SPECTROSCOPIC SIGNATURES AND DYNAMIC CONSEQUENCES OF
MULTIPLE INTERACTING STATES IN MOLECULAR SYSTEMS

by

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Abstract

The development of the experimental techniques in the area of physical chemistry and advances in the *ab initio* methods over last decades may give an impression that every possible propriety of relatively small molecules and radicals in a vacuum can be easily measured and/or accurately calculated. However, *ab initio* theory only deals with the electronic part of the problem (in the Born-Oppenheimer approximation); whereas in experiment a complete interacting molecular system is observed. Nuclear dynamics plays a critical role in understanding the experimental data and cannot be excluded from consideration. Solving the nuclear problem at the same level as the electronic part can be solved is prohibitively expensive with the current computational tools even for small molecules.

The focus of the work presented in this thesis is on filling the gap between advanced *ab initio* techniques and state of the art experiments by creative use of simple models and approximations for nuclear dynamics to interpret the observed data. A brief overview of the methods is given in Chapter 1.

In Chapters 2-4 we discuss the effect of a high molecular symmetry on the topology of the potential energy surfaces. In particular, the difference between conical and glancing intersections, and how both types of intersections shape the photoelectron spectra.
and the dissociation dynamics. We used cyclic $N_3$ and \textit{sym}-triazine molecules as prototype examples, however the same effects can be observed in the molecular systems with high symmetry.

Chapters 5 and 6 focus on the photoelectron spectra calculations for hydroxycarbene diradicals and oxyallyl radical using various approximations to the vibrational wave functions.
Chapter 1

Introduction and overview

A molecular spectrum can not be completely understood and interpreted without theoretical models and calculations. This work is focused on the interconnection of the \textit{ab initio} electronic structure calculations with the experimentally observed data. The task would be trivial if one could solve the full Schrödinger equation of a molecular system. But this is a problem of enormous complexity even for molecules of just several atoms. Therefore, the Born Oppenheimer approximation, a corner stone of quantum chemistry, is used to separate a full Schrödinger equation (SE) into electronic and nuclear parts (in the assumption that electronic and nuclear motion have different time scales); these two parts are solved sequentially, which significantly reduces the dimensionality of the problem.

Considerable efforts over last decades were dedicated into developing sophisticated \textit{ab initio} methods to solve the electronic part of the problem. Current progress in the electronic structure methods and computer hardware allows to achieve so called “chemical accuracy” for reactive energies (about 1 kcal/mol) and about 0.1 eV for electronic excitation energies. Equilibrium structures accuracy of 0.001Å for most molecular systems of up to 20-50 atoms in the order of weeks of CPU time. However, even with smaller molecules, some additional complications for the \textit{ab initio} theory are caused by for example multi-radicals and molecules with degenerate and interacting electronic states.
Regardless of this progress in the electronic structure theory, nuclei and electrons are not well separated in the experiment, and some additional approximations have to be used to predict or interpret the experimental data.

Solution of the nuclear Schrödinger equation in the Born Oppenheimer approximation requires a multidimensional potential energy operator. In most cases it is a potential energy surface (PES) represented either on the grid or by the analytical fit of the \textit{ab initio} results. In practice, the size of the surface is limited by 10-15 dimensions (but can be higher for symmetric molecules): e.g. if only 4 points are obtained along each of the 10 dimensions, more than $10^6$ \textit{ab initio} single point calculations must be performed. Therefore, the lacking symmetry, six- or seven-atomic molecules are the largest for which nuclear Schrödinger equation can be solved. If the time dependent SE has to be solved to predict dynamics of the nuclei, the size of the molecule is limited to about 4 atoms (the limit is approximately 7 dimensions for the wave packet propagation methods). Vibrational part of the Schrödinger equation is solved based on \textit{ab initio} results.

To summarize, \textit{ab initio} methods can predict the electronic structure of a relatively large molecules compared to the limits of the tools to solve the nuclear SE. Therefore in order to compare \textit{ab initio} results to the experimental data, some approximations must be used to describe the missing link: nuclear dynamics.

In the rest of this chapter, we briefly overview approximations used in this work to incorporate the nuclear dynamics into the \textit{ab initio} description of the experiments.
1.1 Born-Oppenheimer approximation, potential energy surfaces, and vibrational wavefunctions

The Born-Oppenheimer (BO) or adiabatic approximation\(^1\) is an efficient approach to a solution of a Schrödinger equation (SE) for problems with slow (nuclear) and fast (electronic) degrees of freedom by separating respective variables. The molecular Hamiltonian operator is the sum of the kinetic energy of nuclei \(T_n\), electrons \(T_e\), and the potential energy of the system \(U(q, Q)\):

\[
H = T_n + T_e + U(q, Q),
\]

where \(q\) and \(Q\) denote the electronic and nuclear coordinates, respectively.

If the kinetic energy of the nuclei were zero, \(T_n = 0\), than Eq. (1.1) would be reduced to the electronic Hamiltonian:

\[
H_e = T_e + U(q, Q)
\]

and the total time independent (TI) SE \(H\Psi = E\Psi\) is reduced to the electron TISE:

\[
H_e\psi_i(q, Q) = \epsilon_i(Q)\psi_i(q, Q)
\]

\(Q\) in Eq. (1.2) and (1.3) is a parameter, not a variable. The assumption is that electrons adjust instantly to any given nuclear configuration \((Q)\), since they are at least three orders of magnitude lighter than the nuclei. Therefore the electronic TISE can be solved independently for every vector parameter \(Q\). Obtained eigen energy \(\epsilon_i(Q)\) is a function
of the nuclear coordinates $Q$ and called a *Potential energy function or (hyper)surface (PES)*.

The total wave function in the BO approximation becomes a product of the electronic and nuclear wave functions:

$$\Psi(q, Q) = \psi(q, Q) \cdot \chi(Q)$$ (1.4)

and the nuclear SE for $\chi(Q)$:

$$[T_n + \epsilon(Q)]\chi(Q) = E \cdot \chi(Q)$$ (1.5)

(electronic indices are omitted for simplicity).

The PES $\epsilon_i(Q)$ can obtained by the electronic structure *ab initio* methods. The brute force method to calculate PES would be running multiple *ab initio* single point calculations for every point $Q$ on some grid. Advanced PES fitting methods allow to significantly reduce required number of *ab initio* points by using irregularly distributed data—with higher density of points calculated around the stationary geometries. The next level of sophistication, is fitting *ab initio* data in a special polynomial basis set, which is by construction invariant with respect to permutation of the nuclei for a given molecule. This helps to further reduce the number of points and ensure that the energy of the fitted surface is exactly the same at the equivalent geometries. The major problem in the PES fitting field is that there is often no single *ab initio* method which produces results of the same quality across all possible nuclear configurations $Q$ (a chemical reaction or dissociation with radical intermediates would be an example of a such complex system).

Once PES is computed, the nuclear SE (Eq. 1.5) can be solved either on the grid using the basis set representation (i.e.basis set of the eigen functions of a harmonic
oscillator). While this methods scales much better than the direct diagonalization of the nuclear Hamiltonian, applications of both approaches are limited because of the computational cost (hundreds of thousands of \textit{ab initio} points must be obtained even for a molecule of just six atoms) and technical problems with multidimensional fits.

Thus in general solution of the nuclear SE is avoided and a combination of simple models and approximations is often used to understand dynamical effects in the molecules.

The simpliest approach is the harmonic approximation—in the vicinity of the equilibrium geometry, the PES is approximated by the second order polynomial function, and eigen energies and vibrational eigen functions are obtained analytically. It could be combined with the Franck-Condon approximation (see Sec. 1.4) to estimate the photoelectron spectra. We explore this approach in our work on oxyallyl (see Chapter 6). However these approximations fail when anharmonic effects and coupling of normal modes is significant. And full vibrational wave functions were obtained in our calculations of the photoelectron spectra of the hydroxycarbene diradicals (see Chapter 5) and compared against the harmonic approximation.

In Chapters 3 and 4 we discuss the dissociation dynamics of the \textit{sym}-triazine not by solving the time dependent SE, but by analyzing the topology of PESes based on the symmetry of the molecule and its electronic wave functions. In Chapter 6 we used a quantum wave packet propagation to estimate the lifetime of the oxyallyl singlet transition state and respective spectral line broadening.

1.2 Complications—conical intersections and GBO

As discussed in the previous section, in the BO approximation the nuclei move on a single PES defined by a fast motion of electrons. When the BO approximation breaks, the
dynamics of the molecular system becomes non-adiabatic and induces electronic transitions between different electronic PESes. In the extreme case of very fast nuclei, the whole concept of PES is looses its significance, however at lower speeds nuclear motion can be described as a motion on several coupled surfaces. Radiationless transitions between the coupled surfaces occur in the vicinity of the PES intersections. In the first order, PESes are linear around the intersection, thus it is called a conical intersection (CI)\(^3,4\).

Fig. 1.1 shows an example of a conical intersection. The ground vibrational wave function is delocalized around CI (x=y=0, \(D_{3h}\) geometry). As shown in the bottom panel of Fig. 1.1 the real adiabatic electronic wave function is not a single valued function: because of the symmetry of the system, real electronic wave function has to change its sign once a conical intersection is encircled; i.e. the geometric or Berry phase\(^6-9\) \(\gamma = \pi\) is acquired.

One can incorporate the geometric phase effects in the calculations of the vibrational wavefunctions following the method proposed by Truhlar and Mead\(^7\). The standard Born-Oppenheimer approximation is generalized (GBO) in a such way that the real adiabatic electronic wave function is multiplied by a complex phase factor:

\[
\psi^{GBO}(q, Q) = \psi(q, Q) \cdot e^{i\frac{2n+1}{2}\gamma(Q)}
\]

(1.6)

where \(\gamma(Q)\) is a phase angle function which changes by \(2\pi\) for every path that encloses the conical intersection, and \(n\) is an integer number. The phase factor \(e^{i\frac{2n+1}{2}\gamma(Q)}\) accounts for the geometric phase effect in the electronic wave function. The molecular SE in the GBO form becomes\(^7\):
Figure 1.1: (Color) (a) A surface plot of the cyclic-N$_3$ PES in hypospherical coordinates around the conical intersection (at x=y=0). (b) A contour plot of the same surface (contour interval is 0.02 eV). Open and closed circles indicate the $B_1$ minima and the $A_2$ transition states for pseudo rotation around the conical intersection (at x=y=0). (c) The BO wave function on the left panel exhibits an abrupt sign change at $\phi = 0$. This problem is removed by multiplying the real BO wave function (left) by a complex phase factor (middle) which exhibits a similar sign change at $\phi = 0$ (with $\phi$ defined only at $[0..2\pi]$). The resultant GBO wave function (right) is complex, single-valued and continuous at the $\phi = 2\pi \rightarrow \phi = 0$ region. (Adapted from Babikov et al.$^5$).

\[
\left[ \frac{1}{2\mu} [-i \nabla - A]^2 + \epsilon \right] \chi^{GBO} = E \cdot \chi^{GBO} 
\]  

(1.7)

where $\epsilon$ is adiabatic PES, and $A$ is a vector potential defined as: $A = \langle \chi^{GBO} | \nabla | \chi^{GBO} \rangle$. 

\[
\begin{align*}
\chi^{BO} & = \left[ \frac{1}{2\mu} [-i \nabla - A]^2 + \epsilon \right] \chi^{GBO} \\
& = E \cdot \chi^{GBO} \\
& = \langle \chi^{GBO} | \nabla | \chi^{GBO} \rangle 
\end{align*}
\]
This approach takes into account the geometric phase effect (i.e. the breakdown of the BO approximation) in the presence of the conical intersection and allows one to evaluate correct vibrational wavefunctions. This method was applied in our calculation of the photoelectron spectrum of the cyclic N$_3$.

### 1.3 Four state glancing intersections

This section describes the electronic structure of the four-state glancing intersections (GIs) derived from the excitations between two degenerate pairs of MOs. Below we explain why the degenerate states in these intersections exhibit negligible JT distortions and demonstrate that the three PES patterns shown in Fig. 1.2 represent all possible topographies of the four-state manifolds.

![Figure 1.2: Cartoons illustrating the behavior of PESs along Jahn-Teller displacements for the conical (a) and glancing-like (b-d) intersections (three different types of four-state manifolds are shown). Solid and dashed lines represent states of different symmetry. Symmetry labels (shown for the example of sym-triazine, see Chapter 3) in (a) are for the $n \rightarrow R_p$ conical intersection, and in (b)—for the glancing intersection of $4 \ n \rightarrow \pi^*$ states. Equilibrium geometries (EG) and transition states (TS) with respect to a pseudo rotation coordinate (rotation around $D_{3h}$ vertical axis) are also shown. See Appendix A for a detailed analysis of the four-states manifolds.](image-url)
In a $D_{3h}$ molecule, the degenerate MOs could be of $e'$ or $e''$ symmetry. In $C_{2v}$ (the highest symmetry in which the degeneracy is lifted), these degenerate orbitals become $A_1 + B_2$ and $A_2 + B_1$, respectively.

Consider excitations from the fully occupied doubly degenerate ($e^\text{occ}_A$ and $e^\text{occ}_B$) MOs to the two degenerate virtual orbitals ($e^\text{virt}_A$ and $e^\text{virt}_B$). Primes and sub indices are omitted for the rest of this section for the sake of generality. Once spin and spatial symmetry is properly accounted for, these transitions give rise to the four electronic configurations (Configuration State Functions, CSFs):

\[
\begin{align*}
\alpha_A : & \quad e^\text{occ}_B \rightarrow e^\text{virt}_B \\
\beta_B : & \quad e^\text{occ}_A \rightarrow e^\text{virt}_B \\
\gamma_B : & \quad e^\text{occ}_B \rightarrow e^\text{virt}_A \\
\delta_A : & \quad e^\text{occ}_A \rightarrow e^\text{virt}_A
\end{align*}
\]

(1.8)

The CSFs of the same symmetry can mix, and at $D_{3h}$ they mix with equal coefficients due to the exact electronic degeneracy of the MOs. Thus, the wave functions of the four excited states are: $\alpha_A \pm \delta_A$ and $\beta_B \pm \gamma_B$ (omitting the normalization coefficients). Only two out of these four states are exactly degenerate, i.e., $e \otimes e \rightarrow E + A + B$ (this is valid for any combination of primes in the MOs symmetry labels).

Let us first consider the topography of the two degenerate states. Assume that these two electronic states are $\alpha_A - \delta_A$ and $\beta_B + \gamma_B$, as in the cyclic $N_3$ cation\textsuperscript{11}. An elegant transformation of the MOs to the complex-valued form proposed by V.I. Pupyshev (private communication) significantly simplifies further derivations:
In these complex-valued MOs, the wave functions of the degenerate states assume the following form:

\[ E_{\pm} = \left( \alpha_A - \delta_A \right) \pm i \cdot \left( \beta_B + \gamma_B \right) \]  

(1.10)

where \( E_{\pm} \) excited states are the single excitations in the complex MOs representation:

\[ E_{\pm}: \quad e_{\text{occ}} \rightarrow e_{\text{virt}} \]  

(1.11)

For example, \( E_+ \) can be written in a shorthand notation as:

\[
E_+ = \left[ (e_{B}^{\text{occ}} \rightarrow e_{B}^{\text{virt}}) - (e_{A}^{\text{occ}} \rightarrow e_{A}^{\text{virt}}) \right] + i \cdot \left[ (e_{A}^{\text{occ}} \rightarrow e_{B}^{\text{virt}}) + (e_{B}^{\text{occ}} \rightarrow e_{A}^{\text{virt}}) \right] \\
= (e_{A}^{\text{occ}} + i \cdot e_{B}^{\text{occ}}) \rightarrow (-e_{A}^{\text{virt}} - i \cdot e_{B}^{\text{virt}}) \\
= e_{+}^{\text{occ}} \rightarrow e_{+}^{\text{virt}}
\]

(1.12)

where \( e_{x}^{\text{occ}} \rightarrow e_{y}^{\text{virt}} \) denotes a determinant in which an electron is excited from the \( e_{x}^{\text{occ}} \) to \( e_{y}^{\text{virt}} \) orbital.

Once the wave functions of the degenerate electronic states are written in the complex MO representation (1.11), it is obvious that the two states are doubly excited with respect to each other. Thus, the matrix element of a one-electron operator (e.g., nuclear derivative) between these two states is exactly zero, suggesting zero gradient along a JT distortion. This propriety of doubly degenerate states has been noted before, for example, in the studies of the benzene excited states\textsuperscript{13,14}. 

\[ e_{\pm}^{\text{occ}} = (e_{A}^{\text{occ}} \pm i \cdot e_{B}^{\text{occ}}) \]  

\[ e_{\pm}^{\text{virt}} = -(e_{A}^{\text{virt}} \pm i \cdot e_{B}^{\text{virt}}) \]  

(1.9)
Below we show that the linear term in the potential energy almost vanishes along any coordinate that lifts the degeneracy in GI, or that the first derivative of the electronic state’s energy is zero along such a coordinate. Neglecting non-Hellmann-Feynman terms, we consider the matrix elements of the derivative of an electronic Hamiltonian along some coordinate $Q$, $\partial H/\partial Q$:

$$
\begin{bmatrix}
\langle \Psi_{E^+} | \frac{\partial H}{\partial Q} | \Psi_{E^+} \rangle & \langle \Psi_{E^+} | \frac{\partial H}{\partial Q} | \Psi_{E^-} \rangle \\
\langle \Psi_{E^-} | \frac{\partial H}{\partial Q} | \Psi_{E^+} \rangle & \langle \Psi_{E^-} | \frac{\partial H}{\partial Q} | \Psi_{E^-} \rangle
\end{bmatrix}
$$

(1.13)

The diagonal matrix elements are equal since $E^+$ and $E^-$ are the complex-conjugates of each other by construction (1.10). Moreover, since the diagonal matrix elements $\langle \Psi_{E^\pm} | \frac{\partial H}{\partial Q} | \Psi_{E^\pm} \rangle$ are always fully symmetric, they can be non-zero only for the Hamiltonian derivatives along a fully symmetric coordinate. Thus, the gradients of both degenerate surfaces along a fully symmetric coordinate are equal and may be non-zero, which means any fully symmetric coordinate is a seam of the intersection. Diagonal elements are exactly zero for the derivative taken along any non-fully symmetric coordinate, i.e., along any coordinate that lifts the degeneracy (a JT distortion). If the derivative of the Hamiltonian, and therefore the derivative of the energy, along the JT coordinate is zero, than the potential energy function has an extremum at the symmetric $D_{3h}$ geometry.

The coupling element is exactly zero only within the 4-electron-in-2-orbital model and for one-electron Hamiltonians. The presence of other electronic configurations in correlated wave functions can, in principle, result in non-zero couplings. However, as demonstrated by highly accurate multi-reference CI calculations of $N_{3^+}^{12}$ (and confirmed by the EOM-CC calculations in the present work), the resulting JT distortions are extremely small.
To conclude, the linear term along JT distortion coordinates is (almost) zero and the extrema of both surfaces are very close to $D_{3h}$. One can easily determine whether these two intersecting surfaces have minima, maxima or both near the intersection, if one considers two other non-degenerate states from the $e \otimes e$ manifold. As shown at the bottom of Fig. 1.2, there are only three possible relative ordering of two degenerate and two non-degenerate states: the degenerate states are the the highest (b), the lowest (d), or in between the two non-degenerate states (c). Solid and dashed lines in Fig. 1.2 denote the electronic states of different symmetry. As described in Ref. 11, each two states of the same symmetry (one non-degenerate and another one from the degenerate pair) due to the symmetry allowed coupling exhibit an avoided-crossing like behavior, as shown in Fig. 1.2(b-d). In few points along the GI seam where an accidental degeneracy of three states occurs, the conical like intersection will be present between two surfaces of the same symmetry.

1.4 Photoelectron spectroscopy and Franck-Condon approximation

Photoelectron spectroscopy is a powerfull tool for probing the electronic structure of molecules. However, the interpretation of the experimental spectra required ab initio calculations.
Figure 1.3: (Color) 1D photoelectron spectrum in the harmonic approximation. $\chi''$ and $\chi'$ are the initial and the target vibrational wavefunctions, respectively; $E_i$ are the energies of the vibrational levels; IE is the adiabatic ionization energy; $\Delta Q$ is the displacement of the target state’s equilibrium geometry along the normal coordinate; $\langle \chi' | \chi'' \rangle$ are the Franck-Condon factors for the $\chi' \leftrightarrow \chi''$ vibronic transition. Vibrational progressions are observed only when the target state (“target state B” in the figure) has a different equilibrium geometry from the initial electronic state, i.e. displaced along at least one normal coordinate $Q_i$.

In the dipole approximation, the intensity of one-electron transition between two vibronic states is proportional to the square of the electric dipole transition moment, which in adiabatic approximation can be expressed as:

$$
\langle \chi'(Q) \cdot \psi'(q, Q) | M(q, Q) | \psi''(q, Q) \cdot \chi''(Q) \rangle = \mu(Q) \cdot \langle \chi'(Q) | \chi''(Q) \rangle,
$$

(1.14)
where \( \psi'' \) and \( \psi' \) are the electronic wave functions, \( \chi'' \) and \( \chi' \)—the vibrational wave functions of the initial and target states, respectively; \( q \) and \( Q \) are the electronic and nuclear coordinates. If the dependence of an electronic transition moment \( \mu(Q) \) on the nuclear coordinates is neglected, the intensity of the transition is proportional to the square of the Franck-Condon factor (FCF)\(^{15,16} \):

\[
\langle \chi'(Q)|\chi''(Q) \rangle .
\] (1.15)

Fig. 1.3 shows an example of a one dimensional photoelectron spectrum (for a diatomic molecule) in the Franck-Condon approximation. In the harmonic approximation vibrational wave functions are products of one dimensional harmonic oscillator wave functions. If normal coordinates of the initial and the target electronic states are assumed to be the same (the parallel approximation), the multidimensional Franck-Condon factors are reduced to the products of one dimensional FCFs:

\[
\langle \chi'(Q)|\chi''(Q) \rangle = \langle \chi_1'(Q_1)\cdot \chi_2'(Q_2)\cdot \ldots|\chi_1''(Q_1)\cdot \chi_2''(Q_2)\cdot \ldots \rangle = \langle \chi_1'(Q_1)|\chi_1''(Q_1) \rangle \cdot \langle \chi_2'(Q_2)|\chi_2''(Q_2) \rangle \cdot \ldots
\]

(1.16)

One-dimensional harmonic FCF can be computed analytically\(^{17} \):
\[
\langle \chi' | \chi'' \rangle = \sqrt{\frac{2\alpha}{\alpha^2 + 1}} \cdot \sqrt{\frac{\nu'' \nu'}{2(\nu'' + \nu')}} \cdot e^{\frac{-\delta^2}{2(\alpha^2 + 1)}} \sum_{L=0}^{L<\min\{\nu'', \nu'\}} \sum_{i=0}^{\nu'-L-1} \sum_{j=0}^{\nu''-L-1} \\
\left[ \frac{1}{L!} \left( \frac{4\alpha}{1 + \alpha^2} \right)^L \frac{1}{i!} \left( \frac{1 - \alpha^2}{1 + \alpha^2} \right)^i \frac{1}{j!} \left( \frac{\alpha^2 - 1}{1 + \alpha^2} \right)^j \right. \\
\left. \frac{1}{\nu' - 2i - L} \left( \frac{-2\alpha \delta}{1 + \alpha^2} \right)^{\nu' - 2i - L} \frac{1}{\nu'' - 2j - L} \left( \frac{2\delta}{1 + \alpha^2} \right)^{\nu'' - 2j - L} \right], 
\]

where

\[
\alpha = \sqrt{\frac{\omega''}{\omega'}} \quad \delta = \Delta Q \sqrt{\omega''},
\]

\(\nu''\) and \(\nu'\) are quantum numbers; \(\omega''\) and \(\omega'\) are harmonic frequencies of the initial and the target electronic state, respectively; \(\Delta Q\) is the displacement of the target electronic state relative to the initial one along a mass-weighted normal mode.

If there are no hot bands in the spectrum (0 K, and only the ground vibrational state of the initial electronic state is populated), using the normal modes of the target electronic state is preferred. Indeed, rotation of the initial ground states’ vibrational wave function does not significantly change the overlap integrals with the target state (see Fig. 1.4); on the other hand, rotation of target state’s vibrational wave functions with many nodes strongly affects the overlap matrices.

When normal modes of the initial and the target electronic state are significantly non-parallel, the nuclear coordinates of the initial and the target vibrational wave functions are different, and the full FCFs \(\langle \chi'(Q') | \chi''(Q'') \rangle\) are not represented accurately by the product of the one-dimensional integrals, Eq. (1.16). In this case, multidimensional
Figure 1.4: (Color) The effect of rotations of normal coordinates on Franck-Condon factors within the parallel-mode approximation. (a) The correct overlap between wave-functions on lower \((q'')\) and upper \((q')\) surfaces. (b) The overlap when lower normal coordinates are rotated to coincide with upper coordinates. (c) The overlap when upper normal coordinates are rotated to coincide with lower coordinates. Note that (b) describes the exact overlap integrals in (a) better than (c).

Franck-Condon factors between two harmonic vibrational wavefunctions can be evaluated analytically\(^\text{18,19}\). For a molecule with \(K\) atoms and \(N\) normal modes \((N = 3K - 6\) or \(N = 3K - 5\) for non-linear and linear molecules, respectively), normal modes of the initial and target states are related by the Duschinsky transformation\(^\text{20}\):

\[
\vec{Q}' = S \cdot \vec{Q}'' + \vec{d},
\]

(1.19)

where the normal modes rotational matrix \(S \ [N \times N]\) is:

\[
S = L'^T L''
\]
and the vector of displacements $\vec{d} [N]$ along the normal coordinates is:

$$\vec{d} = L'^T \sqrt{T}(\vec{x}' - \vec{x}_0)$$

where $L'' [N \times 3K]$ and $L' [N \times 3K]$ are rectangular matrices composed of $N$ mass-weighted normal vectors (in Cartesian coordinates) of the initial and the target electronic states, respectively; $\vec{x}'_0 [3K]$ and $\vec{x}_0' [3K]$ are the Cartesian vectors representing the equilibrium geometries of the initial and the target states respectively; and matrix $T [3K \times 3K]$ is the diagonal matrix composed of atomic masses: $T = \text{diag}\{m_1, m_1, m_1, m_2, m_2, ..., m_K, m_K, m_K\}$.

The overlap integral (FCF) between the ground vibrational states of the initial and target electronic states is given by:

$$\langle \chi'_0 | \chi''_0 \rangle = \frac{2^{N/2}}{\sqrt{\text{det}(S)}} \prod_{\eta=1}^{N} \left( \frac{\omega''_{\eta}}{\omega'_{\eta}} \right)^{1/4} \sqrt{\text{det}(Q)} \left[ e^{-\frac{1}{2} \sqrt{T}^{T}(1-P)T} \right]$$

(Note that there is a typo in this equation in Ref. 19) FCFs for transition from the ground vibrational state of the initial electronic state are calculated recursively$^{19}$ from the $\langle \chi'_0 | \chi''_0 \rangle$ integral as:

$$\langle \chi'_{\nu'_1,..,\nu'_N} | \chi''_0 \rangle =$$

$$\sqrt{\frac{2}{\nu'_\xi + 1}} \left[ (1 - P) \delta \right]_{\xi} \langle \chi'_{\nu'_1,..,\nu'_N} | \chi''_0 \rangle +$$

$$\sum_{\theta=1}^{N} \sqrt{\frac{\nu''_{\theta}}{\nu'_{\xi} + 1}} [2P - 1]_{\xi\theta} \langle \chi'_{\nu'_1,..,\nu'_{\theta-1},\nu'_{\theta},..,\nu'_N} | \chi''_0 \rangle$$

(1.21)
Hot bands (transitions from the vibrationally excited initial electronic state) are given by:

\[
\langle \chi'_{\nu_1',...\nu_N'} | \chi''_{\nu_1'',...\nu_N''} \rangle = -\sqrt{\frac{2}{\nu''_{\eta} + 1}} \left[ R \vec{\delta}_{\eta} \right] \langle \chi'_{\nu_1',...\nu_N'} | \chi''_{\nu_1'',...\nu_N''} \rangle + 
\sum_{\theta=1}^{N} \sqrt{\frac{\nu''_{\theta}}{\nu''_{\eta} + 1}} [2Q - 1]_{\eta\theta} \langle \chi'_{\nu_1',...\nu_N'} | \chi''_{\nu_1'',...\nu_N''-1} \rangle + 
\sum_{\xi=1}^{N} \sqrt{\frac{\nu''_{\xi}}{\nu''_{\eta} + 1}} R_{\eta\xi} \langle \chi'_{\nu_1',...\nu_N'-1,...\nu_N'} | \chi''_{\nu_1'',...\nu_N''} \rangle
\]

(1.22)

where \( \nu_i \) is a number of vibrational quanta in the \( i \)-th normal mode. \( J, Q, P, \) and \( R \) are square \([N \times N]\) matrices:

\[
J = \lambda' S \lambda''^{-1} \\
Q = (1 - J^T J)^{-1} \\
P = J Q J^T \\
R = Q J^T
\]

\( \vec{\delta} \) is a vector \([N]\):

\[
\vec{\delta} = \lambda' \vec{d}
\]
\( \lambda'' \) and \( \lambda' \) are \([N \times N]\) diagonal matrices:

\[
\lambda'' = \text{diag}\{\sqrt{\omega''_1}, \sqrt{\omega''_2}, \ldots, \sqrt{\omega''_N}\}
\]

\[
\lambda' = \text{diag}\{\sqrt{\omega'_1}, \sqrt{\omega'_2}, \ldots, \sqrt{\omega'_N}\}
\]

where \( \omega''_i \) and \( \omega'_i \) are the frequencies of the \( i \)–th normal mode in atomic units.

Total number of vibrational states with up to \( K \) quanta for the molecule with \( N \) normal modes is given by\(^1\):

\[
\left[ 1 + \sum_{k=1}^{K} \frac{(N + k - 1)!}{(N - 1)!k!} \right]^2
\]

\( (1.23) \)

### 1.5 Time dependent Schrödinger equation and wave packet propagation

Throughout our work we tried to avoid explicit description of the nuclear dynamics by solving time dependent SE (TDSE), with the exception of our studies of oxyallyl (see Chapter 6) where we employed a wave packet propagation to estimate the lifetime at the transition state and the respective line broadening.

In nuclear problem, one solves the TDSE and the propagator can be obtained as:

\[
i \frac{\partial}{\partial t} \Psi(R, t) = H \Psi(R, t)
\]

\( (1.24) \)

\(^1\)Please refer to the “stars and bars” combinatorial problem elsewhere, e.g. [http://en.wikipedia.org/wiki/Stars_and_bars](http://en.wikipedia.org/wiki/Stars_and_bars) (probability)
by separating the variables and integrating both sides of the equation:

\[ \int_{\Psi(0)}^{\Psi(t)} \frac{d\Psi}{\Psi} = \int_0^t \frac{1}{i} \, H \, dt' \]  \hspace{1cm} (1.25)

thus

\[ \ln \frac{\Psi(t)}{\Psi(0)} = -iHt \]  \hspace{1cm} (1.26)

and

\[ \Psi(R, t) = e^{-iHt} \Psi(x, 0) \]  \hspace{1cm} (1.27)

This introduces the evolution operator, or propagator, \( U(t) = e^{-iHt} \), which can be applied to a solution of the time independent SE–eigen function \( \psi(R, 0) \) —to obtain a solution of the TDSE at any time \( t \) (for time independent Hamiltonian).

In this work we used the Split Operator method to propagate a nuclear wave function on the grid. The propagator \( U(t) \) represented as a product of propagators over short time intervals \( \Delta t \):

\[ U(t) = e^{-iH \Delta t} \cdot e^{-iH \Delta t} \cdot \ldots \cdot e^{-iH \Delta t} \]  \hspace{1cm} (1.28)

And each short time propagator is a product of the kinetic and potential energy factors (if the Hamiltonian is separable into a sum of kinetic and potential energy):

\[ e^{-iH \Delta t} = e^{-iT \Delta t} \cdot e^{-iV \Delta t} + O(\Delta t^2) = e^{-iV \Delta t/2} \cdot e^{-iT \Delta t} \cdot e^{-iV \Delta t/2} + O(\Delta t^3) \]  \hspace{1cm} (1.29)

This representation of the propagator operator allows using a Fourier Grid representation of the Hamiltonian. And by applying a very efficient FFT transformation of the wave function between the position and momentum representation and back at every time step, the propagation is reduced to multiplication by matrices \( e^{iV \Delta t} \) and \( iT \Delta t \) which are diagonal in momentum and position representations, respectively.
Whenever a wave function $\Psi(R, t)$ is obtained as a function of time a spectrum can be calculated as a Fourier transform of the autocorrelation function:

$$\sigma(E) = \int_{-\infty}^{\infty} dt \cdot e^{i\omega t} \langle \Psi(R, 0) | \Psi(R, t) \rangle = \sum_n |c_n|^2 \delta(E - E_n)$$  \hspace{1cm} (1.30)

The resolution of the spectrum is inverse of to the total time of propagation: $\Delta E = 2\pi/t_{\text{max}}$, and the energy range is inverse of the time step: $E_{\text{max}} = 2\pi/\delta t$.

Figure 1.5: Characteristic times of the decaying autocorrelation function (left) and respective characteristic spectral line width and peak spacing (right) are related as shown above. The spectrum on the right panel is the Fourier transformed autocorrelation function from the left panel. (Adapted from Heller\textsuperscript{22}).
1.6 Chapter 1 reference list


Chapter 2

Conical and glancing Jahn-Teller intersections in the cyclic trinitrogen cation

2.1 Chapter 2 introduction

Interest in homonuclear triatomic molecules has a long history. This is the smallest non-linear system that can have a non-Abelian point group symmetry containing irreducible representations of the order higher than one, which results in symmetry required degeneracies between some electronic states at high symmetry geometries ($D_{3h}$, or equilateral triangle) and the intersections between the corresponding potential energy surfaces (PESs).

According to the Jahn-Teller (JT) theorem$^{1-3}$, high-symmetry intersection points in non-linear systems are not stationary points on PESs, that is, degenerate states follow first order JT distortions to a lower symmetry, which lifts the degeneracy. The linear dependence of states’ energies near the intersection gives rise to singularity points on adiabatic PESs. More precisely, the theorem states that for any geometry with symmetry required degeneracy between the electronic states there exists a nuclear displacement along which the linear derivative coupling matrix element between the unperturbed states and the difference between the diagonal matrix elements of the perturbation are
not required to be zero by symmetry. The theorem does not guarantee the intersection in real physical problems and the above vibronic terms can become zero due to additional symmetries, properties of the potential, or other reasons. For example, as mentioned in the original paper, the energy splitting can be negligible if the orbital dependence on the displacement is weak, as in the case of lone pairs.

An interesting situation arises when such JT pair interacts with other closely lying states, as it happens in cyclic $\text{N}_3^+$. In this case the overall energy dependence at the intersection point becomes purely quadratic and high symmetry configurations can become stationary points on adiabatic PESs.

In triatomics, degenerate PESs usually form a conical intersection (CI) extensively characterized over the years for a variety of systems\textsuperscript{4,5}. An important feature of such intersection is that the real electronic wave function calculated within the Born-Oppenheimer approximation gains a phase, i.e., a sign change, along any path on the PES, which encircles a conical intersection and thus contains the singularity point\textsuperscript{6–9}. This geometric phase has a profound effect on the nodal structure of the vibrational wave functions, the order of vibrational states, and the selection rules for the vibrational transitions\textsuperscript{10,11}.

A common motif in these systems is an unpaired electron in one of the doubly degenerate molecular orbitals (MOs) in the ground electronic state. Alternatively, CIs can be formed by the excited states derived from electron transitions between doubly degenerate and non-degenerate orbitals, e.g., non-degenerate HOMO and doubly degenerate LUMO in NO$_3$.

Similarly to many other $X_3$ systems, the cyclic $\text{N}_3$ radical features CI in the ground state\textsuperscript{12}, with unusually strong geometric phase effect that changes the nodal structure of the vibrational wave function and the ordering of vibrational levels\textsuperscript{11}. 

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Cyclic N$_3$ was described as a metastable molecule ten years ago$^{13}$, which was confirmed by later calculations$^{14,15}$. The first experimental evidence of cyclic N$_3$ was obtained by Wodtke and coworkers$^{16-18}$, who reported the cyclic N$_3$ production in the ClN$_3$ photodissociation and measured its ionization threshold$^{18}$. These experiments motivated recent theoretical studies of N$_3$, as well as the present work targeting the cyclic N$_3^+$ ground and excited states, in order to facilitate interpretation of photoelectron experiments. In contrast to the neutral, only limited information is available about the cation states$^{19}$.

The cyclic N$_3$ cation is a closed shell molecule of D$_{3h}$ symmetry with doubly degenerate HOMO and LUMO. Thus, the lowest excited states of each multiplicity are almost quadruply degenerate (with two exactly degenerate states) and exhibit JT-like behavior.

A similar quadruple set of the excited states occurs in other systems with doubly degenerate HOMO and LUMO, for example, in benzene$^{20}$, a rather popular JT system. Interestingly enough, most theoretical studies of the JT effects in benzene were focused on the benzene cation, which exhibits the usual JT conical intersection. As for the neutral molecule, most of the computational studies reported only the vertical excitation energies$^{21,22}$ for these four almost degenerate excited states.

The effect of other closely lying electronic states on JT intersections has been discussed by several researchers$^{23-25}$. For example, Perrin and Gouterman$^{23}$ analyzed (E+A)$\otimes$e vibronic coupling problem. In their treatment, degenerate E states that form CI were considered not as isolated states (e.g., as in the E$\otimes$e vibronic coupling problem$^{26}$), but as being coupled to a closely lying A state. Similar interactions were characterized in Na$_3$$^{24}$, where the interpretation of the experimental data required the inclusion of the non-degenerate A$_1$ state and treating all three states as a pseudo Jahn-Teller system.
In this chapter we present a comprehensive analysis of the cyclic $\text{N}_3^+$ excited states. We found that two HOMO→LUMO exactly degenerate states do not form a familiar $A_2/B_1$ conical intersection because of the presence of the two other closely lying HOMO→LUMO states of the $A_2$ and $B_1$ symmetries. Non-degenerate states are coupled to the degenerate ones forming a $(E+A+B)\otimes e$ vibronic problem, and the energy dependence on the displacement from the intersection becomes purely quadratic, except for the points of an accidental degeneracy of three states. Such glancing intersection is similar to Renner-Teller glancing intersections in linear molecules. It exhibits pseudo Jahn-Teller distortions, as opposed to CI and the usual JT effect characterized by linear dependence of the energy along the displacements, and has no geometric phase effect in the electronic wave functions.

The structure of this chapter is as follows. The next section describes computational details. Molecular orbital framework and the nature of low-lying states is presented in sections 2.3 and 2.4, respectively. Formal analysis of the $(E+A+B)\otimes e$ JT problem is presented in Sec. 2.5. Sec. 2.6 discusses ionization energy and photoelectron spectrum. Our final remarks are given in Sec. 2.7.

### 2.2 Computational details

Excited states equilibrium geometries, frequencies, vertical and adiabatic excitation energies were calculated at the EOM-CCSD\textsuperscript{29,30}/cc-pVTZ\textsuperscript{31} level of theory with frozen 1$s$ core orbitals. Potential energy surfaces of the excited states were obtained at the EOM-CCSD level with the 6-311G*\textsuperscript{32} basis set. EOM-CCSD/cc-pVTZ PESs presented in this work was discussed in more details elsewhere\textsuperscript{33}. The ground state of cyclic $\text{N}_3^+$ was characterized using the CCSD model with perturbative triples corrections, CCSD(T)\textsuperscript{34}, and the cc-pVTZ\textsuperscript{31} basis set.
Figure 2.1: Leading electronic configurations of the ground (top panel) and the lowest excited states (lower panel). HOMO → LUMO excitations give rise to four singlet and four triplet CSFs labeled $\alpha$, $\beta$, $\gamma$ and $\delta$. HOMO-2 → LUMO excitations yield two additional CSFs of each multiplicity: $(\mu)$ and $(\nu)$.

The ionization energy of cyclic N$_3$ was calculated as the energy difference between the neutral and the cation using the CCSD(T) total energies with the following bases$^{31}$: cc-pVDZ → cc-pVTZ → cc-pVQZ → cc-pV5Z (1s core orbitals were frozen). The three latter basis sets were used for the three point basis set extrapolation, CBS-3pa$^{35,36}$, of the neutral and cation total energies:

$$E_{cc-pV XZ}(X) = E_{BSL} + b \cdot e^{-cX}$$
where $E_{cc-pVXZ}$ is the total energy obtained with cc-pVXZ basis set, X denoting a cardinal number: $X = \{T, Q, 5\}$, $E_{BSL}$ is the extrapolated basis set limit energy, $b$ and $c$ are the fitting constants. The EOM-SF-CCSD$^{37,38}$/cc-pVTZ equilibrium geometry of the neutral cyclic $N_3$ and the CCSD(T)/cc-pVTZ equilibrium geometry of the cation were used in the IP calculations. Zero point energy (ZPE) of neutral cyclic $N_3$ including the geometric phase effect is from Ref.$^{11}$. Cation’s ZPE is calculated at the harmonic approximation at the CCSD(T)/cc-pVTZ level of theory.

EOM-EE-CCSD and EOM-SF-CCSD results were obtained with the Q-CHEM$^{39}$ ab-initio package. CCSD(T) calculations were performed with the ACES II$^{40}$ electronic structure program.

### 2.3 Molecular orbital picture

The ground state equilibrium geometry of cyclic $N_3^+$ is an equilateral triangle ($D_{3h}$) with $R_{NN} = 1.313 \text{ Å}$. Fig. 2.2 shows MOs and the ground state electronic configuration of $N_3^+$, which is a closed shell molecule with $A'_1$ ($A_1$ in $C_{2v}$) electronic wave function. MOs are derived from: (i) the $sp^2$ hybridized $2s$, $2p_x$ and $2p_y$ atomic orbitals, which form nine molecular orbitals – three $\sigma$-bonding, three $\sigma$-antibonding ($\sigma^*$), and three lone pair ($lp$) orbitals, and (ii) $2p_z$ atomic orbitals that form three $\pi$-like MOs. Each triple set of MOs (i.e. $\sigma$, $\sigma^*$, $lp$, or $\pi$) exhibits a similar pattern – one fully bonding MO lies below two exactly degenerate orbitals. There is no clear energy separation between the $\pi$ and $lp$ sets. An interesting feature of this molecule is that both HOMO and LUMO are doubly degenerate. HOMOs ($lp$’s) are of $e'$ symmetry, whereas LUMOs ($\pi^*$) are of $e''$ symmetry. At $C_{2v}$, the HOMO pair splits into $a_1$ and $b_2$, and LUMO — into the $a_2$ and $b_1$ orbitals.
2.4 Lowest excited states

The least symmetric configuration of a triangular molecule is $C_s$. We use $C_{2v}$ symmetry labels for the twelve lowest excited states, which all are of either $A_2$ or $B_1$ symmetry and therefore become $A''$ at $C_s$. $D_{3h}$ labels are also given when appropriate.

Fig. 2.1 shows leading configurations of the ground and the lowest excited states. Different determinants are combined in configuration state functions (CSFs) that have...

Figure 2.2: Molecular orbitals and the ground state electronic configuration of cyclic $N^+_3$ (equilateral triangle, $D_{3h}$). Both HOMO and LUMO are doubly degenerate. $C_{2v}$ labels are given in parentheses.
appropriate spin and spatial symmetry and represent a convenient basis for describing excited states.

The lowest excited states of cyclic $N_3^+$ are derived from the eight possible single excitations from doubly degenerate HOMO to doubly degenerate LUMO ($lp \rightarrow \pi^*$, top panel). The symmetries of respective CSFs are given by: 

$$(a_1 + b_2) \otimes (a_2 + b_1) = (A_2 + A_2 + B_1 + B_1),$$

and each of these can be either a singlet or a triplet. Thus, total of eight different CSFs can be formed, as shown in Fig. 2.1 (lower panel). Labels $\alpha$, $\beta$, $\gamma$ and $\delta$ denote different types of CSF, whereas minus or plus signs correspond to singlet or triplet configurations, respectively. Next two singlets and triplets ($\mu$ and $\nu$) are derived from the excitations from non-degenerate HOMO-2 to LUMO.

Only CSFs of the same spin and irrep can mix in the excited states wave functions. For example, two singlet $A_2$ states are described as linear combinations of two singlet $A_2$ CSFs:

$$| (\alpha + \delta)^1A_2 \rangle = \frac{1}{\sqrt{\kappa^2 + \lambda^2}} \left[ \kappa \cdot | (\alpha)^1A_2 \rangle + \lambda \cdot | (\delta)^1A_2 \rangle \right]$$

$$| (\alpha - \delta)^1A_2 \rangle = \frac{1}{\sqrt{\kappa^2 + \lambda^2}} \left[ \lambda \cdot | (\alpha)^1A_2 \rangle - \kappa \cdot | (\delta)^1A_2 \rangle \right]$$

(2.1)

The wave functions of two triplet $|(\alpha \pm \delta)^3A_2 \rangle$ states can be formed in a similar way. Likewise, four $B_1$ states (two singlets and two triplets), $|(\beta \pm \gamma) B_1 \rangle$, are linear combinations of $|(\beta) B_1 \rangle$ and $|(\gamma) B_1 \rangle$ CSFs. The coefficients $\kappa$ and $\lambda$ are both equal to one at $D_{3h}$, whereas along $C_{2v}$ distortions (e.g., along the bending normal mode) their ratio changes. In other words, at $D_{3h}$ the excited state wave functions are simply a sum or a difference of basis CSFs, and a $C_{2v}$ distortion collapses each state into single CSF (see Fig. 2.3). Thus, these CSFs represent an approximate diabatic basis. Overall,
at $D_{3h}$ geometries four singlet and four triplet excited state wave functions are formed from four CSFs with $\lambda = \kappa = 1$: $|\alpha + \delta\rangle^{1,3}A_2$, $|\alpha - \delta\rangle^{1,3}A_2$, $|\beta + \gamma\rangle^{1,3}B_1$ and $|\beta - \gamma\rangle^{1,3}B_1$. Since all CSFs are derived from the single excitations between the two pairs of doubly degenerate orbitals, the resulting states are also nearly degenerate and form a rather complicated $D_{3h}$ intersection. The $|\mu\rangle^{1,3}A_2$ and $|\nu\rangle^{1,3}B_1$ states derived from HOMO-2 → LUMO excitations do not mix at $D_{3h}$ geometry and form a regular JT pair.

![Diagram of excited states](image)

**Figure 2.3:** Changes in the excited states’ characters and potential energy surfaces upon distortions from an equilateral ($D_{3h}$) geometry to an obtuse (left) and an acute (right) isosceles $C_{2v}$ triangles.

Using $D_{3h}$ symmetry labels, the symmetries of the HOMO $\rightarrow$ LUMO states are:

$$e' \otimes e'' \rightarrow A_1'' + A_2'' + (E'') \xrightarrow{C_{2v}} A_2 + B_1 + (A_2 + B_1),$$

(2.2)

i.e., among these four excited states only one $A_2$ and one $B_1$ state are exactly degenerate $E''$ states forming a JT pair. These degenerate states are $|\alpha - \delta\rangle A_2$ and $|\beta + \gamma\rangle B_1$. 

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HOMO-2 → LUMO states, $(\mu)^{1,3}A_2$ and $(\nu)^{1,3}B_1$, form another E’ JT pair. Calculated vertical excitation energies for the twelve lowest excited states are summarized in Table 2.1. As explained above, only two of the four HOMO-LUMO states are exactly degenerate, however the order of the states is different for singlets and triplets.

Table 2.1: Vertical excitation energies (eV) of the twelve lowest excited states of cyclic N$^+_3$ calculated at the EOM-CCSD/cc-pVTZ level of theory. Two out of four HOMO → LUMO ($\alpha - \delta, \beta + \gamma$) and two HOMO-2 → LUMO ($\mu, \nu$) excited states are exactly degenerate pairs at D$_{3h}$. The ground state geometry and total energy is given in Table 2.2.

<table>
<thead>
<tr>
<th></th>
<th>Singlets</th>
<th></th>
<th>Triplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\nu)^{1}A_2$</td>
<td>7.669</td>
<td>$(\nu)^{3}A_2$</td>
<td>7.014</td>
</tr>
<tr>
<td>$(\mu)^{1}B_1$</td>
<td>7.669</td>
<td>$(\mu)^{3}B_1$</td>
<td>7.014</td>
</tr>
<tr>
<td>$(\alpha - \delta)^{1}A_2$</td>
<td>5.334</td>
<td>$(\alpha + \delta)^{2}A_2$</td>
<td>4.333</td>
</tr>
<tr>
<td>$(\beta + \gamma)^{1}B_1$</td>
<td>5.334</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\beta - \gamma)^{1}B_1$</td>
<td>5.314</td>
<td>$(\beta + \gamma)^{3}B_1$</td>
<td>3.921</td>
</tr>
<tr>
<td>$(\alpha + \delta)^{1}A_2$</td>
<td>4.914</td>
<td>$(\alpha - \delta)^{3}A_2$</td>
<td>3.921</td>
</tr>
</tbody>
</table>

PES scans along the bending normal coordinate are shown in Fig. 2.4 separately for each irrep and multiplicity. The coordinate origin ($Q_b = 0.0$) corresponds to N$^+_3$ at the equilateral D$_{3h}$ geometry ($R_{NN} = 1.313$ Å), whereas left and right wings of the plots correspond to C$_{2v}$ distortions. The scale along the bending normal mode is as follows: $Q_b = 0.4$ corresponds to $\theta = 45.3$ deg and $R_{NN} = 1.430$ Å, whereas $Q_b = -0.4$ — to $\theta = 77.2$ deg and $R_{NN} = 1.220$ Å.

The ground $X^{1}A_1$ state, which has D$_{3h}$ equilibrium geometry, is shown by the solid line and empty circles on each plot. The lowest excited states (filled squares, triangles and circles) have singly occupied degenerate orbitals and undergo JT distortions to C$_{2v}$.
Figure 2.4: The EOM-CCSD/6-311G* potential energy surface scans along the bending normal coordinate for the ground \((X \ ^1A_1,\) shown on each plot) and the excited \(^1A_2, ^1B_1, ^3A_2, ^3B_1\) states of cyclic \(N_3^+\) (upper left, upper right, lower left and lower right, respectively). Data points (squares, triangles and filled circles) correspond to the calculated adiabatic surfaces; dashed lines represent approximate diabats and connect points with the same leading character of the wave function (see Fig 2.1).

Let us first discuss the \((\mu)^{1,3}A_2\) and \((\nu)^{1,3}B_1\) states derived from the excitations from non-degenerate HOMO-2 to doubly degenerate LUMO (two lowest CSFs in Fig. 2.1). These states are shown in the each plot in Fig. 2.4 by the very top dashed line. The two
Figure 2.5: Adiabatic potential energy surfaces and contour plots of the \((\mu) A_2\) and \((\nu) B_1\) singlet (left) and triplet (right) states. Polar radius and angle are hyperspherical coordinates \(\theta\) and \(\phi\), which are similar to the bending and asymmetric stretch normal mode, respectively. Stereographic projection is taken with fixed hyperradius (overall molecular size, or symmetric stretch) \(\rho = 3.262\) corresponding to the cyclic \(N_3^+\) ground state equilibrium geometry. Both surfaces feature conical \((\mu) A_2/(\nu) B_1\) intersection at \(D_{3h}\). Stationary points on the surfaces are located along two \(C_{2v}\) distortions to acute and obtuse isosceles triangles. Energies of the transition state and the conical intersection relative to the minima are: \(E_{TS} = 0.05\) eV, \(E_{CI} = 0.97\) eV and \(E_{TS} = 0.24\) eV, \(E_{CI} = 1.03\) eV on the singlet and triplet \((\mu/\nu)\) PES, respectively.

Singlets, \((\mu)^1A_2\) and \((\nu)^1B_1\), are exactly degenerate at \(D_{3h}\) and undergo JT distortions to \(C_{2v}\). The stereographic projections of PESs using hyperspherical coordinates \(^1\) of PESs shown in Fig. 2.5 reveal the similarity of this intersection to the \(^2B_1/^2A_2\) intersection in neutral cyclic \(N_3\).\(^{11}\) Transition from the acute to the obtuse triangle stationary points through the \(D_{3h}\) point (i.e., along the bending normal mode) encounters a relatively high potential barrier, however the molecule can go around the conical intersection with

\(^1\)Polar radius and angle are hyperspherical coordinates \(\theta\) and \(\phi\), which are similar to the bending and asymmetric stretch normal mode, respectively. For the precise definition stereographic coordinates, see Ref.\(^{12}\) and references therein.
almost no barrier following the asymmetric normal mode that corresponds to pseudo rotation. The seam of this conical intersection is along the fully symmetric stretch. The pair of the \( (\mu)^3A_2 \) and \( (\nu)^3B_1 \) triplet states follows the same pattern, although the energy differences between the respective equilibrium geometries (EG) and the transition states (TS) is slightly larger (see Table 2.2), and the barrier for pseudo rotation is higher. Such \( A_2/B_1 \) intersection causes the electronic wave function to gain a phase (change of a sign) along any path on the adiabatic PES that encircles CI\(^{11}\).

**Figure 2.6:** (Color) PESs of the ground (X) and the first eight excited states of cyclic \( N_3^+ \). Coordinates are as in Fig. 2.5. Three out of four states in each multiplicity are almost degenerate at \( D_{3h} \) geometry, two being exactly degenerate.
The four lower excited states ($\alpha$, $\beta$, $\gamma$, and $\delta$) show a different and more complicated behavior, due to the double degeneracy of initial and target MOs (Fig. 2.1). Instead of a JT pair, they form a JT quartet: four almost degenerate electronic states, which are all unstable at $D_{3h}$ and distort to lower symmetries. Calculated PES of this intersection are presented in Fig. 2.6, and the excited state characters around the intersection point are sketched in Fig. 2.3 (see also PES cuts along $C_{2v}$ distortions in Fig 2.4.) Obviously, this is not a quadruply degenerate intersection – only two out of the four electronic states are exactly degenerate at $D_{3h}$, as described above. Nevertheless, all four states around the intersection strongly interact, which results in a fascinating pattern. For example, the intersection of the two degenerate states is *glancing* rather than *conical*, and the energy depends only quadratically on the displacements from the intersection point$^{6,7}$, as explained in details in section 2.5. Note that the singlets (left panel, Fig. 2.3) form almost a triply degenerate intersection: $(\beta - \gamma)^1B_1$ state is only 0.02 eV (Table 2.1) lower than the $(\alpha - \delta)^1A_2((\beta + \gamma)^3B_1$ pair. Interestingly, the order and the character of the excited states at $D_{3h}$ is different for singlets and triplets, although it becomes the same for the geometries distant from the equilateral triangle as shown by the labels on the left and right sides of the plots in Fig. 2.3.

The intersection topology is further clarified by the additional scan along the fully symmetric stretch normal bond $Q_{ss}$ that corresponds to changing the overall size of the equilateral triangle (Fig. 2.7). All four states of each multiplicity remain close in energy along $Q_{ss}$, and the two exactly degenerate states retain their degeneracy (solid line in Fig. 2.7) forming the seam of the glancing intersection. However, the non-degenerate states (filled circles and squares) slightly change their energy position relative to the
glancing intersection, which changes the order of the triplet states and even leads to additional accidental degeneracies of the $(\alpha + \delta)^3A_2$ or $(\beta - \gamma)^3B_1$ states with the glancing intersection at some $D_{3h}$ geometries (encircled in Fig. 2.7).

**Figure 2.7:** EOM-CCSD/6-311G* potential energy surface scans along symmetric stretch normal coordinate for the lowest $A_2$ and $B_1$ excited states. Singlets are shown on the left plot, triplets – on the right. Solid line shows two exactly degenerate states the $(\alpha - \delta)^1A_2$ and $(\beta + \gamma)^1B_1$, i.e. the seam of the intersection. Circles and squares correspond to the non-degenerate $(\alpha + \delta)^1A_2$ and $(\beta - \gamma)^1B_1$ states, respectively. Big circles on the right plot show two three-state PES intersections. $R_{NN}$ is a bond length of equilateral triangle, vertical dashed line points at the cyclic $N_3^+$ ground state equilibrium geometry.

Optimized geometries, frequencies and adiabatic excitation energies of the excited states described above are presented in Table 2.2. As in many JT triatomics, one sheet of $(\beta)/(\gamma)$ singlet and triplet PES has a minimum (EG), and another — a transition state, the later corresponding to the potential barrier for pseudo rotation motion between the equivalent EG minima. $(\alpha)/(\delta)$ states could follow the similar pattern, however, the $(\alpha)$ singlet and triplet states are dissociative along the $C_{2v}$ distortion. If the $C_{2v}$ constrain is lifted, the $(\alpha)$ states relax to linear structures: the $(\alpha)^1A_2$ assumes $C_{\infty v}$ geometry.
with $R_{NN} = 1.178 \text{ Å}$, whereas the triplet $(\alpha)^3A_2$ becomes $D_{\infty h}$ with $R_{12} = 1.123 \text{ Å}$ and $R_{23} = 1.279 \text{ Å}$.

The shape of the $\alpha/\delta$ and $\beta/\gamma$ PESs crossings is different from that of $\mu/\nu$ CI (and also from the $^2B_1/^2A_2$ intersection in neutral cyclic $N_3$), as the surfaces $\alpha/\delta$ and $\beta/\gamma$ have only a quadratic dependence on a displacement from the intersection point. Thus, even though there are two exactly degenerate JT states, the intersection is glancing rather than conical and adiabatic PESs do not have singularities.

This changes the behaviour of electronic wavefunction in the vicinity of the intersection: although character of the electronic wave function changes along the path around the intersection, the point group symmetry remains the same, and, therefore, the electronic wave function does not gain a sign change. Thus, there is no geometric phase effect along any path that stays on one of the four adiabatic PESs and encircles this intersection$^6$, which is not surprising, in view of the absence of a singularity point.

### 2.5 The analysis of the $(E+A+B) \otimes e$ problem in cyclic $N_3^+$

The electronic Hamiltonian $H = T_e + U(r, Q)$ can be expanded as Taylor series with respect to small nuclear displacements $Q_\rho$ from a reference high symmetry configuration ($Q_\rho = 0$):

$$H = H^0 + \sum_\rho \frac{\partial H}{\partial Q_\rho} Q_\rho + \sum_{\rho, \sigma} \frac{\partial^2 H}{\partial Q_\rho \partial Q_\sigma} Q_\rho Q_\sigma + \ldots = H^0 + V \quad (2.3)$$
We truncate this expansion at linear terms and start by solving Schrödinger equation for Hamiltonian $H^0$. The perturbation $V$ thus includes linear vibronic coupling terms $\sum_{\rho}(\partial H/\partial Q_\rho) Q_\rho^{1,2}$.

Instead of taking eigenfunctions of $H^0$ as a basis set for a subsequent perturbative treatment, we choose to employ a diabatic basis of $\text{HOMO} \rightarrow \text{LUMO}$ CSFs (see Fig. 2.1). These CSFs are close to adiabatic states for $C_{2v}$ distorted geometries, whereas at $D_{3h}$ ($Q_\rho = 0$) the corresponding adiabatic states (i.e., eigenstates of $H^0$) are the linear combinations of CSFs, as given by Eq. (2.1).

We employ normal coordinates: bending $Q_b$, asymmetric stretch $Q_{as}$, and symmetric stretch $Q_{ss}$, which are of $a_1$, $b_2$ and $a_1$ symmetry (in $C_{2v}$), respectively. We will consider $Q_b$ and $Q_{as}$, which constitute the $e'$ degenerate vibration. The third normal coordinate, $Q_{ss}$, describes breathing motion, which does not lift the degeneracy between MOs and CSFs. This mode will be discussed in the end of the section.

The matrix elements $V_{ij}$ of the vibronic coupling term are:

$$V_{ij} = \langle \Psi_i | \sum_{\rho} \frac{\partial H}{\partial Q_\rho} Q_\rho | \Psi_j \rangle = \sum_{\rho} \langle \Psi_i | \frac{\partial U}{\partial Q_\rho} | \Psi_j \rangle Q_\rho = \sum_{\rho} F_{ij}^{Q_\rho} Q_\rho$$  \hspace{1cm} (2.4)

where $\{\Psi_k\}$ are the diabatic $\{(\alpha)A_2, (\delta)A_2, (\beta)B_1, (\gamma)B_1\}$ basis functions.

Selection rules for $F_{ij}^{Q_\rho}$, derivative or linear vibronic coupling constant, are readily derived from the group theory considerations. $V_{ij}$ is non-zero only if $\Gamma_{(i|} \otimes \Gamma_{Q_\rho} \otimes \Gamma_{|j)}$ includes totally symmetric irrep $A_1$, where $\Gamma_{(i|}$, $\Gamma_{|j)}$ and $\Gamma_{Q_\rho}$ are the irreps of the $\Psi_i$, $\Psi_j$ diabats and the $Q_\rho$ normal mode, respectively. Thus, the linear vibronic coupling is non-zero between the states of the same symmetry only along the bending normal coordinate, e.g., $\Gamma_{(B_1|} \otimes \Gamma_{Q_b(a_1)} \otimes \Gamma_{|B_1)} \supset A_1$. For the states of different symmetry, i.e. $A_2$ and $B_1$, it is non-zero only along the asymmetric stretch: $\Gamma_{(A_2|} \otimes \Gamma_{Q_{as}(b_2)} \otimes \Gamma_{|B_1)} \supset A_1$. Thus, the vibronic coupling matrix elements $V_{ij}$ are:
\[
\langle \Psi_i^{A2} | V | \Psi_j^{A2} \rangle = F_{ij}^{Q_b} Q_b
\]
\[
\langle \Psi_i^{B1} | V | \Psi_j^{B1} \rangle = F_{ij}^{Q_b} Q_b
\]
\[
\langle \Psi_i^{B1} | V | \Psi_j^{A2} \rangle = F_{ij}^{Q_{as}} Q_{as}
\] (2.5)

The $H^0$ off-diagonal matrix elements are non-zero only between the states of the same symmetry:

\[
\langle \Psi_i^{A2} | V^0 | \Psi_j^{A2} \rangle = V_{AA}^0
\]
\[
\langle \Psi_i^{B1} | V^0 | \Psi_j^{B1} \rangle = V_{BB}^0
\]
\[
\langle \Psi_i^{B1} | V^0 | \Psi_j^{A2} \rangle = 0
\] (2.6)

Using Eqs. (2.5) and (2.6), the Hamiltonian in the diabatic basis set \{$(\alpha)A_2$, $(\delta)A_2$, $(\beta)B_1$, $(\gamma)B_1$\} assumes the following form:

\[
H(Q_b, Q_{as}) = \begin{pmatrix}
E_A + k_A Q_b & V_{AA}^0 & F_{\alpha\beta} Q_{as} & F_{\alpha\gamma} Q_{as} \\
V_{AA}^0 & E_A - k_A Q_b & F_{\delta\beta} Q_{as} & F_{\delta\gamma} Q_{as} \\
F_{\alpha\beta} Q_{as} & F_{\delta\beta} Q_{as} & E_B + k_B Q_b & V_{BB}^0 \\
F_{\alpha\gamma} Q_{as} & F_{\delta\gamma} Q_{as} & V_{BB}^0 & E_B - k_B Q_b
\end{pmatrix}
\] (2.7)

where $k_A = F_{\alpha\alpha}^{Q_b} = -F_{\delta\delta}^{Q_b}$ and $k_B = F_{\beta\beta}^{Q_b} = -F_{\gamma\gamma}^{Q_b}$.

Along the bending normal mode $Q_b$, when $Q_{as} = 0$, CSFs of the different symmetry are not coupled, and Hamiltonian (2.7) assumes a block diagonal form. Thus,
pairs \{((\alpha)A_2, (\delta)A_2)\} and \{((\beta)B_1, (\gamma)B_1)\} form two pairs of non-crossing adiabats (see Fig. 2.8, compare to Fig. 2.3).

\[
\begin{pmatrix}
E_A + k_A Q_b & V_{AA}^0 & 0 & 0 \\
V_{AA}^0 & E_A - k_A Q_b & 0 & 0 \\
0 & 0 & E_B + k_B Q_b & V_{BB}^0 \\
0 & 0 & V_{BB}^0 & E_B - k_B Q_b
\end{pmatrix}
\]

\[
U_A^\pm = E_A \pm \sqrt{(k_A Q_b)^2 + (V_{AA}^0)^2} \\
U_B^\pm = E_B \pm \sqrt{(k_B Q_b)^2 + (V_{BB}^0)^2} \\
U_A^+ = U_B^+
\]

Figure 2.8: The Hamiltonian in the diabatic (left) and adiabatic (right) representations along the bending normal mode \(Q_b\). Since the Hamiltonian is block diagonal, the pairs of states of the same symmetry do not interact with each other, and form two non-crossing pairs (see text).

At \(D_{3h}\), i.e. when \(Q_b = 0\) and \(Q_{as} = 0\), it is required by symmetry, Eq. (2.2), that one of the \(A_2\) states (\(U_A^\pm\)) is degenerate with one of the \(B_1\) states (\(U_B^\pm\)), i.e., in the example shown in Fig. 2.8 the intersection condition is \(U_A^+ = U_B^+\), which gives rise to

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the additional condition $E_A + |V_{AA}^0| = E_B + |V_{BB}^0|$. By shifting the energy scale such that one of the diabatic energies at the intersection is zero, this condition becomes:

$$|V_{BB}^0| = |V_{AA}^0| - E_B$$

$$E_A = 0$$

(2.8)

The coupling between the two degenerate states at $(Q_b = 0, Q_{as} = 0)$ is zero by virtue of Eqs. (2.5) and (2.6). Thus, the derivatives of the potential energy surfaces ($U_i$) along the bending coordinate (see Fig. 2.8) are zero:

$$\left. \frac{\partial U_i}{\partial Q_b} \right|_{Q_{as}=Q_b=0} = 0, \; i = 1 \ldots 4,$$

(2.9)

which means that the linear terms are absent and the intersection is glancing rather than conical.

The Hamiltonian along the asymmetric stretch $Q_{as}$ is obtained from matrix (2.7) by using $Q_b = 0$ and condition (2.8). If only two intersecting states are considered, the problem is similar to the familiar conical intersection$^4,5$ of $E''$ degenerate states:

$$H = \begin{pmatrix} k_A Q_b & F_{\alpha\beta} Q_{as} \\ F_{\alpha\beta} Q_{as} & k_B Q_b \end{pmatrix}$$

(2.10)

However, because of the two other states $A_2$ and $B_1$, which are almost degenerate with $E''$ pair, the linear vibronic coupling constants $F_{ij}^{Q_{as}}$ are non-zero and the 4x4 full Hamiltonian should be considered at the first order of perturbation theory.
This 4x4 problem can be solved analytically, e.g., by using MATHEMATICA\(^2\). The resulting (rather tedious!) expressions for eigenvalues can be differentiated, which reveals that the eigenvalues’ derivatives along the asymmetric stretch coordinate are also zero, similarity to the derivatives along \(Q_{bh}\). Thus:

\[
\frac{\partial U_i}{\partial Q_{\text{as}}} \bigg|_{Q_{\text{as}}=Q_{bh}=0} = 0, \; i = 1 \ldots 4
\]  

(2.11)

and, therefore all four potential energy surfaces \((E'' + A_2 + B_1)\) depend only quadratically on the displacements along the degenerate vibration \(e'' = Q_{bh} + Q_{\text{as}}\) from \(D_{3h}\) geometry, i.e. they have an extremum at the symmetric configuration. Note, that the inclusion of the second order terms in the perturbation does not change the derivatives in Eqs. (2.9) and (2.11).

Thus, the intersection of four HOMO-LUMO excited states is glancing\(^{42-44}\), and all four \((E + A + B) \otimes e\) vibronically coupled states follow a pseudo Jahn-Teller distortion. Contrary to the conical intersection case, there is no geometric phase effect along any path that encircles the intersection point\(^7,24,26\).

The absence of linear terms can also be demonstrated by considering 2x2 block of the Hamiltonian in the basis of adiabatic JT states (i.e., two degenerate eigenstates of \(H^0\)), as elegantly shown by Pupyshev\(^3\) The proof requires the construction of complex \(e'\) and \(e''\) MOs obtained from \(a_1/b_2\) HOMOs and \(a_2/b_1\) LUMOs:

\[
e'_{\pm} = \frac{1}{\sqrt{2}} (a_1 \pm i b_2)
\]

\[
e''_{\pm} = \frac{1}{\sqrt{2}} (-b_1 \pm i a_2)
\]

\(2.12\)


\(^3\)V.I. Pupyshev, private communication.
In this basis, two degenerate adiabatic states $\Psi_{E+}$ and $\Psi_{E-}$ are simply single $e'_+ \rightarrow e''_+$ and $e'_- \rightarrow e''_+$ excitations:

$$\Psi_{1,3}^{E+} = \frac{1}{\sqrt{2}} (|e'_+\alpha e'_-\alpha e''_+\beta\rangle \pm |e'_+\beta e'_-\alpha e''_+\alpha\rangle)$$

$$\Psi_{1,3}^{E-} = \frac{1}{\sqrt{2}} (|e'_+\alpha e'_-\beta e''_+\alpha\rangle \pm |e'_+\alpha e'_-\beta e''_+\beta\rangle)$$  \hspace{1cm} (2.13)

The above can be derived by either transforming the original adiabatic states into the new MO basis, or by symmetry considerations. In terms of diabatic CSFs from Fig. 2.1, these states are:

$$\Psi_{1,3}^{E \pm} = \frac{1}{\sqrt{2}} \left[ (|\langle \alpha \rangle A_2 \rangle - |\langle \delta \rangle A_2 \rangle \pm i (|\langle \beta \rangle B_1 \rangle + |\langle \gamma \rangle B_1 \rangle) \right]$$  \hspace{1cm} (2.14)

As clearly seen from Eq. (2.13), $\Psi_{E+}$ is *doubly excited* with respect to $\Psi_{E-}$. Neglecting the changes in MOs upon small geometric distortion, the perturbation operator $\frac{\partial U}{\partial Q}$ is a one-particle operator, and, therefore, the corresponding matrix element is zero. There is no linear dependence in $\langle \Psi_{E\pm} | \frac{\partial U}{\partial Q_{ss}} | \Psi_{E\pm} \rangle$ and $\langle \Psi_{E\pm} | \frac{\partial U}{\partial Q_b} | \Psi_{E\pm} \rangle$ diagonal terms because of the symmetry. Note that double degeneracy of both initial and target MOs (e.g., HOMO and LUMO) is required for the two respective electronic states to be doubly excited w.r.t. each other. Thus, both proofs show that the cancellation of linear terms occurs due to the presence for 4 interacting CSFs.

Change of the overall size of cyclic $N^+_3$ under $D_{3h}$ constraint corresponds to the symmetric stretch (triangle breathing) $Q_{ss}$ ($a_1$) motion, with $Q_b = Q_{cas} = 0$. The $E''$, or $A_2 + B_1$ pair of states remains degenerate at any point along $Q_{ss}$. Both zero- and first-order coupling terms between the states of different symmetry are identically zero by symmetry, which means that the $A_2$ states do not interact with the $B_1$ states along $Q_{ss}$,
as well as along $Q_b$ normal mode of the same $a_1$ symmetry. However, the derivative coupling between two states of the same symmetry, e.g., $|\langle \alpha \rangle A_2 \rangle$ and $|\langle \delta \rangle A_2 \rangle$, is non-zero along the $Q_{as}$, and can accidentally cancel out the zero-order coupling term $V_{AA}$, which results in a triple degeneracy $(E'' + A_2)$. By setting $Q_{as}$ to be equal zero at such triple degeneracy point, and taking into account conditions (2.8), Hamiltonian (2.7) assumes the following form:

\[
\begin{pmatrix}
  k_A Q_b & 0 & F_{\alpha\beta} Q_{as} & F_{\alpha\gamma} Q_{as} \\
  0 & -k_A Q_b & F_{\delta\beta} Q_{as} & F_{\delta\gamma} Q_{as} \\
  F_{\alpha\beta} Q_{as} & F_{\delta\beta} Q_{as} & E_B + k_B Q_b & -E_B \\
  F_{\alpha\gamma} Q_{as} & F_{\delta\gamma} Q_{as} & -E_B & E_B - k_B Q_b
\end{pmatrix}
\]

(2.15)

In this case, both derivatives $\partial U_i / \partial Q_b$ and $\partial U_i / \partial Q_{as}$ for $i = 1 \ldots 4$ at $Q_{as} = Q_b = 0$ are non-zero, and the intersection has a conical shape in $(Q_{as}, Q_b)$ coordinates: triple conical intersection and a non-degenerate fourth surface with the singularity in the origin ($Q_{as} = 0, Q_b = 0$). Triple CIs, which are not defined by the high nuclear symmetry, were characterized by Matsika and Yarkony\cite{45} as an accidental intersection of two seams of conical intersections. In triatomics, this type of CI was found, for example, in $H_2+H^46$. In cyclic $N_3^+$, however, the triple CI is formed by two crossing seams of $A''/A''$ conical intersection (in $C_s$) and the $A_2/B_1$ glancing intersection (along $D_{3h}$).

To conclude, interactions of a JT pair of states with other states removes linear terms and change the intersection from conical to glancing thus eliminating geometric phase effects.
2.6 Ionization energy and photoelectron spectrum

The cyclic $N_3^+$ ionization energy was calculated by CCSD(T) with the basis set extrapolation, as described in Sec. 2.2. The results are presented in Fig. 2.9. Energy of both the neutral and the cation were calculated with four different basis sets. The energy difference extrapolated to the basis set limit is 10.52 eV. Zero point energy (ZPE) of the cation in the harmonic approximation is 0.239 eV (see Table 2.2), and for the neutral cyclic $N_3$ E-symmetry vibrational ground state — 0.164 eV$^{11}$. Thus, with the ZPE correction, the adiabatic $I_{P_{00}}$ is 10.595 eV. This result supports the experimental measurement of IE for cyclic $N_3^{18}$ of 10.62±0.07 eV.

Figure 2.9: $I_E_{ee}$ (not ZPE corrected) calculated as a difference between neutral’s and cation’s CCSD(T) total energies in the basis set limit. ZPE corrected IE, $I_{E_{00}}$, is 10.595 eV.
IE of the linear N\textsubscript{3} radical is 11.06 eV\textsuperscript{47}. Therefore, the difference in IEs of the cyclic and linear N\textsubscript{3} is only 0.44 eV, which is comparable to vibrational energy of possibly hot photofragments. Thus, more detailed analysis of photoelectrons is required to unambiguously assign the observed product as cyclic N\textsubscript{3}. Below we discuss general features of the cyclic N\textsubscript{3} photoelectron spectrum. The calculation of the spectrum and the comparison with the experiments was reported elsewhere\textsuperscript{33}.

The lowest electronic states of the cation that are bright in a photoelectron experiment, are those that are derived from neutral cyclic N\textsubscript{3} by one electron ionization: the ground X\textsuperscript{1}A\textsubscript{1} and (\(\alpha\)), (\(\beta\)), (\(\nu\)) excited states, as well as (\(\gamma\)), (\(\delta\)), and (\(\mu\)) for the photoionization from \(^2\text{B}_1\) (EG) and \(^2\text{A}_2\) (TS), respectively. Since neutral’s vibrational wave function is delocalized along the pseudorotation coordinate over \(^2\text{B}_1\) and \(^2\text{A}_2\) states\textsuperscript{12}, both sets of the cation’s excited states can be produced in one electron photoionization.

Thus, all lowest excited states discussed in this work can contribute to the photoelectron spectrum, and, since they are close in energy and strongly coupled, calculation of the full photoelectron spectrum become a challenging problem.

The Franck-Condon factors, however, are very different for many of the states. For example, the lowest excited states, (\(\alpha\))\textsuperscript{1}\text{A}_2 and (\(\alpha\))\textsuperscript{3}\text{A}_2, are almost dissociative along \(C_{2v}\) distortion (see Table 2.2) and collapse to linear equilibrium structures. Because of this geometry difference, the Franck-Condon factors for these \(\alpha\) states and neutral N\textsubscript{3} are small, and they should produce only a background signal in the photoelectron spectrum. All other excited states are at least 3.8 eV higher than the cation ground state. Thus, the lower energy part (\(E_{ex} < 14\) eV) of the photoelectron spectrum can be well described as a transition from the \(^2\text{B}_1/^2\text{A}_2\) pair of states of the neutral to the ground X\textsuperscript{1}A\textsubscript{1} state of the cation. Such calculation should include the geometric phase effect in neutral N\textsubscript{3}\textsuperscript{33}. 

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2.7 Chapter 2 conclusions

In this chapter we described twelve lowest excited states of cyclic N$_3^+$. Eight lowest states (four singlets and four triplets) derived from single electronic excitations from doubly degenerate HOMO to doubly degenerate LUMO are close in energy at the ground state equilibrium geometry ($D_{3h}$) and exhibit a complicated Jahn-Teller behavior. Only two out of four states in each multiplicity are exactly degenerate and form an intersection seam along the symmetric stretch normal mode. However, this intersection is glancing rather than conical, because it is affected by interactions with two other non-degenerate states. Thus, adiabatic PESs do not have singularities at the intersection point, unless accidental triple degeneracy occurs. Therefore, these glancing intersection do not cause a geometric phase effect, which occurs in cyclic N$_3$ ground state or any other system with CI.

Stationary points of the excited states PES were also characterized. Cyclic N$_3$ ionization energy was estimated to be 10.595 eV, in a good agreement with recent experiments. Photoelectron spectrum of cyclic N$_3$ in the energy range $E_{ex} < 14$ eV predicted to be dominated by the transitions between the lowest electronic states of neutral N$_3$ and the ground state of the cation.
Table 2.2: $C_{2v}$ constrained optimized geometries, harmonic vibrational frequencies, total ($E_{\text{tot}}$) and adiabatic excitation ($E_{\text{ex}}$) energies of the ground ($X^1A_1$) and the lowest excited states calculated at the EOM-CCSD/cc-pVTZ level of theory. $\omega_1$, $\omega_2$ and $\omega_3$ are the frequencies of the symmetric stretch, bending and asymmetric stretch, respectively.

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<td>1.343</td>
<td>1.244</td>
<td>1.475</td>
<td>1.365</td>
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$^a$ ZPE for the transition states were calculated only for normal coordinates with real frequencies, i.e., bending and symmetric stretch.

$^b$ We were not able to calculate frequencies for the $(\mu)$ and $(\nu)$ states because of the numerical instability of finite difference procedure in the vicinity of the conical intersection.
2.8 Chapter 2 reference list


Chapter 3

Jahn-Teller distortions in the electronically excited states of sym-triazine

3.1 Chapter 3 introduction

In this chapter we present our study of the electronic structure of the excited states of sym-triazine. The next chapter describes the experimental consequences of the topology of the excited states of sym-triazine.

Triazine is the simplest member of azobenzenes family, and its isomers have attracted considerable experimental and theoretical attention\(^1\)\(^-\)\(^12\). Triazines are isoelectronic with benzene, the simplest aromatic molecule, however, the presence of heteroatoms introduces an interesting twist in their electronic structure and allows one to investigate how chemical and physical properties of benzene (e.g., aromaticity) are modulated in homologous series.

One important difference between azobenzenes and benzene is their very dense electronic spectra\(^1\). In addition to the benzene-like (\(\pi \rightarrow \pi^*\) and \(\pi \rightarrow R\)) transitions, they include numerous transitions derived from the \(n \rightarrow \pi^*\) and \(n \rightarrow R\) excitations. Owing to the complexity of the electronic spectroscopy of azobenzenes, they have become popular benchmark systems for electronic structure methodology\(^5\)\(^,\)\(^8\)\(^,\)\(^10\)\(^,\)\(^12\).
Chemically, azobenzenes are less stable than benzene and, consequently, have a propensity to undergo three body dissociation. Among the three isomers of triazine, sym-triazine (Tz) is of special importance due to its high symmetry and the ability to dissociate into the three identical fragments, which motivated a number of experimental and theoretical studies of this system \(^2,6,7,9,11,13\)–\(^{15}\). The central question in these studies was whether the mechanism of the three-body break-up is concerted or stepwise. Recent experiments in Continetti group, in which HCN fragments were detected in coincidence with time and position resolution \(^{16}–^{18}\), demonstrated that both dissociation channels are open. While the mechanisms of concerted and stepwise dissociation have not yet been fully elucidated, most researchers agree that dissociation occurs following radiationless transition of electronically excited Tz to the ground electronic state \(^9,11,13\). Theoretical investigations of the ground state potential energy surface (PES) of Tz have found that the lowest transition state between the Tz molecule and the three HCN product is of \(D_{3h}\) symmetry \(^6,11\), thus fulfilling a necessary condition for the concerted symmetric dissociation. The two channels have been explained in terms of different initial conditions using reflection principle. The symmetric distribution of energy and momentum among three HCN fragments (concerted dissociation) ensues when the dynamics on the ground state PES is initiated from the symmetric wave packet, whereas asymmetric momentum distribution results from the wave packet with vibrational excitation in the asymmetric vibrational modes. Using Franck-Condon arguments (and assuming that the excited state lifetimes are sufficiently long such that the vibration wave packet can equilibrate prior to radiationless relaxation to the ground state), symmetric wave packet can be attributed to the relaxation from the electronic state with a symmetric PES, whereas the transition from an electronic state with an asymmetric (non-\(D_{3h}\)) PES will produce a non-symmetric wave packet. Thus, characterizing equilibrium geometries of the excited
electronic states of Tz played an important role in the theoretical interpretation of the Continetti’s experiments\textsuperscript{16–18}.

Due to the high symmetry of Tz ($D_{3h}$), many of its electronic and ionized states are derived from the transitions involving degenerate molecular orbitals (MOs), and, consequently, many of them are subject to Jahn-Teller (JT) distortions. Whereas the ionized states or states derived from the transitions in which either initial or target MOs are degenerate form a familiar ‘Mexican-hat’ two-state Jahn-Teller manifold, the states derived from the transitions between the pairs of degenerate MOs from a more complicated four-state manifold, in which the JT distortions of the two exactly degenerate states are so small that their intersection appears to be glancing rather than conical. This type of intersections have been characterized in $N_3^+$ both formally and computationally\textsuperscript{19,20}.

The focus of this chapter is on characterizing the two types of Jahn-Teller intersections in Tz. We further analyze the topologies of these manifolds and present a simple recipe of predicting whether a particular state from the glancing-like manifold have a distorted or nearly symmetric equilibrium structure from only one single point calculation at a symmetric geometry and the analysis of the electronic structure of the excited states. We also present optimized equilibrium geometries for the selected states to validate the predictions of this simple analysis and to quantify the magnitude of the JT distortions. Finally, we analyze the optimized geometries in terms of the displacements along normal modes of the ground-state Tz to make a connection with the Continetti’s experiments\textsuperscript{16–18}.

3.2 Theoretical methods and computational details

The ground state equilibrium geometry and vibrational frequencies were computed by the coupled-cluster with single and double substitutions (CCSD) method\textsuperscript{21} with the
cc-pVTZ basis set. Excitation energies and optimized structures of the electronically excited states were computed by equation-of-motion for excitation energies CCSD (EOM-EE-CCSD). The EOM-EE methods are capable of reproducing electronic degeneracies (e.g., in Jahn-Teller systems), as well as balanced description of interacting states of different character (e.g., Rydberg and valence), which is crucial in the case of Tz in view of its dense electronic spectrum and multiple JT manifolds. Equilibrium geometries and frequencies of the cation were computed by EOM-CCSD for ionization potentials (EOM-IP-CCSD) and the cc-pVTZ basis set. All geometry optimizations were conducted using analytic nuclear gradients EOM-CCSD and CCSD codes.

All electrons were correlated in geometry optimizations and excitation energy calculations. All calculations were performed using the Q-CHEM electronic structure program.

Basis set effects were investigated using a series of Pople basis sets with a varying number of diffuse and polarization basis functions. Vertical excitation energies of Tz at the CCSD/cc-pVTZ geometry calculated with different bases are summarized in Table 3.1. Most of the excited states energies of states are almost converged at the 6-311++G** level, e.g., the differences in the excitation energies relative to aug-cc-pVTZ do not exceed 0.05 eV for all the states below 8 eV, except some Rydberg and higher $n \rightarrow \pi^*$ states. For example, adding a second set of diffuse functions lowers excitation energies of the Rydberg states by 0.1 eV on average. Extra polarization functions increase energies of all the states by about 0.1 eV. Higher $n \rightarrow \pi^*$ states are mixed with a high density manifold of the Rydberg states in this energy region, which results in a stronger basis set dependence of the high valence states of the same symmetry as $n \rightarrow R_{\pi}$ states. The differences in excitation energies between the aug-cc-pVTZ basis
and a corresponding (but slightly smaller) Pople basis, 6-311(2+,+)G(3df,3pd), do not exceed 0.08 eV, and for most states are within 0.02 eV. Overall, the 6-311++G** basis set provides a balanced description of the valence states of Tz, and the results for the Rydberg states are close to the aug-cc-pVTZ ones due to the cancellation of errors. Thus, most of the excited states calculations presented below employ this basis set.

3.3 Electronically excited states at the neutral and the cation geometries: Assignments and symmetry analysis

Excitation energies and symmetries of the lowest excited states of Tz at the equilibrium geometries of the neutral and the cation are shown in Fig. 3.1. Both singlet and triplet manifolds are very dense and feature extensive (near)-degeneracies. All the excited states from Fig. 3.1 can be classified as belonging to the several different manifolds: Rydberg, valence $n \rightarrow \pi^*$, and valence $\pi \rightarrow \pi^*$, as described in Ref. 17.

All the relevant valence MOs of Tz are degenerate at $D_{3h}$: the HOMO ($\pi$, $e''$) and closely lying HOMO-1 ($n$, $e'$) pairs, as well as the Rydberg LUMO+1 ($R_{p}$, $e''$) and LUMO+2 ($\pi^*$, $e''$) pairs. The only low-lying non-degenerate orbital is the s-like Rydberg LUMO ($R_{s}$, $a'_1$).

Owing to this degeneracy pattern, all the states from Fig. 3.1 are derived from the transitions involving degenerate MOs, and, consequently, many of them are subject to JT distortions, as evidenced by the splittings between the degenerate states at the cation ($C_{2v}$) geometry (right panel of Fig. 3.1).
The $\pi \rightarrow R_s$ and $n \rightarrow R_s$ Rydberg states form a familiar two-state JT manifold, and undergo distortions to lower-symmetry, pretty much like in the cation. One of the states relaxes to the minimum, and another—to the transition state along the pseudorotation coordinate. The symmetries of these $n \rightarrow R_s$ states are $E'$: $e' \otimes a'_1 \rightarrow E'$, where $e'$ and $a'_1$ are symmetries of $n$ and $R_s$ orbitals, respectively. The behavior of the corresponding PES along a JT distortion coordinate is shown on the left panel of Fig. 1.2. Note that the symmetry of the lowest adiabatic state changes along the pseudorotation coordinate, which gives rise to the geometric phase effect causing the break down of Born-Oppenheimer approximation.

Excitations between the two doubly degenerate orbitals results in the four-states manifolds, two states being exactly degenerate as follows from the symmetry considerations. For example, symmetries of the electronic states in the $n \rightarrow \pi^*$ manifold can be obtained according to the irreducible representation multiplication rules: $e' \otimes e'' \rightarrow A''_1 + A''_2 + E''$, where $e'$ and $e''$ are the symmetry of the $n$ and $\pi$ orbitals, respectively. Relative ordering of the states in these manifolds can be different, and three possible cases are shown in Fig. 1.2, (b)-(d). The distinctive feature of the four-states manifolds is that all four states are strongly coupled together. As shown both formally and numerically for the $N_{3h}^+$ example\textsuperscript{19,20}, the result of these interactions is that the linear JT terms in the degenerate PESs in these manifolds almost vanish at the high symmetry geometry, and, consequently, the magnitude of the JT distortion is very small (e.g. 0.001 Å and $10^{-4}$ eV in $N_{3h}^+$). Thus, all four surfaces have extrema either at or very close to the symmetric geometry, and the intersection appears to be glancing rather than conical, resembling avoided crossing in diatomics. Consequently, the symmetries of all four adiabatic PESs do not change as one moves around a $D_{3h}$ point, provided that the radius
of the rotation is greater than their minute JT distortions. Thus, one can safely employ adiabatic PESs for calculating vibrational wave functions.

The analysis of the three different degeneracy patterns in the four-state manifolds presented in Sec. 1.3 reveals that the two upper surfaces always have symmetric minima, as depicted in Fig. 1.2(b-d). Thus, just from a degeneracy pattern at a symmetric configuration, the overall topology of the intersection can be mapped out. Note that without this analysis additional single-point calculation at a lower symmetry geometry (as in the right panel of Fig. 3.1), or even at optimized equilibrium geometry of a distorted state, is not very informative, e.g., the conical and glancing degeneracies split in a similar way, whereas the PES topologies are rather different.
Figure 3.1: Singlet and triplet excited states at the neutral $D_{3h}$ (left panel) and the distorted cation $C_{2v}$ (right panel) geometries. The frontier MOs ordering and the electronic configuration of the ground electronic state are shown in the insert. $\pi$ and $\pi^*$ orbitals are similar to those of benzene, whereas orbitals denoted by $n$ are derived from the nitrogens’ lone pairs. $R_s$ and $R_p$ denote Rydberg orbitals of $3s$ and $3p$ character, respectively.
Table 3.1: Total ground state energies (Hartrees) and vertical excitation energies (eV) of Tz calculated by EOM-CCSD.

<table>
<thead>
<tr>
<th>Ground state</th>
<th>6-311(+,+)$G^{**}$</th>
<th>6-311(2,+)$G^{**}$</th>
<th>6-311(+,+)$G(3df,3pd)$</th>
<th>6-311(2,+)$G(3df,3pd)$</th>
<th>aug-cc-pVTZ</th>
</tr>
</thead>
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<tr>
<td></td>
<td>HF, Hartree</td>
<td>CCSD, Hartree</td>
<td>HF, Hartree</td>
<td>CCSD, Hartree</td>
<td>HF, Hartree</td>
</tr>
<tr>
<td>Singlets</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>4.99</td>
<td>4.96</td>
<td>4.96</td>
</tr>
<tr>
<td></td>
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<td>5.04</td>
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<td>5.02</td>
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<td>5.06</td>
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<td>8.11</td>
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Table 3.2: Geometrical parameters of the ground electronic state of Tz, the Tz$^+$ cation, the $n \rightarrow \pi^*$ and $n \rightarrow R$ singlet excited states optimized equilibrium structures. Bond lengths are given in Angstroms, and angles are in degrees. The relaxation energies are calculated relative to the energy of the ground electronic state geometry.

<table>
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<tr>
<th>$\Delta E$, eV</th>
<th>Ground electronic state</th>
<th>Singlet $n \rightarrow \pi^*$ excited states</th>
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<th>Cation</th>
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<td>EOM-CCSD 6-311+G**</td>
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<td>$2^1B_1$</td>
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3.4 Optimized equilibrium geometries of the excited states in conical and glancing-like manifolds

In this section we present and discuss equilibrium geometries of the states from the valence $n \rightarrow \pi^*$ and $n \rightarrow R_s$ manifolds. The latter structures are very similar to that of the cation, whose ground state is derived by ionization from the $n$ orbital. These manifolds give rise to the two dissociation channels of Tz initiated by the charge exchange between Cs and Tz$^+$, and represent two different types of the JT intersections: four-state glancing like and two-state conical ones. Optimized geometries and relaxation energies are summarized in Table 3.2. The definitions of geometrical parameters (angles and distances) are presented in Fig. 3.2(c).

![Figure 3.2: CN bond lengths (a) and deviations from 120 degrees of hexagon ring angles (i.e., 120-NCN$_1$, 120-NCN$_2$, and 120-CNC) for the neutral Tz, the cation, and the $\pi^* \leftarrow n$ excited states. The definitions of structural parameters are shown in (c). The neutral and the top $\pi^* \leftarrow n$ states are of $D_{3h}$ symmetry, and the $2^1B_1$ state is nearly $D_{3h}$ symmetric.](image)

The Tz cation exhibits relatively strong JT distortions from $D_{3h}$ geometry, which results in 0.47 eV energy gain, a difference between vertical and adiabatic ionization energies of Tz. The potential energy profile along pseudorotation around the conical
intersection is almost barrierless, as the transition state \((^2B_2)\) is only about 0.01 eV higher than the ground \(^2A_1\) state at the EOM-IP-CCSD/6-311++G** level of theory. These values can be compared to JT distortions in the benzene cation, whose ground state is derived from ionization from the degenerate \(\pi\)-orbitals: relaxation of the cation from \(D_{6h}\) to \(D_{2h}\) is 0.18 eV with a transition state barrier for the pseudorotation only 0.003 eV above the ground state\(^{30}\). We attribute this difference to a stronger perturbation of the \(\sigma\) system by ionization form the \(n\) orbitals.

The barrier for pseudo-rotation is below ZPE, and, therefore, the lowest vibrational wavefunctions of the cation are delocalized around the conical intersection. Note that proper account of geometric phase effect is crucial for obtaining even qualitatively correct vibrational states\(^{35,36}\). The complications due to geometric phase can be avoided entirely by switching to diabatic representation, see, for example, Ref.\(^{37}\) and references therein.

Although glancing-like manifold of the four \(n \to \pi^*\) states have more complicated electronic structure, the vibrational wave functions of the top two states can be computed within BO approximation, due to special features of the four-states manifolds, which are explained in the Sec. 1.3. Note that the displacements from \(D_{3h}\) symmetry are indeed minute, as evidenced by the data in Table 3.2 and Fig. 3.2.

Fig. 3.2 allows one to quantify the magnitude of JT displacements in terms of bond-lengths and angles. Tz has \(D_{3h}\) symmetry if the three CN bonds are of equal length, and the sum of CNC and NCN angles is 240 deg, that is, if CNC and NCN deviate from 120 deg to an equal extent but with the opposing sign. Fig. 3.2 shows that this is exactly the case for the top \(^21A_2\) state from the \(n \to \pi^*\) manifold. The \(^21B_1\) state is also almost symmetric, as it is expected for the glancing-like manifold. The two lowest states from
this manifold ($1^1A_2$ and $1^1B_1$) are significantly distorted to $C_{2v}$ geometry, as the corresponding PESs have a maximum at $D_{3h}$. Note that the relaxation energies (difference between the Tz ground state geometry and the excited-state optimized structures) from Table 3.2 are similar in magnitude for all states (0.4-1.0 eV), however, for the two top states the relaxation occurs along the $D_{3h}$ “seam” of glancing-like intersection, whereas the two lowest states relax along the JT coordinate to $C_{2v}$.

Note that equilibrium geometries of the Rydberg $n \rightarrow \pi^*$ states are indeed very close to those of the cation: the differences are less than 0.008 Å for the CN bonds and less than 0.8° for the angles. Likewise, the energy gain upon the JT relaxation is also very similar (within 1 kcal/mol).

Finally, the magnitude of geometric relaxation can be analyzed in terms of the displacements along the normal modes of the neutral Tz, as presented in Table 3.3. The units for normal coordinates, which are the eigenstates of the mass-weighted Hessian, are Å/√amu. The two nearly symmetric $n \rightarrow \pi^*$ states are distorted mostly along the three fully symmetric $a'_1$ normal modes, the two other states and the cation are distorted along the in-plane normal modes of lower symmetries. The two lowest $n \rightarrow \pi^*$ states, $1^1A_2$ and $1^1B_1$, are asymmetric and the most active non-symmetric normal mode for the both states is $5e'$, with -11.07 and 0.34 displacements, respectively. This mode corresponds to the JT coordinate of the $n \rightarrow \pi^*$ states. Coupling between the normal modes is considerable at larger geometry relaxations, and several other non-$a'_1$ modes are active in the $1^1A_2$ state.

Normal mode mixing is even stronger in the cation (and the $n \rightarrow R_s$ excited state) due to larger distortion relative to the neutral $D_{3h}$ equilibrium geometry. Nevertheless, only two non-$a'_1$ normal modes contribute considerably: $5e'$ and $2a'_2$ with 6.92 and
-11.09 displacements, respectively, which are the most active normal modes. JT coordinate is 5e′ with opposite displacements of -1.58 and 1.26 for $^2A_1$ ground and $^2B_2$ transition states of the cation respectively.

In the recent study\textsuperscript{16–18}, it has been concluded that Tz dissociates symmetrically when prepared in the $2^1A_2 \rightarrow \pi^*$ state, and follows asymmetric dissociation from the Rydberg $n \rightarrow R$ excited state. Displacements along the normal modes of the neutral Tz molecule from the neutral equilibrium geometry shown in Table 3.3 demonstrate the suggested mechanisms. Indeed, the symmetric excited state, whose structure is different from the $D_{3h}$ ground state only by displacements along $a'_1$ normal modes ($2^1A_2$), will acquire symmetric ($a'_1$) vibration quanta upon the relaxation to the ground state, and in the case of fast, ballistic, dissociation to the three HCN, this vibrational excitation will transform into symmetrically distributed momenta of the fragments. Vibrational excitation of the non-$a'_1$ normal modes acquired via the Rydberg state will lead to the asymmetric momentum partitioning.

### 3.5 Chapter 3 conclusions

In this chapter we characterized electronically excited states of Tz at the equilibrium ground state geometry and at the geometry of the cation. Moreover, full geometry optimizations of the selected excited states were performed. JT distortions in the cation and the excited states were analyzed both formally and numerically. Analysis of the electronic structure of the excited states allows one to predict symmetry of the equilibrium geometry of the states derived from excitations between the two pairs of doubly degenerate orbitals from a single-point calculation at a symmetric geometry. This was demonstrated by discussing possible PES topologies and symmetries of the states from
the two- and four- manifolds giving rise to the conical and glancing intersections, respectively. Formal conclusions are supported by the optimized equilibrium geometries of the selected excited states.

This analysis can be applied to predict symmetries of the equilibrium structures of the states from four-states manifolds in other benzene-like aromatic molecules, whose electronic structure is similar to that of Tz.

In the next Chapter, we suggest that these two different types of manifolds give rise to two different dissociation mechanisms, concerted and stepwise\textsuperscript{16,17}. The difference between the two manifolds would also manifests itself in the vibrational spectra of the respective excited states. The order of vibrational states for the electronic state with the conical intersection should be affected by the geometric phase effect as it was observed in Na\textsubscript{3}\textsuperscript{38,39} and theoretically documented in N\textsubscript{3}\textsuperscript{35,36}, however, we expect no signature of the geometric phase effect in the case of the glancing-like intersections.
Table 3.3: Harmonic frequencies (cm\(^{-1}\)) and infrared intensities (km/mol, in parenthesis) of the \(n \rightarrow \pi^*\) excited states and the cation. The displacements from the neutral ground-state geometry along normal modes (\(\AA/\sqrt{amu}\)) are also shown whenever is greater than 0.01 \(\AA/\sqrt{amu}\). In plane and out of plane vibrations are labeled with (p) and (o) respectively.

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<thead>
<tr>
<th>Normal modes</th>
<th>Frequencies</th>
<th>Displacement from GS equilibrium geometry(^a)</th>
<th>Cation</th>
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</thead>
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<td>Ring(o)</td>
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<tr>
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3.6 Chapter 3 reference list


Chapter 4

The role of the excited state topology in three-body dissociation of sym-triazine: conical for stepwise, glancing for concerted.

4.1 Chapter 4 introduction

Dissociation of energetic molecules is one of the most fundamental processes in chemistry\(^1\). In atmospheric, planetary and biochemical reactions, dissociation is often induced by photoexcitation, whereas in high temperature environments (e.g., combustion) there is sufficient thermal energy to break bonds.

Proliferation of novel experimental and theoretical techniques have enabled physical chemists to gain increasingly more detailed mechanistic insights into dissociation processes. Experimentally, it has become possible to observe chemical transformations in a more direct fashion, e.g., to investigate dynamics of a well-characterized initial state rather than ensemble averages, and even monitor bond-breaking in real time by means of femtosecond spectroscopy. The development of experimental techniques has been paralleled by advances in theory, which progressed from qualitative interpretations to rigorous quantitative predictions in electronic structure and dynamics.
Yet, our understanding of the dissociation of polyatomic molecules is rather incomplete, even for processes as fundamental as three-body break-up\textsuperscript{2,3}. Since the first report of a three-body dissociation of azomethane in 1929\textsuperscript{4}, only about 30 systems capable of three-body photodissociation were characterized\textsuperscript{2}. Among these, there are only six molecules that produce three molecular fragments: azomethane, s-tetrazine, triazine, acetone, DMSO, and glyoxal. More examples of three-body break up have been observed in dissociative recombination and photodetachment\textsuperscript{5}. In dissociative recombination, where more energy is available, three-body dissociation becomes a dominant channel for many systems. Unfortunately, the dynamical information available in those studies is quite limited because those experiments are typically performed in ion storage rings at very high beam energies.

For almost every one of the above examples of three-body break-up, there is a history of controversy of whether the dissociation proceeds in a stepwise or a concerted fashion. The mechanistic controversy stems from the challenges of characterizing the dissociation of a polyatomic system at the molecular level. Several of the reactions are believed to be true “triple whammy” events proceeding through symmetric transition states and involving simultaneous (i.e., within one rotational period) breaking of two bonds. These reactions become even more fascinating when one realizes that the reverse reaction is a termolecular association reaction, and is generally improbable on account of collision statistics. Yet, termolecular reactions are important, the most prominent example being ozone formation in which a three-body reactive collision is essential part of the mechanism\textsuperscript{6}: \( \text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M} \).
Sym-triazine (Tz), the largest among the few molecules studied to date capable of photoinduced three body break-up, is the only one that produces three polyatomic products. Moreover, due to its high symmetry, it produces three identical fragments:

$$C_3N_3H_3^* \rightarrow 3HCN$$  

(4.1)

This unique feature of Tz facilitates unambiguous mechanistic interpretation of the dynamics — indeed, the symmetric kinetic energy distribution among the three fragments can only be observed in the concerted three-body process.

The concerted mechanism proposed in earlier studies of Tz dissociation has been a subject of considerable debate\textsuperscript{7–12}. In the photofragment translational spectroscopy (PTS) experiments\textsuperscript{7,8}, dissociation was initiated by 248 and 193 nm photo-excitation most likely into the $\pi^* \leftrightarrow n$ and $\pi^* \leftrightarrow \pi$ manifolds, respectively, but dissociation to three HCN occurs ultimately through decay to the ground state, as dictated by symmetry correlation arguments and energy balance\textsuperscript{13}. The original PTS study by Ondrey and Bersohn assumed that the HCN photoproducts were produced in a concerted fashion and, therefore, received an equal kinetic energy release (KER)\textsuperscript{7}, however, the later work by Gejo et al. presented evidence in favor of stepwise dissociation\textsuperscript{8}. \textit{Ab initio} calculations of transition states along with classical trajectory studies have found that the barrier to a symmetric concerted reaction lies lowest in energy, but have suggested that at higher excitation energies the stepwise mechanism could become more prevalent\textsuperscript{9–12}.

In this chapter we discuss the first direct observation of the symmetric three-body break up of Tz by using coincidence detection of neutral products coupled with translational spectroscopy, which allows a full kinematic description of the process. Coincidence experiments, which are capable of unambiguously distinguishing between symmetric and asymmetric dissociation, are no longer limited to ionic products\textsuperscript{14}. Continetti
and coworkers extended this technique to neutral species, and it has been applied to H$_3$.$^{15,16}$

Dissociation is initiated by charge exchange (CE) between Tz$^+$ and cesium, a technique for producing electronically excited neutral molecules$^{17–19}$. We have observed products with both symmetric (i.e., equal between the three fragments) and C$_{2v}$ (further referred to as “asymmetric”) momentum partitioning corresponding to two fast and one slow or two slow and one fast fragments. The former case suggests a concerted three-body breakup, while the latter is consistent with stepwise decomposition. While the underlying dissociation dynamics may be very complex and involve multiple electronic states, the reflection principle$^{20}$ suggests that the two processes proceed through at least two different electronic states with symmetric (D$_{3h}$) and asymmetric equilibrium geometries, as illustrated in Fig. 4.1.

A key feature noted for CE experiments is the potential to excite multiple initial electronic states$^{17}$. If CE occurs in a resonance regime, Tz is expected to be excited above its ground state by 6.12 eV$^{21}$, i.e., the difference between ionization energies of Tz and cesium (10.01 eV and 3.89 eV respectively). However, the amount of energy deposited in neutrals created by CE of keV cation beams and alkali electron donors can also occur off resonance, with transition probabilities depending on the energy defect, coupling strength, and relative velocity between the cation and electron donor$^{17,18,22}$. We found that the relative ratio of symmetric vs. asymmetric momentum partitioning depends on the beam velocity, which suggests that different excited states are populated and consequently decay via different mechanisms. To elucidate the nature of the initially excited state, and to determine how it influences the mechanism of the three-body breakup, we performed ab initio calculations of excited state potential energy surfaces
Figure 4.1: (Color) Two-dimensional representation of the ground and excited-state PESs demonstrating mapping of the initial wave function into the product distribution, i.e., reflection principle. The two coordinates are the reaction coordinate for the three-body dissociation and a symmetry lowering displacement, e.g., Jahn-Teller deformation. The reflection principle, which assumes ballistic dissociation on the lowest PES, predicts symmetric energy partitioning for the process initiated on the symmetric PES, and asymmetric for a distorted one.

The calculations and analysis of several Jahn-Teller (JT) manifold topologies allowed us to identify the most likely initially populated states as the $A_1$ 3s Rydberg and the $A_2 \pi^* \leftarrow n$ valence states.

It should be noted that the influence of initially excited electronic states on the outcome of a reaction on the ground state is not new to chemistry. For example, mechanisms of photochemical reactions are often explained by structures of relevant conical
intersections, as was done Mebel and coworkers in their study of Tz photodissociation. Recently, Suits and coworkers argued that the selection between different channels of propanal cation dissociation occurs because the molecule finds itself in different configurations on the ground state given different starting points (i.e., cis or gauche conformations) on the excited state. The motif suggested by the present work is different. As evidenced by geometry optimizations of electronically excited states and the PES scans presented below, the distortions of electronically excited Tz are relatively small owing to relatively rigid π-system. Thus, the molecule is unlikely to sample vastly different conformations, and the momentum partitioning is influenced by whether or not there is a vibrational excitation in asymmetric modes.

4.2 Experimental methods and computational details

4.2.1 Experimental methods

The fast-beam translational spectrometer capable of detecting multiple neutral fragments in coincidence is a modified version of a previously described apparatus. Tz was produced using an electrical discharge in a 1 kHz pulsed supersonic expansion (25 psig backing pressure) of a mixture of room temperature Tz (97%, Alfa Aesar) vapor seeded in 250 psig He. Cations were then skimmed, electrostatically accelerated to 12 or 16 keV, and re-referenced to ground using a high-voltage switch. The cation of interest (m/z=81) was mass-selected by time of flight and electrostatically guided through a 1 mm interaction region containing Cs vapor (approximately 10⁻⁵ torr). Any unreacted cations were deflected out of the beam path and monitored with an ion detector. Neutrals formed in the interaction region were allowed to propagate 110 cm forward to a time- and position-sensitive microchannel plate based delay-line anode. The neutral particle
detector was capable of coincidence detection of the time and position of arrival for up to eight particles in a single event given a favorable recoil geometry. Given the beam energy, parent cation mass, and fragment masses, a full three-dimensional kinematic description of the dissociation process was obtained, including the center-of-mass-frame KER and product momentum partitioning.

Empirical product KER distributions were constructed for the three-body dissociation of Tz upon CE of the Tz\(^+\) with Cs at both 12 and 16 keV cation beam energies. Due to the finite size of the neutral particle detector, certain events were not detected. Monte Carlo simulations of the detector’s geometric efficiency were used to correct the empirical distributions to produce true probability distributions, denoted as \(P(\text{KER})\)\(^{16,27}\). A similar procedure employing Monte Carlo simulations was also used to correct the Dalitz plots presented below.

**The Dalitz plot**

Momentum and energy partitioning in three-body dissociation can be most clearly examined using a correlated method of displaying the data such as a Dalitz plot\(^{28}\), which is an equilateral triangle with each axis corresponding to the fractional square \((f_i)\) of the momentum imparted to a single neutral fragment:

\[
f_i = \frac{|\vec{p}_i|^2}{\sum_i |\vec{p}_i|^2}
\]

(4.2)

In short, a single point on the three-axis plot within the inscribed circular region of momentum conservation represents a specific arrangement of three momentum vectors pointing from the center-of-mass (c.m.) of the system to the c.m. of the recoiling fragments, as shown in Fig. 4.2. Thus, the Dalitz plot is a histogram of events and
the intensity on the plot corresponds to the number of recorded events with a particular momentum distribution. Since Tz dissociates to three indistinguishable equal-mass HCN fragments, the plot exhibits a six-fold degeneracy and three-fold symmetry. Note that the momentum vectors represented in the Dalitz plot are constructed from final c.m. frame trajectories. For concerted dissociation, the Dalitz plot can be used to identify an instantaneous impulsive force driving the fragments apart. However, the final c.m. frame trajectories in a stepwise process are the result of several intermediate events and not readily apparent in the Dalitz plot alone.

Figure 4.2: The Dalitz plot represented as a map of the momentum partitioned to three equal-mass fragments. Each axis of the Dalitz plot corresponds to the squared fraction of the momentum imparted to one of the three fragments. The center point of the plot corresponds to the equal momentum partitioning. Dashed lines represent regions of $C_{2v}$ symmetry within the plot, which correspond to one fast and two slow (acute feature) or to one slow and two fast (obtuse feature) fragments.
Monte Carlo simulations were used to interpret characteristic features observed in Dalitz distributions in the present experiment. While the symmetric Dalitz feature discussed below represents a concerted process, the mechanism giving rise to the $C_{2v}$ feature is not as apparent. To determine how a stepwise mechanism would manifest itself in the Dalitz plot, we conducted ad hoc Monte Carlo simulations. The simulations demonstrated that the acute feature can indeed be interpreted as the result of a stepwise reaction.

4.2.2 Theoretical methods and computational details

Electronically excited states of Tz were computed using the equation-of-motion coupled-cluster method with single and double substitutions (EOM-EE-CCSD)\textsuperscript{29–32} employing the 6-311++G** basis set. The cation states were described by the EOM-CC method for ionized states, EOM-IP-CCSD\textsuperscript{33,34}. Electronic states of the combined (Cs-Tz)$^+$ system were characterized by EOM-EE-CCSD using a closed-shell reference state corresponding to the lowest electronic state of the Cs$^+$-Tz system. The Hay-Wadt effective core potential basis set with an additional polarization function with an exponent of 0.19 for a Cs atom as suggested by Glendenning \textit{et al.}\textsuperscript{35}, and 6-311+G* basis set for C, H and N atoms.

The advantage of EOM-CC methods is that it allows a balanced description of multiple electronic states of different nature, e.g., Rydberg and valence, degenerate JT states, interacting charge-transfer (e.g., Cs$^+$-Tz$^*$ and Cs-Tz$^+$) states, etc. Moreover, the EOM-CC wave-functions for the electronically excited and ionized states of Tz employ the same closed-shell reference, i.e., the ground electronic state of Tz. This feature facilitated calculation of electronic coupling elements governing the CE process.
The EOM-EE wave functions of the combined (Cs-Tz)$^+$ system were used to evaluate the diabatic electronic couplings ($h_{ab}$) between the Cs-Tz$^+$ and Cs$^+$-Tz$^*$ states (i.e., quantities that control CE) by the generalized Mulliken-Hush (GMH) method$^{36,37}$. The GMH method developed by Cave and Newton to compute the diabatic-adiabatic transformation matrix and the coupling elements is based on the assumption that there is no dipole moment coupling between the diabatic states, and thus the dipole moment matrix is diagonal in this representation. This corresponds to the two states with the largest charge separation, i.e. charge localized on the reactants and products. The so-defined transformation matrix can hence be applied to the Hamiltonian matrix in the adiabatic representation yielding the coupling as the off-diagonal element. This leads to the following expression:

$$h_{ab} = \frac{\mu_{12}\Delta E_{12}}{[\Delta\mu_{12}^2 + 4(\mu_{12})^2]^{1/2}},$$

(4.3)

where the letter and number subscripts refer to diabatic and adiabatic quantities, respectively, $\mu_{12}$ is the transition dipole moment, $\Delta\mu_{12}$ is the difference between the permanent dipole moments, and $\Delta E_{12}$ is energy gap between the states. These couplings were used to evaluate probabilities of populating different electronic states in CE process using the Demkov model$^{38}$, as described below.

PES scans for the (Cs-Tz)$^+$ electronic states were computed in two steps. First, the total energies for the (Cs-Tz)$^+$ system were calculated for the triazine part at the neutral ground state geometry and Cs atom on the $C_3$ symmetry axis of Tz$^+$ by varying the Cs-Tz$^+$ distance. Asymptotic values of these energies are identical to the excitation energies of Tz and are given in Table 4.1. Then, the energies were shifted to account for the JT relaxation of the Tz$^+$ core such that each excited state of the (Cs-Tz)$^+$ complex asymptotically approaches vertical excitation energies of Tz at the cation geometry at infinite separation (15 Å). This is done by subtracting differences in excited energies at

84
the neutral and cation geometries from Table 4.1. In addition, the energies of Cs-Tz\(^+\) excited states (i.e., neutral Cs atom, initial state of Tz in the experiment) were shifted to match the asymptotic value of 6.12 eV at infinite separation (the difference between the experimental IE of cesium and Tz, 3.89 eV and 10.01 eV respectively).

Table 4.1: Vertical EOM-EE-CCSD/6-311++G\(^{**}\) excitation energies (eV) for Tz at the neutral (D\(_{3h}\)) and the cation (C\(_{2v}\)) ground-states geometries. All energies are relative to the ground-state energy of neutral Tz at the respective geometries. To recalculate energies relative to three ground-state HCN molecules, 1.86 eV should be subtracted.

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The PES scans for the ground and electronically excited states of Tz along the symmetric three-body dissociation coordinate were computed by EOM-EE-CCSD/6-311++G\(^{**}\) using the geometries obtained by Pai \textit{et al.}\(^\text{12}\) for the dissociation reaction coordinate on the MP2/6-31G\(^{**}\) ground state PES.

All calculations were performed using the Q-Chem electronic structure program\(^\text{39}\).
4.3 Results and discussion

Reaction mechanisms are ultimately defined by the shape of the underlying PES, and both the interpretation of the experimental observations and theoretical predictions require the knowledge of structures and energies of the PES stationary points, e.g., barriers and local minima along the reaction coordinates. The mechanisms of processes that span more than one electronic state also depend on the couplings and crossings between different PESs. Below we will discuss important features of the relevant PESs, as well as calculations of electronic couplings determining CE probabilities.

A necessary condition for concerted dissociation is the existence of an energetically accessible appropriate transition state, and many theoretical studies of the interplay between concerted and stepwise mechanisms have focused on locating and comparing different transition states\textsuperscript{40–45}. Tz has an accessible symmetric transition state for the three-body dissociation\textsuperscript{12}, however, a complete picture of the mechanism requires information about dynamics, which depends on how the process was initiated. This aspect of the dynamics — the effect of initial conditions on the reaction outcome — can be understood within the reflection principle framework\textsuperscript{20}. In photodissociation, the reflection principle assumes a ballistic process (i.e., no vibrational equilibration) on the excited state surface, which therefore acts as a mirror reflecting the initial wave packet onto the final states of the products. In the present experiment, the roles of excited and ground state surfaces are reversed — Tz is prepared in an electronically excited state, and the dissociation occurs ultimately on the ground electronic state. For the three-body breakup on the PES with the symmetric transition state, the reflection principle predicts a symmetric KER for the initially symmetric wave packet, and asymmetric — for the initial conditions described by asymmetric wave packet, as explained in Fig. 4.1. The shape of the initial wave packet is determined by the shape of the corresponding excited state.
surface on which Tz is produced by CE. Since all of the electronically excited states of Tz in the relevant energy region are derived by transitions between doubly-degenerate orbitals, some of them will themselves be degenerate and therefore subject to asymmetric JT distortions. However, some of the states have symmetric PES by virtue of double degeneracy of both the initial and the target molecular orbitals (MOs), and can, therefore, result in a symmetric wave packet.

4.3.1 Kinetic energy release and Dalitz plots

Fig. 4.3 shows the P(KER) distribution for dissociation following CE of a 16 keV beam of Tz$^+$ with Cs, accompanied by the relevant dissociation limits, calculated electronic state minima, and energy thresholds. P(KER) distributions obtained at 12 and 16 keV are similar, and extend from 0 to 5 eV with a major feature peaked at 2.6 eV and a minor feature at 0.5 eV relative to the three ground-state HCN molecules. Based on the Tz enthalpy of formation ($\Delta H_f=225.87$ kJ/mol), CE in the resonance regime should produce Tz$^*$ 4.26 eV above the 3 HCN$(X^1\Sigma^+)$ limit. However, the maximum observed KER extends well beyond this limit suggesting a degree of non-resonant excitation in the CE process.

We found that the three-body momentum distribution depends strongly on the KER. To illustrate this dependence, P(KER) distributions were divided into 32 KER bins, and Dalitz representations (see Sec. 4.2.1) were used to visualize the momentum partitioning for the events contained within each KER bin. Several Dalitz representations constructed from the 12 and 16 keV Tz data are shown in Fig. 4.4, and correspond to the labeled KER ranges in Fig. 4.3. A two-fold symmetric acute feature (two slow and one fast HCN fragment) dominates the Dalitz representations between intervals B and E at both beam energies. A weaker feature corresponding to a three-fold symmetric
Figure 4.3: (Color) Energy diagram for the three-body dissociation of Tz. The P(KER) distribution obtained with a 16 keV cation beam is shown on the left. Labeled KER intervals correspond to the following energies: A(0.51-0.68 eV), B(1.69-1.86 eV), C(2.70-2.87 eV), D(3.38-3.54 eV), E(4.05-4.22 eV). The hatched boxes labeled 'KER (acute)' and 'KER (symmetric)' mark the region over which the mechanism was observed. The hatched boxes labeled '3s Rydberg' and '$\pi^* \leftarrow n$' denote the regions between the lowest and the highest lying states (triplets included) in each manifold, as computed at the cation equilibrium geometry ($C_{2v}$). Zero energy corresponds to the ground-state energy of three HCN.
partitioning of momentum is also present, and the Dalitz distributions in Fig. 4.4 have been slightly cropped near the intense acute apexes in order to highlight it. While more apparent in the 16 keV Dalitz plots, the symmetric feature is present (along with the acute feature) for intervals C and D at both beam energies. This symmetric feature also exhibits slight asymmetries extending towards the two-fold symmetric obtuse region of the Dalitz plot.

Dalitz distributions were constructed for intervals spanning the entire P(KER) distribution and reveal the ranges over which the acute and symmetric Dalitz features were observed as 1.5-5 eV and 2-4 eV, respectively (denoted in Fig. 4.3). These two seemingly independent features and the dependence of their relative ratio on the beam energy suggest that dissociation proceeds by two different mechanisms, the origins of which were an impetus for the \textit{ab initio} investigation into electronic structure of Tz.

Without performing non-adiabatic dynamics simulations in full dimensionality (as, for example, in Refs.\textsuperscript{49,50}) and on multiple PESs, one can gain mechanistic insight by using simple Franck-Condon considerations and the reflection principle\textsuperscript{20}, as sketched in Fig. 4.1. In our energy range, the three-body dissociation necessarily proceeds on the ground state, and the transition state for this process is symmetric\textsuperscript{9–12}. Assuming ballistic dissociation on the ground-state PES (and neglecting possible involvement of other electronic states in the non-adiabatic relaxation from the initially populated electronic state to the ground state), the reflection principle states that dumping a symmetric nuclear wave packet on the ground-state PES results in the symmetric dissociation, whereas a non-symmetric process corresponds to a non-symmetric nuclear wave function. Asymmetric wave packets give rise to vibrational excitation of asymmetric modes, which ultimately leads to asymmetric momentum partitioning. Thus, the symmetric and asymmetric channels can be explained by two different initial electronic states of
Figure 4.4: (Color) Dalitz representations of the momentum correlation in the three-body breakup of Tz obtained over KER intervals denoted in Fig. 4.3. A symmetric partitioning of momentum yields intensity in the center of the Dalitz plots, whereas intensity near the apexes (i.e., acute features) corresponds to one fast and two slow fragments.

neutral Tz — one with three-fold symmetry ($D_{3h}$) and one with lower symmetry (e.g., $C_{2v}$) assuming the vibrational wave function equilibrates on the excited state prior to
electronic relaxation. To elucidate the nature of the initially populated states, we performed electronic structure calculations of the excitation energies, coupling elements, and PES scans as described below. In light of the dense electronic spectrum of Tz, only by considering several characteristics of the excited states — their excitation energies, non-adiabatic couplings, and the topologies of the corresponding JT manifolds — we were able to identify the most likely initially populated states as the $A_1$ 3s Rydberg and the $A_2$ $\pi^* \leftarrow n$ valence states.

4.3.2 Electronic states of sym-triazine and electronic couplings between the Cs-Tz$^+$ and Cs$^+$-Tz states

The electronic spectrum of Tz consists of dense manifolds of valence $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ states$^{21,51-54}$, as well as Rydberg states derived from the transitions from nitrogen lone pairs ($n$) and $\pi$ orbitals. While in the ground electronic state, Tz is of $D_{3h}$ symmetry, many of the excited states, as well as the cation$^{55,56}$, are distorted by virtue of the JT theorem.

Our calculations$^{24}$ identified more than twenty states of neutral Tz below 9 eV. Examination of the energy diagram in Fig. 4.3 and the computed excitation energies summarized in Table 4.1 reveals that several singlet and triplet states are accessible energetically, i.e., all of the $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ states, as well as the lowest Rydberg $R_s \leftarrow n$ state.

Electronic couplings between the Cs-Tz$^+$ and Cs$^+$-Tz states (i.e., initial and final states in a CE event) computed by the GMH approach$^{36,37}$ (see Section 4.2.2) are presented in Table 4.2. In agreement with qualitative considerations$^{17}$, the calculations show that the couplings between the Cs-Tz$^+$ and different Cs$^+$-Tz$^*$ states are at least 400 times larger for the Rydberg states than for the valence states. Furthermore, the
$\pi^* \leftarrow \pi$ values are nearly zero due to the two-electron character of the corresponding electronic transition (the ground state of $Tz^+$ has a hole in a lone pair orbital). The same arguments apply to the corresponding triplet states, which are accessible in CE experiments. Thus, considerable electronic coupling matrix elements for the $3s$ Rydberg and $\pi^* \leftarrow n$ manifolds suggest these states as the most likely initially populated electronic states. However, the coupling for the Rydberg state is two orders of magnitude larger than that of the $\pi^* \leftarrow n$ state. As noted by Peterson and coworkers, CE transitions between loosely-bound orbitals (hence, characterized by large couplings) would yield large cross sections, whereas CE between tightly bound orbitals occurs mostly in close collisions and is characterized by small cross sections. More quantitative analysis of how couplings of these magnitudes will manifest themselves in branching ratios of the two channels can be obtained using the Demkov model, as described in the next section.

### 4.3.3 Evaluation of CE probabilities using the Demkov model

To discriminate between the different states, we employ the simple two-state Demkov model to evaluate transition probabilities for the CE process. The transition probability derived from this model depends upon the potential energy difference (i.e., the off-resonant energy defect), the potential parameter in the coupling matrix element, and the relative velocity between the cation and atomic electron donor:

$$\omega = sech^2 \left( \frac{\pi}{2\sqrt{2mI}} \cdot \frac{\Delta E}{V} \right) sin^2 \left( \int_{-\infty}^{+\infty} h_{ab} dt \right), \quad (4.4)$$
Table 4.2: The GMH couplings \( (h_{ab}) \) for CE between Cs and the triazine cation at 5Å and 8Å Cs-Tz\(^+\) separation. The couplings are computed by Eq. (2) using dipole moment difference \( (\Delta \mu_{12}) \), energy separation \( (\Delta E_{12}) \) and transition dipole moments \( (\mu_{1,2}) \).

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</tr>
<tr>
<td>( R_p \leftarrow n )</td>
<td>-0.36</td>
<td>2.00</td>
<td>1.563</td>
</tr>
</tbody>
</table>

where \( \Delta E \) is the energy defect (energy difference between the Cs-Tz\(^+\) and Cs\(^+\)-Tz states), \( h_{ab} \) is a matrix coupling element between the two states, \( V \) is the relative velocity, and \( t, m, \) and \( I \) denote time, mass, and the smaller of the ionization energies of electron donor or acceptor, respectively. This semiclassical model is derived assuming that the coupling \( h_{ab} \) increases exponentially at short distances and approaches zero as the fragments scatter apart. The maximum value of the coupling should be the order of the energy defect \( \Delta E \), and the latter is assumed to be constant in the exchange region.

The first term in Eq. (4.4), \( sech^2(\ldots) \), is the CE transition probability amplitude, which increases with the relative velocity \( V \) and asymptotically approaches unity. At 12 keV energy beam this term can be rewritten as \( sech^2(\alpha_{12keV}^e \Delta E) \), where all constants and the scattering velocity dependence are included in the effective cross section parameter \( \alpha_{12keV}^e \). At any other beam energies, \( E_b \), the cross section term equals
\[ sech^2(\alpha_{12\text{keV}}^{\text{eff}} \Delta E \sqrt{\frac{12}{E_b}}), \]

where \( \alpha_{12\text{keV}}^{\text{eff}} \) is the effective cross section parameter at 12 keV. Fig. 4.5 shows the CE cross sections as a function of beam energy for the two states with energy defects of 0.2 eV and 1.0 eV using two different values of \( \alpha_{12\text{keV}}^{\text{eff}} \) (5 and 1 eV\(^{-1} \)). The top panel showing the cross section for \( \alpha_{12\text{keV}}^{\text{eff}} \!=\! 5 \text{ eV}^{-1} \) corresponds to the \( \alpha \)-value before the saturation, which seems to be the case in the present experiment. As one can see from Fig. 4.5, the cross section increases (and saturates) faster for smaller energy defects.

The second term, \( \sin^2(\ldots) \) in Eq. (4.4), describes the population oscillation between the two states, Cs-Tz\(^+ \) and Cs\(^+\)-Tz. The frequency of the oscillation is proportional to the electronic coupling matrix element integrated over the interaction time. For the Rydberg Cs\(^+\)-Tz states, the coupling \( h_{ab} \) is about 1 eV (0.037 hartree, see Table 4.2). Assuming an interaction region of \( \sim 15 \) a.u., the time of interaction between Tz\(^+ \) and Cs is about \( 5 \times 10^{-15} \) sec (200 a.u.) at 12 keV beam velocity. With the exponential increase of the coupling from zero to 0.037 hartree and decrease back to zero over 200 a.u. of time, the value of the effective coupling

\[ h_{\text{eff}}^{12\text{keV}} = \int_{-\infty}^{+\infty} h_{ab} dt, \]

is estimated as 5 a.u. For a beam energy \( E_b \) other than 12 keV, the effective coupling is given by:

\[ h_{\text{eff}}(E_b, \text{keV}) = \sqrt{\frac{12}{E_b}} h_{\text{eff}}^{12\text{keV}}, \quad (4.5) \]

since the interaction time is inversely proportional to the square root of the relative velocity. The top panel in Fig. 4.6 shows strong oscillations in the value of the \( \sin^2(\ldots) \) term with the phase depending strongly on the exact value of the coupling. In the experiment, there are variations in the effective coupling due to the variety of the impact parameters and orientations of Tz, and the \( \sin^2(\ldots) \) term values are averaged \(^1\) with

\(^1\)The averaging is performed as follows. The average of \( \sin^2(x) = \int_{0}^{\pi} \sin^2(x) dx \cdot \pi = \frac{\pi}{2} \cdot \pi = \frac{\pi}{2}. \)

However, we have the average of \( \sin^2(\frac{\pi}{2}) \), which is \( \frac{1}{2} \) at the region of oscillations and then decreases to

94
Figure 4.5: The CE cross sections as a function of beam energy for the two states with energy defects of 0.2 eV (solid line) and 1.0 eV (dashed line) at 12 keV beam energy. The upper and lower panels show the results for the effective cross section parameter \( \alpha_{12\text{keV}}^{\text{eff}} \) equals 5 eV\(^{-1}\) and 1 eV\(^{-1}\), respectively.

an effective value of \( \sim 0.5 \) for the Rydberg states (see Fig. 4.6). The coupling for the valence states from the \( \pi^* \leftarrow n \) manifold are two orders of magnitude smaller, which zero when oscillations die down at large \( x \). Thus, we employ averaging over the period, which yields an effective value of 0.5.
results in an almost constant value of the $\sin^2(\ldots)$ term with respect to the $\text{Tz}^+$ beam velocity. The value of this oscillating term is $\sim 400$ times smaller for the valence $\pi^* \leftarrow n$ state than for the Rydberg state, as shown in the bottom panel in Fig. 4.6.

Figure 4.6: The state switching probability term $\sin^2(\ldots)$ in Eq. (4.4) as a function of the $\text{Tz}^+$ beam energy for selected values of effective couplings (4.5) of the order of magnitude corresponding to the $R \leftarrow n$ (top panel) and $\pi^* \leftarrow n$ (bottom panel) states at 12 keV.

Thus, for a given interaction time determined by the neutral-ion relative velocity, the model predicts a larger probability for populating states with: (i) smaller energy defect (i.e., in resonance); and (ii) larger coupling. The velocity dependence of the branching
ratios between different channels is non-linear and is determined chiefly by the energy defect through the cross section, Eq. (4.5). The probability of populating the state with a smaller energy defect increases more rapidly than that of the state with a larger defect as the relative ion-atom velocity increases. Thus, the observed velocity-dependent change in relative intensity of the two features from Fig. 4.3 suggests that two different initial electronic states of the neutral give rise to the observed dissociation channels. The dominant character of the asymmetric channel suggests stronger couplings for the respective initial state, whereas the increased intensity for the symmetric dissociation at 16 keV argues in favor of the smaller off-resonant energy defect of the corresponding state.

Energy defects of the Rydberg and $\pi^* \leftarrow n$ states (0.75 and 0.66 eV asymptotically) reveal that neither state is in exact resonance, although the valence state is 0.1 eV closer. However, as will be demonstrated in Sec. 4.3.5, at short Cs-Tz$^+$ distances the valence state becomes nearly degenerate with the Cs-Tz$^+$ state, whereas the energy defect of the Rydberg state increases.

Thus, the Demkov model predicts a much higher probability of populating the Rydberg state, even though it is further off-resonance compared to the $\pi^* \leftarrow n$ state. The respective equilibrium geometries of these states can be considered as starting points on the neutral ground-state surface by virtue of the reflection principle (see Fig. 4.1).

4.3.4 Analysis of the excited states topology

It is possible to determine which of the excited states have symmetric equilibrium structures, and which are distorted, by simply analyzing symmetries and the electronic configurations of the corresponding wave functions, as in recent studies of $N_3^{++}$46,47. All of the states discussed above are derived from transitions involving degenerate MOs,
and can, therefore, be potentially subject to JT distortions. States derived from the transitions between degenerate and non-degenerate MOs \((e \otimes a \rightarrow E)\) form a familiar 'Mexican hat'-shaped PES shown in Fig. 4.7. The pair of \(R_s \leftarrow n\) Rydberg states in Tz is of this type. A qualitatively different type of intersection occurs for the states derived from excitations between two degenerate MO pairs producing two exactly degenerate and two nearly degenerate states, i.e., \(e \otimes e \rightarrow E + A + B\). It can be shown that all four states are scrambled around the intersection, and the linear terms for the degenerate states are very small\(^{46,47}\). Consequently, the intersection appears to be glancing rather than conical, as shown in Fig. 4.7. Although the minimum of the upper degenerate PES is not exactly at \(D_{3h}\), a small magnitude distortion (e.g., 0.001 Å and \(10^{-4}\) eV in cyclic \(N^+_3\)) suggests a negligible effect on the corresponding nuclear wave functions, which, therefore, could be treated as derived from the symmetric PES. As will be discussed in the previous chapter, the minimum of the top \(\pi^* \leftarrow n\) state of Tz is numerically almost exactly at \(D_{3h}\).

4.3.5 The PES scans

Fig. 4.8 shows the PES scans along the symmetric three-body dissociation coordinate for the ground and the lowest electronically excited states of Tz. Note that none of the excited states correlates with the dissociation limit of the three ground-state HCN. Moreover, the excited states curves are rather parallel to the ground state one and feature a barrier along the three-body dissociation coordinate. Thus, Fig. 4.8 suggests that there are no obvious conical intersections between the ground and the excited states in the proximity of the dissociation coordinate. A non-dissociative character of the excited states PES suggests that non-adiabatic relaxation is likely to occur in the FC region. One can therefore expect slow radiationless relaxation to the ground state, which will allow
Figure 4.7: (Color) Topology of regular (upper panel) and four-fold (lower panel) Jahn-Teller intersections. The former case corresponds to the states derived from the transitions between doubly degenerate and non-degenerate MOs. Four-state intersections occur for the states originating from the transitions between the two sets of doubly-degenerate MOs. Symmetry analysis predicts that two out of four states will be exactly degenerate at $D_{3h}$. While the topology and degeneracy pattern might differ, the PES of the upper state always has a (nearly)-symmetric minimum.

electronically excited Tz$^*$ to vibrationally equilibrate prior to the transition. Of course, only non-adiabatic dynamics calculations in full dimensionality can reveal where (and how fast) Tz$^*$ reaches the ground-state PES, however, the presently available data support the above mechanism for symmetric dissociation. The $S_1$-$S_0$ conical intersection reported by Dyakov et al.$^9$ is at the opened ring geometry, and thus would lead to the asymmetric momenta partitioning among the fragments. 

Fig. 4.9 shows a scan of the calculated PESs for Cs approaching Tz$^+$ in a direction perpendicular to the molecular plane. Bold and light curves correspond to the Cs-Tz$^+$
Figure 4.8: (Color) Potential energy curves for the ground and excited states of Tz along the symmetric three-body dissociation coordinate.

and Cs\(^+\)-Tz states, respectively. At infinite separation, the state ordering is exactly as in neutral Tz at the cation geometry. The pictograms on the right show the topology of each PES around D\(_{3h}\). Note that the diffuse R\(_s\) ← n states become perturbed by approaching Cs at 7 Å, while the PESs of the valence states remain flat up to about 3.5 Å. This numerically demonstrates the qualitative statement made by Peterson and coworkers\(^{17}\) regarding the necessity of close collisions for electron capture into valence states.

Analysis of the topology shows that among the states in the energy range corresponding to the symmetric dissociation, the only states with a symmetric equilibrium structure are the upper \(\pi^* ← n\) states, as denoted by the pictograms in Fig. 4.9. Thus, we conclude that these states are responsible for the symmetric channel. The asymmetric dissociation may occur via all other states accessible energetically, however, the
Figure 4.9: Potential energy curves for the relevant singlet electronic states of the (Cs-Tz)\(^+\) system in a T-shaped configuration. Bold and light curves correspond to Cs-Tz\(^+\) and Cs\(^+\)-Tz states, respectively, whereas solid and dashed lines distinguish between the valence and Rydberg excited states. The geometry of the triazine fragment is that of the cation. The pictograms on the right show the PES topology for each state along JT coordinate. As in Fig. 4.3, the shaded boxes denote the KER regions for which symmetric and asymmetric dissociation were observed. Energies are relative to the the ground-state energy of three HCN.

most likely candidate is the lowest Rydberg \(R_s \leftarrow n\) state for which the GMH coupling is two orders of magnitude larger than that for the valence states. Thus, we conclude that acute and symmetric dissociation occur following initial excitation into the 3s Rydberg and \(\pi^* \leftarrow n\) manifolds, respectively. This assignment is supported by qualitative agreement between the observed intensity of these channels and the GMH matrix coupling elements.
The energetic locations of the 3s Rydberg and $\pi^* \leftarrow n$ manifolds in the cation Franck-Condon region correlate well with the KER range over which each Dalitz feature was observed. The maximum observed KER of 5 eV associated with the acute feature is close to the vertical energy for the Rydberg states (i.e., 5.17 and 5.11 eV above the three HCN limit for the singlet and triplet, respectively). Monte Carlo simulations support the acute Dalitz feature being the result of a stepwise dissociation. The maximum observed KER of 4 eV for symmetric dissociation lies 0.33 eV higher in energy than vertical energy of the highest $\pi^* \leftarrow n$ state ($^1A_2$), which is located at 3.67 eV above the three HCN limit and has $D_{3h}$ equilibrium structure. The small separation between singlet and triplet states does not allow us to discriminate between these manifolds. However, due to the three-fold degeneracy of the triplets one might expect triplets being populated more frequently. On the other hand, the rate of electronic relaxation to the ground-state singlet PES is likely to be much slower for the triplets.

Finally, we would like to comment on the obtuse lobes of the ’symmetric’ Dalitz feature, which shows slight asymmetries associated with the symmetric mechanism. Possible explanations for these features are: (i) the electronic transition to the ground-state PES occurs too fast, i.e., while the molecule still has vibrational excitation in an asymmetric mode (expected to be populated because of the JT distorted geometry of the cation), as suggested by Dyakov et al.; (ii) crossing to an intermediate lower-symmetry electronic state occurs prior to dissociation; (iii) contributions from initial population of nearby distorted $\pi^* \leftarrow n$ states. Interestingly, it was observed that excitation into the $\pi^* \leftarrow n$ manifold results in a partially asymmetric ’symmetric’ dissociation, which agrees with recent theoretical predictions aimed at resolving past debate on the dissociation of $Tz$.9–12.
4.4 Chapter 4 conclusions

In this chapter we discussed the first direct observation of two unique three-body dissociation mechanisms of Tz and the first observation of experimental signatures of the dynamics proceeding through both conical and glancing JT intersections within one molecule. We found that the observed KER in the CE-induced three-body dissociation of Tz results from two different electronic states. The analysis of product momentum partitioning obtained in coincidence experiments revealed both symmetric and asymmetric dissociation. The former was observed in the KER region between 2 to 4 eV, whereas the latter occurred between 1.5 and 5 eV. This energy dependence suggests that the symmetric dissociation proceeds through an excited electronic state of Tz populated in the resonance regime, while an off-resonant electronic state is responsible for the asymmetric breakup. Neglecting possible involvement of other electronic states, these observations can be explained within the reflection principle framework, assuming vibrational equilibration of the initially populated electronic state prior to a non-adiabatic transition to the ground state and fast dissociation on the ground state PES. With the above provisions, the reflection principle attributes symmetric dissociation to an initial electronic state with symmetric equilibrium geometry, and asymmetric dissociation to one with lower symmetry. *Ab initio* calculations and the analysis of the topology of the JT manifolds identified these states as the two highest valence states from the $\pi^* \leftarrow n$ manifold and the lowest 3s Rydberg state, respectively. The energy defect for $\pi^* \leftarrow n$ states is smaller than that of the Rydberg state, however, the coupling strength for the latter is two orders of magnitude larger, which explains dominant presence of asymmetric breakup. These results are in agreement with the conclusions made by Ondrey et al., who suggested that Tz does not reach an equilibrium prior to dissociation and thus the partitioning of momentum to the HCN products depends heavily on
the region of configuration space in which the ground state surface was accessed (i.e., the entrance-channel), while the final partitioning of internal energy in the products is determined by evolution on the dissociative surface\textsuperscript{7}. 
4.5 Chapter 4 reference list


Chapter 5

Ab initio calculation of the photoelectron spectra of the hydroxycarbene diradicals

5.1 Chapter 5 introduction

Hydroxycarbene, HCOH, is a high-energy diradicaloid isomer of formaldehyde. It is believed to play a role in formaldehyde photochemistry and its “roaming hydrogen” dynamics, the interstellar medium, and reactions of carbon atom with water\textsuperscript{1–5}. HCOH production is a major channel in the photodissociation of hydroxymethyl radical, CH\textsubscript{2}OH, in the 3p Rydberg state\textsuperscript{6}. Reisler and coworkers determined the heat of formation of the deuterated isotope HCOD to be 24±2 kcal/mol\textsuperscript{7}. Recently its synthesis and spectroscopic characterization were reported by Schreiner et al\textsuperscript{8}, who isolated the \textit{trans}-HCOH and HCOD in argon matrix at 11K and identified several infrared (IR) band origins. The experiment was supported by variational calculations of the anharmonic energies using the CCSD(T)/cc-pVQZ quartic force field. In an independent study, the vibrational levels and IR intensities for the ground states of neutral \textit{cis}- and \textit{trans}-HCOH were reported\textsuperscript{9}. The calculated lines and intensities matched the experimental data of Schreiner \textit{et al.} closely. It was found that anharmonicities were crucial for correctly describing IR intensities as well as energies. The harmonic approximation described
the lowest fundamental frequencies accurately, although is overestimated the stretching modes by approximately 200 cm$^{-1}$ in both isomers. Several combination/overtone bands acquired intensity in the low-energy region (0-3,000 cm$^{-1}$) and complicated the spectrum.

The cation HCOH$^+$ has also been studied. Berkowitz$^{10}$ and also Burgers$^{11}$ observed the species by mass spectroscopy in the dissociative photoionization of methanol. Near the dissociation threshold of hydrogen elimination, HCOH$^+$, rather than H$_2$CO$^+$, was the dominant product$^{10}$. Radom and coworkers characterized trans-HCOH$^+$, formaldehyde cation, and the transition state using molecular orbital theory$^{12}$. They were the first to suggest that HCOH$^+$ is the most stable isomer of ionized formaldehyde. The following year, McLafferty and coworkers$^{13}$ performed collision-activated mass spectroscopy experiments and were able to infer the stability of a product in the correct energy range, which they attributed to HCOH$^+$. The heat of formation, based on careful comparison between theoretical calculations and experimental data (reverse activation energy and isotope effects were found to be crucial in analysis of appearance energy experiments), was established by Radom and coworkers$^{14}$. The energy difference between the formaldehyde cation and HCOH$^+$ was found to be poorly reproduced by perturbation theory (MP2) due to convergence issues in the perturbative series. Finally, Wiest$^{15}$ characterized energy and structure for both cis- and trans- isomers in a DFT study of the methanol radical cation surface.

Neutral HCOH tunnels effectively through the barrier to formaldehyde$^{8}$. The calculated rate constant for the forward reaction is almost an order of magnitude higher than for the reverse reaction$^{16}$, as would be expected from energetics. Whereas on the neutral surface, HCOH is much higher than formaldehyde, the energy gap between HCOH$^+$
and \( \text{H}_2\text{CO}^+ \) is much smaller (1,811 cm\(^{-1}\), see Fig. 5.1). Thus, it might be easier to observe HCOH isomer in the ionized rather than neutral state.

![Diagram showing stationary points on the HCOH (lower, CCSD(T)/cc-pVTZ) and HCOH\(^+\) (upper) PES. Vertical arrows represent ionization to the Franck-Condon regions and vertical (regular print) and adiabatic (underline) IEs are given. Energies of stationary points are listed on each surface relative to their global minimum (trans- structure). The formaldehyde isomer was not included in our PES, and associated barrier (marked with *) was calculated with CCSD(T)/cc-pVTZ at B3LYP/cc-pVTZ optimized transition state.](image-url)

Figure 5.1: Stationary points on the HCOH (lower, CCSD(T)/cc-pVTZ) and HCOH\(^+\) (upper) PES. Vertical arrows represent ionization to the Franck-Condon regions and vertical (regular print) and adiabatic (underline) IEs are given. Energies of stationary points are listed on each surface relative to their global minimum (trans- structure). The formaldehyde isomer was not included in our PES, and associated barrier (marked with *) was calculated with CCSD(T)/cc-pVTZ at B3LYP/cc-pVTZ optimized transition state.
From the electronic structure point of view, HCOH is an example of substituted carbenes, diradical species playing important role in organic chemistry\textsuperscript{17}. Spectroscopically, prototypical substituted carbenes have been studied by Reid and co-workers\textsuperscript{18–21}. Using high-resolution spectroscopy, they characterized the singlet-triplet gaps, spin-orbit couplings, and mode-specific dynamics of several triatomic carbenes\textsuperscript{18–21}. Halogen substitution reduces diradical character resulting in the singlet ground state. The OH group has similar effect — the ground state of hydroxycarbene is a singlet, and the singlet-triplet gap is about 1 eV\textsuperscript{2–5,22,23}.

In this chapter we describe the vibrational levels of ground-state HCOH\textsuperscript{+}, and the associated photoelectron spectra from ground vibrational states of \textit{cis-} and \textit{trans-}HCOH. Photoelectron spectroscopy is a sensitive tool that provides information about electronic structure and nuclear motion. Positions of band heads yield ionization energies (IEs) and an electronic spectrum of the ionized system. The information about changes in electronic wave functions can be inferred from the vibrational progressions due to structural changes by using Koopmans-like arguments. Although the Koopmans theorem\textsuperscript{24} neglects electron correlation and orbital relaxation effects, it provides useful qualitative guideline for rationalizing and predicting structural changes upon ionization. Moreover, a simple one-electron picture of the ionization process can be developed for correlated wave functions by using Dyson orbitals\textsuperscript{25}.

Vibrational progressions give frequencies and anharmonicities on the upper state, and information about structural differences between the two states. The structure of the paper is as follows. Section 5.2 discusses theory and computational details, including basis set convergence, details of the vibrational configuration interaction (VCI) basis, and calculation of the Franck-Condon factors. Section 5.3 discusses the molecular
orbitals and structural changes upon ionization, as well as barriers on the PES. Section 5.4 discusses the vibrational levels of HCOH$^+$ and presents the photoelectron spectra, and section 5.5 does the same for the deuterated isomers HCOD. Section 5.6 compares the VCI photoelectron spectra with the harmonic parallel-mode approximation, and shows that better accuracy is obtained by calculating displacements along the cation normal coordinates. Finally, section 5.7 presents our conclusions.

5.2 Theory and computational details

The calculations employed potential energy surfaces (PESs) for the neutral and cation ground states. The neutral PES is described in an early publication$^9$. The new cation surface covers the cis- and trans- wells and the space connecting them. Both PES are available for download along with precompiled ezPES software$^{26}$.

The PES is a 9$^{th}$ degree polynomial in Morse variables of the set of interatomic distances, represented in a specially constructed basis invariant to permutations of like nuclei. The Morse variables are defined as: $y(i,j) = e^{-r(i,j)\lambda}$. $r(i,j)$ is the internuclear distance between atoms $i$ and $j$, and, based on previous optimization studies, the value of $\lambda$ is set to 2 bohr, although any value in the range 1.5 to 2.5 bohr will yield similar fitting precision, based on our extensive experience using Morse variables in fitting potential energy surfaces. The polynomial contains 2,649 terms fitted by weighted data to 26,221 ab initio single point energies, calculated by the CCSD(T) method$^{27,28}$ with the cc-pVTZ basis set$^{29}$. The restricted orbital Hartree-Fock (ROHF) was used as a reference to mitigate the effects of spin contamination. The PES was fitted to 22,263 points in the range [0,0.1) a.u. above the global minimum (trans-HCOH$^+$ equilibrium structure), 1,903 points in the range [0.1,0.2) a.u., and 1,894 points in the range [0.2,0.5) a.u. The least squares was weighted to ensure low-energy points were well fitted and
harmonic frequencies reproduced *ab initio* values. The rms fitting errors are 24 cm$^{-1}$ below 3000 cm$^{-1}$, 44 cm$^{-1}$ below 5000 cm$^{-1}$, and 62 cm$^{-1}$ below the highest barrier at 7085 cm$^{-1}$. Points above 0.1 a.u. were included to enforce asymptotes for fragmentation and small internuclear distances. The calculations were performed using MOLPRO$^{30}$. The core electrons were frozen in all PES calculations. Similarly constructed PESs have been used in several dynamics and spectroscopy studies$^{31-37}$; details of constructing the symmetrized polynomial basis are given elsewhere$^{38}$.

Basis set effects were considered by examining equilibrium structures and frequencies with aug-cc-pVTZ$^{39}$ and cc-pVQZ bases$^{29}$ (Fig. 5.2). Bond lengths and angles are well converged at the cc-pVTZ level. The largest differences are a 0.005 Å decrease in the CO bond length and a 0.4° increase in the HOC angle. Harmonic frequencies are also well converged. Average absolute differences are 7.9 cm$^{-1}$ between cc-pVTZ and aug-cc-pVTZ and 5.0 cm$^{-1}$ between cc-pVTZ and cc-pVQZ. Basis set convergence is better with respect to polarization than diffuse functions, implying some diffuse character of the electron density. The OH stretch is most sensitive to this: its frequency decreases by 16 cm$^{-1}$ upon adding diffuse functions, but remains unchanged with added polarization.

The PES replicates equilibrium CCSD(T)/cc-pVTZ bond lengths to 0.001 Å, and bond angles to 0.2° in *trans*- and 0.5° in *cis*-HCOH$^+$ (Fig. 5.2). Frequencies on the PES were calculated numerically using 5-point central difference formulas. They reproduce CCSD(T) finite difference frequencies with an average (absolute) difference of 5.8 and 4.3 cm$^{-1}$ for *cis-* and *trans*-HCOH$^+$, respectively, and maximum differences of 14 and 12 cm$^{-1}$ (Tables 5.2, 5.1). To emphasize the character of the motion, we refer to some bending motions as “in-plane” and “out-of-plane” bends, instead of the conventional “bend” and “wag” terms used to describe planar and non-planar motions, respectively.
Figure 5.2: Equilibrium structures on cation PES. CCSD(T)/cc-pVTZ (regular print), CCSD(T)/aug-cc-pVTZ (underline), CCSD(T)/cc-pVQZ (italic), and PES (bold) for cis- (left) and trans-HCOH\textsuperscript{+} (right). E\textsubscript{nuc} = 31.858717 a.u. and 31.825806 a.u. at the CCSD(T)/cc-pVTZ (frozen core) geometries. All calculations were performed with core electrons frozen.

Table 5.1: Comparison of harmonic frequencies (cm\textsuperscript{-1}) and IR intensities (km/mol, in parentheses) for trans-HCOH\textsuperscript{+}.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Sym.</th>
<th>cc-pVTZ\textsuperscript{a}</th>
<th>cc-pVTZ\textsuperscript{b}</th>
<th>PES\textsuperscript{c}</th>
<th>aug-cc-pVTZ\textsuperscript{b}</th>
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<td>ν\textsubscript{6}</td>
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<td>ip bend</td>
<td>a’</td>
<td>998 (213)</td>
<td>999</td>
<td>997</td>
<td>994</td>
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<tr>
<td>ν\textsubscript{4}</td>
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<td>a’</td>
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<tr>
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<td>CH stretch</td>
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<td>3073</td>
<td>3069</td>
<td>3066</td>
</tr>
<tr>
<td>ν\textsubscript{1}</td>
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<td>a’</td>
<td>3529 (413)</td>
<td>3511</td>
<td>3499</td>
<td>3495</td>
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</tbody>
</table>

\textsuperscript{a} ACES II using analytic gradients, all electrons are correlated.

\textsuperscript{b} MOLPRO using total energies, core electrons are frozen.

\textsuperscript{c} Finite-differences calculations using PES fitted to the cc-pVTZ (frozen core) results.

Vibrational energies and wave-functions were calculated by diagonalizing the Watson Hamiltonian\textsuperscript{40} for \( J = 0 \) (pure vibration) in a basis of vibrational self-consistent field\textsuperscript{41} (VSCF) functions. The basis for VSCF optimized modals was the set of harmonic oscillator wave-functions along the normal coordinates, with quantum numbers from 0 to 15. Multimode interactions in the PES were included up to the 4-mode level. The
Table 5.2: Comparison of harmonic frequencies (cm\(^{-1}\)) and IR intensities (km/mol, in parentheses) for cis-HCOH\(^+\).

<table>
<thead>
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<th>Mode</th>
<th>Sym.</th>
<th>cc-pVTZ(^a)</th>
<th>cc-pVTZ(^b)</th>
<th>PES(^c)</th>
<th>aug-cc-pVTZ(^b)</th>
<th>cc-pVQZ(^b)</th>
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<td>a”</td>
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<td>921</td>
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<tr>
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<td>ip bend</td>
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<td>988 (65)</td>
<td>987</td>
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<td>1711</td>
<td>1710</td>
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<tr>
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<td>3085 (45)</td>
<td>3055</td>
<td>3054</td>
<td>3047</td>
</tr>
<tr>
<td>(\nu_1)</td>
<td>OH stretch</td>
<td>a’</td>
<td>3464 (339)</td>
<td>3448</td>
<td>3442</td>
<td>3428</td>
</tr>
</tbody>
</table>

\(^a\) ACES II using analytic gradients, all electrons are correlated.
\(^b\) MOLPRO using total energies, core electrons are frozen.
\(^c\) Finite-differences calculations using PES fitted to the cc-pVTZ (frozen core) results.

Rovibrational corrections were treated in an approximate manner. The Watson correction term was calculated in the n-mode representation along with the potential, up to the 4-mode level\(^{42}\). Coriolis coupling terms that coupled two modes were integrated over a 2-mode representation of the inverse moment of inertia tensor. The basis for VCI calculations consisted of all VSCF product wave-functions with maximum of 10 total quanta excited from the VSCF ground state reference, with a maximum of 5 modes simultaneously excited. Matrix elements of the Hamiltonian were calculated numerically using Gauss-Hermite quadrature with 20 integration points for 1D and 2D integrals, 15 points for 3D integrals, and 10 points for 4D integrals.

Franck-Condon factors were calculated as full-dimensional (i.e., 6-dimensional) integrals over the normal coordinates of the cation PES. The neutral ground-state wave-function at each point was obtained by aligning the molecules according to center of mass and the principal axis system, transforming between the normal coordinates, and evaluating the VCI wave-function. Thus, no approximations were made in evaluating
Franck-Condon factors via full-dimensional integration conducted using exact transformation between the two sets of normal coordinates. Only transitions from the ground vibrational states of the neutral are considered in photoelectron spectrum calculations as these are most likely to be of relevance to future experiments.

Non-zero Franck-Condon factors were calculated for levels up to 7,000 cm$^{-1}$ above the zero-point energy. With the present VCI basis, convergence in the VCI energies was converged to 1 cm$^{-1}$ for most states below 4,000 cm$^{-1}$, with the exception of four combination/overtones of $\nu_6$, which are converged to about 2 cm$^{-1}$. This mode leads towards the out-of-plane transition state connecting cis- and trans-; large VCI bases lead to inefficient convergence probably because they sample this flat region. Above 4,000 cm$^{-1}$, convergence in these states is about 5-10 cm$^{-1}$. $\nu_6$ is the only out-of-plane mode and is not active in the photoelectron spectrum. The active states are converged to about 5 cm$^{-1}$ up to 7,000 cm$^{-1}$.

Single point energies for the PES fitting were calculated using MOLPRO$^{30}$. Harmonic frequencies were calculated using MOLPRO and ACES II$^{43}$, and harmonic infrared intensities using ACES II. The core orbitals were frozen in all MOLPRO calculations, and correlated in ACES II and Q-Chem$^{44}$ calculations. ACES II was used only to calculate harmonic frequencies using analytic gradients for comparison versus MOLPRO, which employs finite differences procedure. MOLPRO harmonic vibrational frequencies were computed by finite-differences using total energies, whereas ACES II calculations employed first analytic derivatives$^{45}$.

Vibrational wave functions and energy level were computed using ezVibe code$^{46}$. For benchmark purposes, we compared VCI levels from ezVibe with the MULTIMODE program$^{47}$. Agreement in the energies was within 1 cm$^{-1}$ for states below 6,000 cm$^{-1}$ (approximately 160 states), and within 2 cm$^{-1}$ below about 7,300 cm$^{-1}$(300 states).
5.3 Molecular orbital framework and structural effects of ionization

The smallest carbene, methylene (CH$_2$), has a triplet ground state, with two unpaired electrons on the divalent carbon atom. The singlet-triplet gap is 0.39 eV\textsuperscript{48,49}. Substituted carbenes have diverse properties, for example in the stereospecificity of their reactions\textsuperscript{17,50–52}. The differences in reactivity can often be explained in terms of the singlet versus triplet character of the ground state.

The triplet state in carbenes has two electrons in nonbonding orbitals on carbon, one $\sigma$ and one $\pi$. The singlet state has the electrons paired in the $\sigma$ orbital, with the $\pi$ orbital unoccupied. The effect of substituents can be explained using simple molecular orbital considerations\textsuperscript{53,54}: substituent groups with $\pi$ type lone pairs (N,O atoms) lead to singlet ground states because these lone pairs can mix with carbon’s $\pi$ orbital. This can raise it enough so that pairing the electrons in $\sigma$ becomes energetically favorable. For example, in HCOH the singlet state is about 1 eV below the triplet.

The vertical (adiabatic) IEs of HCOH are 9.45 (8.76) and 9.44 (8.79) eV for the cis- and trans- isomers, respectively, as computed at the CCSD(T)/cc-pVTZ level (ZPE excluded). The highest occupied molecular orbital (HOMO) on HCOH is a lone pair on carbon with a minor contribution on OH which provides antibonding character along the CO bond. (Fig. 5.3). The first ionization removes an electron from the HOMO, with large geometrical changes in equilibrium structure. The CO bond is shortened by 0.097 and 0.093 Å in the cis- and trans- isomers, respectively. Ionization from an sp$^2$ orbital on carbon increases the carbon’s overall s character; the HCO angle increases by 25.5 and 22.6°. The HOC angle also increases, by 6.1 and 9.9°.
Figure 5.3: (Color) Highest occupied molecular orbital of cis- (left) and trans-HCOH (right).

The displaced equilibrium structures strongly affect the shape of the PES, and harmonic frequencies show strong differences upon ionization (Table 5.3). The largest change is in the CO stretch, which increases by 370 cm$^{-1}$ in both isomers upon ionization. This is due to the shortening of the CO bond. The CH stretching frequency increases upon ionization, by 286 and 216 cm$^{-1}$. The remaining four frequencies decrease. The OH stretch decreases by 213 and 255 cm$^{-1}$; this follows from the longer OH bond in the cation, due to increased donation into the electron-depleted carbon. The remaining three are bending modes involving the OH group; the oxygen lone pairs encounter less steric hindrance with a single electron on C in these motions.

Table 5.3: Comparison of harmonic frequencies (cm$^{-1}$) between neutral and cation PESs.

<table>
<thead>
<tr>
<th></th>
<th>op wag</th>
<th>ip bend</th>
<th>ip bend</th>
<th>CO stretch</th>
<th>CH stretch</th>
<th>OH stretch</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-HCOH</td>
<td>1014</td>
<td>1238</td>
<td>1476</td>
<td>1335</td>
<td>2768</td>
<td>3655</td>
</tr>
<tr>
<td>cis-HCOH$^+$</td>
<td>931</td>
<td>996</td>
<td>1159</td>
<td>1711</td>
<td>3054</td>
<td>3442</td>
</tr>
<tr>
<td>trans-HCOH</td>
<td>1098</td>
<td>1214</td>
<td>1508</td>
<td>1326</td>
<td>2853</td>
<td>3754</td>
</tr>
<tr>
<td>trans-HCOH$^+$</td>
<td>970</td>
<td>997</td>
<td>1254</td>
<td>1694</td>
<td>3069</td>
<td>3499</td>
</tr>
</tbody>
</table>
Two barriers on the HCOH\(^+\) PES, which separate the \textit{cis}- and \textit{trans}- wells, are 6,190 and 7,085 cm\(^{-1}\) above the \textit{trans}- minimum (Fig. 5.1). The respective transition states represent in-plane and out-of-plane rotation of H around the oxygen, respectively. These transition states are lower in energy relative to the neutral (by 6,717 cm\(^{-1}\) for the linear, and by 3,578 cm\(^{-1}\) for the out-of-plane). This also is due to decreased repulsion between the electrons on O and C: in out-of-plane rotation, the HOC angle remains essentially constant. In in-plane-rotation, this angle changes and the oxygen’s electron density is brought closer to the carbon center. The ionized carbon atom presents a much smaller barrier for this interaction, hence the disproportionate effect of ionization on the two barriers.

In addition, the neutral PES was optimized to replicate harmonic frequencies; we have since created a similar PES that replicates barrier heights accurately with only a moderate decline in the accuracy of the harmonic frequencies. Both PESs are available for download from the iOpenShell website.

### 5.4 Photoelectron spectra of HCOH

Vibrational levels of HCOH\(^+\) up to 3,600 cm\(^{-1}\) are listed in Table 5.4. Considering the fundamental excitations, the first four levels (up to 1,700 cm\(^{-1}\)) are accurately described by the harmonic approximation, with an average deviation between harmonic and VCI excitation energies of 35 cm\(^{-1}\). The higher stretches show large deviations from the harmonic approximation; VCI decreases the CH and OH stretch fundamental frequencies by approximately 150 and 190 cm\(^{-1}\), respectively.

The photoelectron spectra for the two isomers are shown in Fig. 5.4, and positions and intensities are tabulated in Tables 5.5 and 5.6. The intensities are unitless; intensity of 1 corresponds to full overlap between the neutral and cation wave-functions.
Table 5.4: HCOH\(^+\) VCI vibrational levels below 3600 cm\(^{-1}\), and corresponding levels for HCOD\(^+\) (cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>No.</th>
<th>State label</th>
<th>cis-HCOH(^+)</th>
<th>cis-HCOD(^+)</th>
<th>trans-HCOH(^+)</th>
<th>trans-HCOD(^+)</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>(\nu_6)</td>
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<td>746</td>
<td>935</td>
<td>781</td>
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<tr>
<td>2</td>
<td>(\nu_5)</td>
<td>949</td>
<td>822</td>
<td>967</td>
<td>822</td>
</tr>
<tr>
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<td>(\nu_4)</td>
<td>1126</td>
<td>1099</td>
<td>1211</td>
<td>1143</td>
</tr>
<tr>
<td>4</td>
<td>(\nu_3)</td>
<td>1684</td>
<td>1671</td>
<td>1664</td>
<td>1655</td>
</tr>
<tr>
<td>5</td>
<td>(2\nu_6)</td>
<td>1811</td>
<td>1475</td>
<td>1858</td>
<td>1547</td>
</tr>
<tr>
<td>6</td>
<td>(\nu_5+\nu_6)</td>
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<td>1575</td>
<td>1915</td>
<td>1604</td>
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<td>(2\nu_5)</td>
<td>1885</td>
<td>1641</td>
<td>1933</td>
<td>1644</td>
</tr>
<tr>
<td>8</td>
<td>(\nu_4+\nu_6)</td>
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<td>1912</td>
</tr>
<tr>
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</tr>
<tr>
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<td>2488</td>
<td>2626</td>
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<td>(3\nu_6)</td>
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<tr>
<td>14</td>
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<td>2826</td>
<td>2365</td>
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<td>2863</td>
<td>2785</td>
</tr>
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<td>2908</td>
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</tr>
<tr>
<td>17</td>
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<td>2825</td>
<td>2395</td>
<td>2903</td>
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<tr>
<td>19</td>
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<td>2784</td>
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<tr>
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<td>3122</td>
<td>3038</td>
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<td>3109</td>
</tr>
<tr>
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<td>3156</td>
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<td>3560</td>
<td>3304</td>
<td>3589</td>
<td>3301</td>
</tr>
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</table>
Figure 5.4: Franck-Condon factors for HCOH ionization producing electronic ground state of HCOH$^+$ in the range from the ZPE (0 cm$^{-1}$) to 7,000 cm$^{-1}$. Top: cis- isomer; bottom: trans- isomer.

The cis-HCOH photoelectron spectrum is given in Fig. 5.4 and Table 5.5. In the low energy region ($0 - 2,000$ cm$^{-1}$), the lowest-frequency mode $\nu_0$ has no intensity.
Table 5.5: Active vibrational levels of cis-HCOH\(^+\) / HCOD\(^+\) in the photoelectron spectrum of cis-HCOH / HCOD. Energies are in cm\(^{-1}\) and intensities are unitless.

<table>
<thead>
<tr>
<th>No.</th>
<th>State label</th>
<th>Energy</th>
<th>Intensity</th>
<th>cis-HCOH(^+)</th>
<th>State label</th>
<th>Energy</th>
<th>Intensity</th>
<th>cis-HCOD(^+)</th>
</tr>
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<td>0 0 0.0104</td>
<td>(\nu_5)</td>
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<tr>
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<td>1126</td>
<td>0.0121</td>
<td>(\nu_4) 1099</td>
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<tr>
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<td>1671</td>
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<tr>
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<td>1885</td>
<td>0.0163</td>
<td>2(\nu_5) 1835</td>
<td>(\nu_5)</td>
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<tr>
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<td>(2\nu_4+\nu_5)</td>
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<td>(\nu_3+2\nu_4)</td>
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<td>0.0131</td>
<td>(\nu_3+2\nu_4+\nu_5) 0.0131</td>
</tr>
<tr>
<td>23</td>
<td>(5\nu_5)</td>
<td>4730</td>
<td>0.0196</td>
<td>(2\nu_3+2\nu_4) 5438</td>
<td>(2\nu_3+2\nu_4)</td>
<td>5438</td>
<td>0.0099</td>
<td>(2\nu_3+2\nu_4) 0.0099</td>
</tr>
<tr>
<td>24</td>
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<td>4740</td>
<td>0.0083</td>
<td>(\nu_3+3\nu_4+\nu_5) 5482</td>
<td>(\nu_3+3\nu_4+\nu_5)</td>
<td>5482</td>
<td>0.0160</td>
<td>(\nu_3+3\nu_4+\nu_5) 0.0160</td>
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</table>
This is the only mode which is not fully symmetric; in the absence of normal mode coupling in the PES, transitions to odd levels of this mode are forbidden by symmetry. The other four fundamentals in this range have appreciable intensity, with \( \nu_5 \) and \( 2\nu_5 \) the strongest. In \( \text{cis-HCOH}^+ \), \( \nu_5 \) is a scissoring of OH and CH which moves the molecule toward linearity. From Fig. 5.5, displacement along this mode brings the cation into the Franck-Condon region. \( \nu_4 \) increases one angle and decreases the other one. It is active because the difference in HCO angles in neutral and cation structures is much larger than the difference in HOC angles. The third active mode is \( \nu_3 \), which is the CO stretch.

![Figure 5.5: Equilibrium structures calculated on the PES for HCOH (regular print) and HCOH\(^+\) (underline) for cis- (left) and trans- (right) isomers. All calculations were performed with core electrons frozen.](image)

In the high energy range (2,000 – 7,000 cm\(^{-1}\)), six peaks have significant intensity (greater than approximately 0.025). Peaks labeled 5, 7, and 17 are composed of primarily one VSCF state, and correspond to combination bands of two modes, \( \nu_5 \) and either \( \nu_4 \) (5 and 17, more intense) or \( \nu_3 \) (7, less intense). Peaks 23, 26, and 29 are combinations in all three active modes and mix several (2-8) VSCF states. All of the intense peaks in the \( \text{cis-HCOH} \) spectrum represent vibrational states with multiple quanta in combinations of \( \nu_5 \) and \( \nu_4 \), and to a smaller extent, \( \nu_3 \).
The trans-HCOH spectrum is given in Fig. 5.4 and Table 5.6. It is qualitatively different than for cis-HCOH: there are fewer intense progressions, and they occur at much lower energies. $\nu_4$ at 1,211 cm$^{-1}$ dominates the low-energy part of the spectrum, with $\nu_3$ having about half the intensity. $\nu_4$ is the bend which brings the molecule to linearity, and $\nu_3$ is the CO stretch. Above 2,000 cm$^{-1}$, the five strongest peaks occur below 4,050 cm$^{-1}$. The dominant progression throughout the spectrum is an overtone of $\nu_4$. Other peaks with lesser intensity are combination bands involving excited quanta in $\nu_3$ and $\nu_4$. Compared to the cis-isomer, trans-HCOH shows a less dense spectrum with most of the intensity in $\nu_4$.

The qualitative differences in the two photoelectron spectra can be rationalized by differences in equilibrium structures upon ionization (Fig. 5.5). As discussed in Section 5.3, the opening up of the HOC angle is the most prominent effect, followed by a smaller opening of the HCO angle. The third difference is a shortening of the CO bond in both isomers. The intensity in the photoelectron spectra of HCOH is dominated by combination bands of the two hydrogen bending modes, whose primary displacement is changing these angles. A smaller amount of intensity is seen in the CO stretch. Thus to a great extent the progressions in the photoelectron spectrum are due to the Condon reflection principle$^{55}$.

### 5.5 Photoelectron spectra of HCOD

The photoelectron spectra for cis- and trans-HCOD are depicted in Fig. 5.6 and tabulated in Tables 5.5 and 5.6. Compared to HCOH, the energies of all the states are decreased due to the larger mass of D; the relative intensities also change because the different mass affects the normal modes. The normal modes tend to localize vibration into H and suppress it in D. This effect is largest in trans-HCOD.
Figure 5.6: Franck-Condon factors for HCOD ionization producing electronic ground state of HCOD$^+$ in the range from the ZPE (0 cm$^{-1}$) to 7,000 cm$^{-1}$. Top: cis- isomer; bottom: trans- isomer.
Table 5.6: Active vibrational levels of \textit{trans-HCOH}^+ / \textit{HCOD}^+ in the photoelectron spectrum of \textit{trans-HCOH} / \textit{HCOD}. Energies are in cm$^{-1}$ and intensities are unitless.

<table>
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<th>No.</th>
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<th>Energy</th>
<th>Intensity</th>
<th>State label</th>
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<th>Intensity</th>
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</table>
5.6 Comparison with the parallel-mode harmonic approximation

Franck-Condon factors between two electronic states are often approximated by assuming that (a) the vibrational wave-functions are harmonic and (b) all normal coordinates on the two surfaces are parallel, i.e., completely neglecting the Duschinsky rotations. In this case the Franck-Condon factors are products of 1D integrals over harmonic oscillator wave-functions, which are shifted by displacement $\Delta Q$ between equilibrium structures along that normal coordinate. Because of the neglect of rotations, $\Delta Q$ depend on the choice of normal modes used for calculation. The spectra of HCOH calculated using the two sets of normal coordinates are compared to the VCI spectrum for both isomers. All spectra were generated using CCSD(T)/cc-pVTZ frequency calculations and the ezSpectrum program.

Fig. 5.7 compares parallel-mode spectra with the VCI spectrum for the cis-isomer. The parallel-mode spectra are calculated using normal coordinates of the neutral (top column in Fig. 5.7) and cation (bottom column) normal coordinates. The displacements differ significantly only along one coordinate, the CO stretch; $\Delta Q$ equals 0.08 and 0.21 Å $\sqrt{amu}$ for neutral and cation normal coordinates, respectively. The differences are due to rotations (mixing); the CO bond is longer in the neutral and other modes, especially the stretches, have relative displacements along CO in their motion. Since the bends have to be displaced significantly to account for the change in HOC and HCO angles (by 0.35 and 0.33 Å $\sqrt{amu}$ in neutral and cation, respectively), $\Delta Q$ along the CO stretch is smaller in the neutral coordinates. Consequently the photoelectron spectrum using the neutral normal coordinates shows negligible intensity in the CO stretch.
fundamental (peak 3 in Fig. 5.7) and underestimates the intensity of all states with quanta in this mode.

Fig. 5.8 compares this approximation with VCI for trans-HCOH. The same effect is seen, except that the $\Delta Q$s differ in one of the bending modes rather than the CO stretch (peak 1 in Fig. 5.8). The displacements are 0.05 and 0.15 Å $\sqrt{amu}$ in the neutral and cation normal coordinates, respectively.

The effect of normal coordinate rotation on the wave-function overlap between states is shown in Fig. 1.4. On the lower state, only the ground vibrational wave-function is considered (in the absence of hot bands). The errors in FCFs due to rotation of the ground vibrational wave-function depend on two factors: the displacement $\Delta Q$ and the difference in frequencies of the active normal modes: if these frequencies are very similar, errors are small [column (b) in Fig. 1.4]. In HCOH, the three active frequencies are within 238 and 294 cm$^{-1}$ of each other for cis- and trans-, respectively. On the upper state, all of the wave-functions are considered. For excited vibrational wave-functions, even small rotations can significantly affect the overlap due to the nodal structure [column (c) in Fig. 1.4]. Therefore, for large relative rotations of normal coordinates, it can be more accurate to use the normal coordinates of the cation within the parallel-mode approximation, especially if the active modes have similar frequencies on the neutral state.

5.7 Chapter 5 conclusions

In this chapter we report accurate configuration interaction calculations of vibrational levels of the cis- and trans- isomers of HCOH$^+$ and HCOD$^+$. The photoelectron spectra from the ground vibrational wave-functions of the two isomers are also presented.
Figure 5.7: (Color) Comparison between VCI (black lines) and parallel-mode harmonic oscillator approximation (red lines) using normal coordinates of the neutral (top) and cation (bottom) for the Franck-Condon factors of cis-HCOH. Harmonic intensities are not scaled to match VCI.
Figure 5.8: (Color) Comparison between VCI (black lines) and parallel-mode harmonic oscillator approximation (red lines) using normal coordinates of the neutral (top) and cation (bottom) for the Franck-Condon factors of \( \text{trans-HCOH} \). Harmonic intensities are not scaled to match VCI.
HCOH$^+$ is derived by removing an electron from a doubly-occupied lone pair orbital on the carbon atom (Fig. 5.3), with antibonding contribution along CO. This leads to large structural changes upon ionization, including shortening of the CO bond and increase in HCO angle due to increased s hybridization on C. Changes in harmonic frequency are due to structural changes and in the reduced repulsion between electrons on O and the C center in the cation.

VCI fundamental excitations are harmonic for the lowest four normal modes, while the CH and OH stretches show anharmonicities over 150 cm$^{-1}$. Due to the large difference in equilibrium structures on the neutral and cation surfaces, non-zero Franck-Condon factors are calculated for energies up to 7,000 cm$^{-1}$. The progressions are localized into select frequencies, namely two in-plane bends and the CO stretch. This is rationalized in terms of the geometrical differences. Photoelectron spectra for the HCOD isotopes are significantly different than for HCOH; this is due to the suppression of D motion in the normal mode vibrations.

The photoelectron spectra in the parallel-mode harmonic approximation were also calculated, and compared with the VCI spectra. This approximation was fairly accurate for the low-energy part of the spectrum, especially in duplicating intensities of the three active fundamental excitations in both isomers. For combinations and overtones, the harmonic intensities for the strong peaks are only accurate to within a factor of 2 for cis-HCOH. However, the parallel-mode harmonic approximation is slightly more accurate for trans-HCOH than for cis-.

The calculated photoelectron spectra for cis- and trans-HCOH are qualitatively different, which should make an experimental identification possible. Moreover, these differences are present even in the low-energy part of the spectrum (below 2,000 cm$^{-1}$) where the VCI method is expected to have the highest accuracy. Our previous work
which calculated infrared spectra of the HCOH isomers achieved excellent agreement with experiment; we expect that current results will be of use in an experimental discrimination of the photoelectron spectra of HCOH.
5.8 Chapter 5 reference list


Chapter 6

Electronic structure and spectroscopy of oxyallyl

6.1 Chapter 6 introduction

Diradicals are commonly encountered as reaction intermediates or transition states and are essential in interpreting mechanisms of chemical reactions\(^1\)–\(^4\). Following Salem\(^5\), diradicals are often defined as species with two electrons occupying two (near)-degenerate molecular orbitals (MOs). As an example of a perfect diradical, consider trimethylenemethane (TMM), which has two exactly degenerate (due to symmetry constraints) frontier molecular orbitals (MOs) hosting two unpaired electrons\(^6\)–\(^8\). The ground state of TMM is triplet, followed by the singlet states at 1.17 and 3.88 eV (vertically)\(^9\)–\(^11\). The adiabatic ST gap is 0.699 eV\(^10\),\(^11\). Other diradicals, such as benzynes, metaxylylene, methylene, etc, feature nearly-degenerate frontier MOs, and their relative state ordering depends on the energy gap between the frontier MOs as well as their characters, e.g., disjoint versus non-disjoint\(^12\).

Oxyallyl (OXA) can be viewed as a derivative of TMM in which one CH\(_2\) group is replaced by oxygen\(^13\). This substitution lowers the symmetry from D\(_{3h}\) to C\(_{2v}\) lifting the degeneracy between the frontier MOs and stabilizing the singlet state. However, the differences in electronic structure between TMM and OXA are more substantial. The lone pairs on oxygen give rise to a second diradical manifold, which can interact with
the TMM-like states. This is similar to other oxygen-containing diradicals, such as Cvetanvić diradicals produced by reactions of atomic or molecular oxygen with unsaturated hydrocarbons\textsuperscript{14–17}.

Fig. 6.1 shows relevant MOs of OXA. The $a_2$ and three $b_1$ orbitals are of \(\pi\)-like character and can be described as the distorted TMM orbitals\textsuperscript{9}. The lowest $b_1$ orbital, which is predominantly an out-of-plane oxygen’s lone pair, lies below two other $b_1$ orbitals derived from carbon’s $p_z$, in agreement with electronegativity considerations. However, above the lowest $b_1$, there is a $b_2$ orbital corresponding to the in-plane oxygen lone pair. This orbital gives rise to several electronic configurations (and low–lying electronic states), which are unique for OXA.

Fig. 6.2 shows electronic configurations of the ground state of the OXA anion and the three lowest electronic states of the OXA diradical (see section 6.2). While the lowest triplet and singlet states, $^3B_2$ and $^1A_1$, are derived from different distributions of two electrons over the TMM-like $a_2$ and $b_1$ MOs, the next electronic state, $^3B_1$ has the unpaired electron on the in-plane oxygen lone pair, $b_2$. Different distributions of the two electrons on the $a_2$ and $b_2$ orbitals give rise to another manifold of diradical states.

Electronic structure calculations of diradicals are challenging due to multi configurational character of the wave functions and small energy gaps between states which require high accuracy and balanced description of multiple states\textsuperscript{18}. The most reliable approach is the equation-of-motion spin-flip coupled-cluster (EOM-SF-CC) method that describes target diradical states as spin-flipping excitations from a well behaved high-spin reference\textsuperscript{18–22}. The SF method describes all target states on an equal footing, includes dynamical and non-dynamical correlation in a single computational step, and does not involve active space selection and state averaging. When CCSD (or OO-CCD) wave function is used as the reference, the typical errors in energy differences are 0.1 eV,
and perturbative inclusion of triple excitations brings the errors below 1 kcal/mol (0.05 eV)\(^ {21} \), provided that an adequate basis set is employed. The calculations become even more challenging when other electronic states (e.g., second diradical manifold, anionic states) are important. To accurately compute energy differences between multiple states of different character one needs to employ appropriate computational strategies with built-in error cancellations (rather than rely on a brute-force approach), which can be achieved by judicious combination of different CC and EOM-CC methods\(^ {23–25} \).
Figure 6.2: (Color) Lowest electronic states of OXA. The $^3\text{B}_2$ state has a open-ring $C_{2v}$ minimum, whereas optimized $C_{2v}$ structure of the $^1\text{A}_1$ state is a transition state (TS). The vertical and adiabatic energy differences of the anion and singlet TS relative to the triplet $^3\text{B}_2$ state are given in Tables 6.1, 6.3, and 6.2. The second leading wave function amplitudes, $\lambda$, are also shown.

Although OXA has been postulated as a reactive intermediate in several classes of organic reactions, its experimental characterization has proven to be difficult, a possible reason being facile ring closure forming cyclopropanone (for a brief history, see Ref. 143).
The results of the neutralization-reionization mass spectrometric study, which attempted to produce neutral OXA from the anion, have not provided sufficient evidence of the production of the neutral²⁶.

The first direct experimental observation of OXA via photodetachment of the oxalyl anion has been reported recently¹³. The authors presented the photoelectron spectrum and assigned the observed progressions to the $^3$B₂ and $^1$A₁ states. They reported the respective adiabatic detachment energies to be 1.997±0.010 eV and 1.942±0.010 eV.

The previous theoretical studies of OXA provide a stark demonstration of methodological challenges posed by diradicals¹³,²⁶–³². For example, the reported values of singlet-triplet (ST) gap vary from -0.22 to +0.87 eV. The answers to another important question, whether or not the singlet OXA diradical can be isolated (i.e., whether there is a minimum on the singlet potential energy surface corresponding to an open-ring diradical structure) also vary wildly. This frustrating for theory situation is reflected in the most recent study¹³, which reports a collection of calculated detachment energies ranging from 1.68 to 2.08 eV.

The purpose of our study is to provide reliable theoretical description of the important aspects of the electronic structure of OXA. The failure of theory to yield converged and accurate results for OXA is not at all surprising owing to the nature of methods employed in previous studies. Indeed, DFT (and broken-symmetry DFT) is not capable of even giving a qualitatively correct description of the diradical wave functions. Moreover, self-interaction error often spoils the treatment of radicals (especially charged ones)³³–³⁵. The multi-reference methods employ more appropriate wave functions, however, obtaining quantitative results is difficult due to a subtle balance between dynamical
and non-dynamical correlation energy, arbitrariness in active space selection, etc. Addi-
tional difficulties arise due to uncertainties in equilibrium geometries, i.e., bare CASSCF
geometries often employed in energy calculations using higher level methods are rather
crude (see, for example, Ref. 9), which may introduce additional errors in small energy
gaps. Moreover, the selection of the active space for CASSCF strongly influences the
shape of the PES even on the CASPT2 level, e.g., in a study of tetramethylene some
stationary points calculated at the lower level of theory disappeared in more accurate
calculations\textsuperscript{36}. Finally, basis sets much larger than used in the previous studies are
required for converged results, as demonstrated below.

In this chapter we report accurate equilibrium geometries and the converged values
of detachment energies and energy gaps between the low-lying OXA states. Our best
estimates of the adiabatic energy differences (including the zero-point energies, ZPE)
between the anion \(^2\)\(A_2\) and the neutral \(^3\)\(B_2\) and \(^3\)\(B_1\) states are: 1.94 and 2.73 eV, respec-
tively. At the equilibrium geometry of the anion, the \(^1\)\(A_1\) state lies above \(^3\)\(B_2\), but geom-
etry relaxation brings the singlet below the triplet. We also present scans of the singlet
\(^1\)\(A_1\) PES demonstrating that there is no minimum corresponding to a singlet diradical
structure. Thus, singlet OXA undergoes prompt barrierless ring closure. However, a
flat shape of the PES results in the resonance trapping on the singlet PES giving rise to
the experimentally observable features in the photoelectron spectrum. Using reduced-
dimensionality wave-packet calculations, we estimated that the wave packet lingers in
the Franck-Condon region for about 170 fs, which corresponds to the spectral line broad-
ening of about 200 cm\(^{-1}\). We also present calculations of the photodetachment spectrum
and compare it with experimental results\textsuperscript{13,37}. 

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Figure 6.3: (Color) Electronic states of neutral OXA and its anion. Vertical energy differences are relative to the $^3\text{B}_2$ triplet state at its equilibrium geometry. The weights of leading electronic configurations as given by the EOM wave functions are shown. The two $^1\text{A}_1$ and $^1\text{B}_2$ states (right) are described by EOM-SF-CCSD(dT) from $^3\text{B}_2$ reference. The two $^3\text{B}_2$ and $^3\text{B}_1$ are described by EOM-IP from $^2\text{A}_2$. Anion-triplet (lowest $^3\text{B}_2$) energy gap is calculated by EOM-EA and EOM-IP from triplet and anion references, respectively. The shaded configurations are not well described. All EOM-CCSD calculations employed ROHF references and the 6-311(+(+,+)G(2df,2pd) basis set.

6.2 Theoretical methods and computational details

Reliable calculations of energy differences between multiple electronic states of different character require appropriate computational strategies that are based on balanced description of different states and have built-in error cancellation (see, for example, Refs. 24, 25), in the spirit of isodesmic reactions\textsuperscript{38}.  

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Fig. 6.3 shows electronic configurations of the low-lying states of OXA and its anion. The wave functions of the doublet anion and high-spin neutral triplet states are of single-configurational character, and can be well described by the ground-state coupled-cluster methods, i.e., CCSD. Chemical accuracy can be achieved by including triples corrections, e.g., within CCSD(T)\textsuperscript{39,40} or CCSD(dT)\textsuperscript{21,41}. To mitigate possible effects of spin-contamination, ROHF references are employed throughout this study. Energy differences between these states can be computed as differences between the respective total CCSD(T) or CCSD(dT) energies\textsuperscript{24,25}.

The \(^1\)A\(_1\) and \(^1\)B\(_2\) states have multi configurational wave functions that can be described by EOM-SF\textsuperscript{22} from the high-spin \(^3\)B\(_2\) reference. Note that some of the configurations of the \(^1\)B\(_2\) state appear as double excitations from \(^3\)B\(_2\), and, therefore, we anticipate larger errors for this state.

The states that are derived from the \(^3\)B\(_1\) manifold (shown on the right side of Fig. 6.3 can be described by SF from that reference. Alternatively, both \(^3\)B\(_2\) and \(^3\)B\(_1\) (as well as higher \(^3\)B\(_2\)) can be described by EOM-CC for ionized states, EOM-IP\textsuperscript{42-47}, using \(^2\)A\(_2\) reference.

Finally, the energy gap between \(^2\)A\(_2\) and \(^3\)B\(_2\) can also be computed by EOM-CC for electron attachment, EOM-EA\textsuperscript{42,48}, from the \(^3\)B\(_2\) reference. Note that the EOM-EA operator in this case corresponds to attaching of a \(\beta\) rather than an \(\alpha\) electron, as was done in the study of para-benzyne anion\textsuperscript{49}.

We also characterized electronically excited states of the anion using EOM-EE-CCSD/6-311(\(+,\+)
G(2df,2pd). The lowest excited state corresponds to the \(b_1 \rightarrow a_2\) excitation and is 1.4 eV vertically. The next excited state lies at 2.5 eV. It corresponds to \(b_2 \rightarrow a_2\) excitation and has low (but not negligible) oscillator strength (\(f_l=0.013\))
owing to its $lp \rightarrow \pi^*$ character. This state is above the onset of the detachment continuum, and, therefore, is of resonance character. Photoexcitation to this state will result in autodetachment and thus can contribute to the photoelectron signal above 2.5 eV.

As demonstrated by the numeric results below, the energy differences are extremely sensitive to the correlation treatment and basis set selection, and a balanced description of the relevant states is crucial for obtaining accurate results.

Calculation of adiabatic energy differences requires accurate equilibrium geometries. The $^2A_2$ (anion) and $^3B_2$ state equilibrium geometries were optimized by CCSD-UHF/6-311+(+,+)G(2df,2pd). The planar C$_2$v structure of the $^1A_1$ state was optimized by EOM-SF-CCSD/6-311+(+,+)G(2df,2pd). This structure is not a minimum but a transition state (TS) with a 203 cm$^{-1}$ imaginary frequency for out of plane symmetric rotation of the CH$_2$ groups. The $^3B_1$ equilibrium geometry was computed by EOM-IP-CCSD/6-311+(+,+)G(2df,2pd).

To investigate the reaction coordinate for ring closure, we performed two-dimensional scans of the $^1A_1$ PES — along the CCC angle and out-of-plane symmetric rotation of the CH$_2$ groups. Reaction path is well described in these two internal coordinates, but some minor relaxation of bond lengths and tilting of CO out of CCC plane (at the beginning of cyclization) is ignored. Note that relaxing other degrees of freedom along the reaction coordinate would only lower the energy and reduce the barriers connecting the fully optimized reactant structure and the product well.

This PES was used for the wave-packet propagation to investigate resonance trapping in the Franck-Condon region. Ab initio 2D PES calculated on the 24 x 16 grid was interpolated using natural cubic spline on the 200 x 200 rectangular uniform grid. The Fourier method$^{50,51}$ was used for the discrete representation of the Hamiltonian.
The time-dependent Schrödinger equation was solved using the split-operator method with a 6 attosecond (0.25 atomic time units) time step. The initial wave function at $t=0$ was represented by a 2D Gaussian corresponding to the ground vibrational state of the anion in the harmonic approximation, i.e., the product of two 1D Gaussians with 449 cm$^{-1}$ (CCC-bend) and 411 cm$^{-1}$ (CH$_2$ out of plane rotation) frequencies. This initial wave function was displaced by 0.12 (3.3$^\circ$) along the mass-weighted CCC-bend normal mode. The absorbing boundary conditions were used to dump the reflections from the boundaries resulting in a slow decay of the wave function norm to 0.9998 and 0.87 at 200 fs and 2 ps, respectively.

The photoelectron spectrum of the anion ($^2A_2$) was computed using double harmonic approximation with Duschinskii rotations with ezSpectrum. Equilibrium geometries and frequencies were computed by CCSD/6-311(+(*)G** ($^2A_2$ and $^3B_1$), EOM-SF-CCSD/6-31G* ($^1A_1$), and EOM-IP-CCSD/6-31G* ($^3B_2$). For the singlet transition state, planar C$_2v$ structure was used and the imaginary frequency was ignored. Such approach can be used to approximately describe a vibrational resonance.

All electronic structure calculations were performed using Q-Chem electronic structure program. The relevant geometries, energies, and frequencies are given in the Supplementary Materials.

### 6.3 Results and discussion

#### 6.3.1 Vertical and adiabatic electronic state ordering

Tables 6.1-6.2 show vertical and adiabatic energy gaps between the anion ($^2A_2$) and the neutral $^3B_2$, $^1A_1$ (planar TS), and $^3B_1$ states (see Fig. 6.2). Additional calculations are
Table 6.1: Vertical energy gaps (eV) relative to the triplet state at its equilibrium geometry calculated with different basis sets. $E_{TA}$ and $E_{TS}$ denote triplet-anion and triplet-singlet energy separations, respectively.

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>$\Delta E_{TA}^{v}$</th>
<th>$\Delta E_{TS}^{v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-311G**</td>
<td>-0.987</td>
<td>0.164</td>
</tr>
<tr>
<td>6-311(++)G**</td>
<td>-1.501</td>
<td>0.111</td>
</tr>
<tr>
<td>6-311(2++,2+)G**</td>
<td>-1.505</td>
<td>0.112</td>
</tr>
<tr>
<td>6-311(++,+)G(2df,2pd)</td>
<td>-1.714</td>
<td>0.071</td>
</tr>
<tr>
<td>6-311(++,+)G(3df,3pd)</td>
<td>-1.767</td>
<td>0.063</td>
</tr>
<tr>
<td>cc-pVTZ</td>
<td>-1.420</td>
<td>0.101</td>
</tr>
<tr>
<td>aug-cc-pVDZ</td>
<td>-1.680</td>
<td>0.061</td>
</tr>
<tr>
<td>aug-cc-pVTZ</td>
<td>-1.803</td>
<td>0.061</td>
</tr>
</tbody>
</table>

Table 6.2: Vertical ($E_{TS}^{v}$) and adiabatic ($E_{TS}^{a}$) energy gaps (eV) between the singlet (planar TS structure) and the triplet states$^a$. The best theoretical estimates are shown in bold.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta$CCSD(T)</th>
<th>EOM-SF-CCSD</th>
<th>EOM-SF-CCSD(dT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{TS}^{v}$</td>
<td>0.249</td>
<td>0.155</td>
<td><strong>0.061</strong></td>
</tr>
<tr>
<td>Relaxation energy</td>
<td>-0.154</td>
<td>-0.153</td>
<td>-0.124</td>
</tr>
<tr>
<td>$E_{TS}^{a}$</td>
<td>0.095</td>
<td>0.002</td>
<td><strong>-0.063</strong></td>
</tr>
</tbody>
</table>

$^a$ Energies are obtained with the aug-cc-pVTZ basis set.

summarized in Supplementary Materials. Our best estimate of the adiabatic VDE of the anion corresponding to photodetachment to the $^3B_2$ state is 1.89 eV (VDE$_{ee}$, i.e., no ZPE). The best value for the singlet-triplet (ST) gap (using planar TS structure of the $^1A_1$ state) is -0.063 eV (the singlet state being below the triplet). Our best estimate of the $^3B_2$-$^3B_1$ adiabatic gap (no ZPE) is 0.77 eV$^1$, which yields 2.66 eV for the $^2A_2-^3B_1$ gap.

$^1$The $^3B_2$-$^3B_1$ adiabatic gap was computed as energy difference between the EOM-IP-CCSD/aug-cc-pVTZ energies from the anion $^3A_2$ reference.
These energy gaps are very sensitive to the methods employed. Table 6.1 demonstrates the basis set dependence of the vertical energy gap between (i) the lowest triplet state and the ground state of the anion; and (ii) the lowest singlet and the lowest triplet states. The gaps in Table 6.1 are computed by the most appropriate correlation methods. The gaps are very sensitive to the basis set size, and the converged values require the basis of an aug-cc-pVTZ quality (e.g., $\Delta E_{TA}^{v}$ changes by 0.4 eV upon adding diffuse functions to the cc-pVTZ basis). The anion-triplet gap converges slower than the ST gap. For example, the difference in $\Delta E_{TA}^{v}$ in the Pople and Dunning triple-zeta bases is 0.4 eV, whereas the difference between the respective $\Delta E_{ST}^{v}$ is only 0.06 eV. This is because $\Delta E_{TA}^{v}$ is computed by $\Delta E$ approach, which relies on converged total energies. Thus, non-dynamical correlation should be recovered, which requires large basis sets. Moreover, diffuse functions are more important for the anion than for the neutral. Our best estimates of the $\Delta E_{TA}^{v}$ and $\Delta E_{TS}^{v}$ are -1.784 and 0.061 eV, respectively, obtained at the CCSD(dT)/aug-cc-pVTZ and EOM-SF-CCSD(dT)/aug-cc-pVTZ levels.

Tables 6.3 and 6.2 present vertical versus adiabatic energy gaps between the anion and the two lowest states of the neutral (see Fig. 6.2). As one can see, the gaps are also sensitive to the correlation treatment. While EOM-CCSD methods provide balanced description of the states involved, the effect of triples excitation is important for the quantitative accuracy.

As Tables 6.3 and 6.2 show, structural relaxation (under $C_{2v}$ constraint) brings the singlet $^1A_1$ state below the triplet $^3B_2$. Our best estimate of the adiabatic singlet-triplet and anion-triplet gaps are 0.063 eV and 1.886 eV, respectively (obtained at the EOM-SF-CCSD(dT)/aug-cc-pVTZ and the CCSD(dT)/aug-cc-pVTZ levels). However, as shown

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$^2\Delta E$ refers to a computational strategy when target energy gap is computed as a difference between the respective total energies, as opposed to the approaches formulated for direct calculation of energy differences, such as EOM-CC.
### Table 6.3: Vertical ($E_{T,A}^{v}$) and adiabatic ($E_{T,A}^{a}$) energy differences (eV) of the anion relative to the lowest triplet state. The best theoretical estimates are shown in bold.

<table>
<thead>
<tr>
<th></th>
<th>EOM-EA-SF</th>
<th>EOM-IP</th>
<th>∆CCSD(dT)</th>
<th>∆CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical, $E_{T,A}^{v}$</td>
<td>-1.654</td>
<td>-1.769</td>
<td>-1.784</td>
<td>-1.803</td>
</tr>
<tr>
<td>Relaxation energy</td>
<td>-0.092</td>
<td>-0.101</td>
<td>-0.102</td>
<td>-0.101</td>
</tr>
<tr>
<td>Adiabatic, $E_{T,A}^{a}$</td>
<td>-1.746</td>
<td>-1.870</td>
<td>-1.886</td>
<td>-1.904</td>
</tr>
</tbody>
</table>

below, the planar singlet structure is not a true minimum but a TS. The true minimum of the $^1A_1$ state corresponding to the closed-ring structure is of course much lower, i.e., 1.71 eV below $^3B_2$ as computed with CCSD/6-311(+(+)G(2df,2pd) (no ZPE).

### 6.3.2 Equilibrium geometries and vibrational frequencies

Fig. 6.4 shows optimized structures of the anion’s $^2A_2$, singlet $^1A_1$, and triplet $^3B_2$. In all three states, the geometry of the CH$_2$ groups is approximately the same, and only three internal coordinates show large differences between the states, i.e., the CCC angle and the CC and CO bonds. Thus, we expect the following two normal modes to be active in the photoelectron spectrum: (i) bending mode in the CCC angle, and (ii) symmetric stretching mode, which simultaneously shortens the CO bond and stretches both CC bonds.

The triplet $^3B_2$ state is displaced mostly along the bending normal mode relative to the anion, and the optimized singlet structure, which is a transition state, differs from the anion along the CO/CC stretching normal mode. This is consistent with the MOs — the triplet and singlet states are derived by removing an electron from the orbitals which are of bonding and antibonding character with respect to the two radical centers, respectively. The $b_1$ orbital is antibonding along the CO bond. The $^3B_1$ state, which is
Figure 6.4: Bond lengths (Å) and angles (degree) of the C$_{2v}$ optimized structures of the $^2A_2$, $^1A_1$, $^3B_2$ and $^3B_1$ states shown in normal, italic, bold, and bold italic fonts respectively. The planar C$_{2v}$ structure of $^1A_1$ is not a minimum but a transition state (TS).

derived by removing the electron from the in-plane oxygen lone pair orbital that also has anti bonding character along the CC bonds, has the longest CO and the shortest CC bonds.

Frequencies of these states are shown in Table 6.4. In agreement with the MO considerations, the largest changes are observed in the CO and CC stretches. Relative to the anion, the former increases in the singlet and decreases in both triplets. The CC stretch becomes softer in $^3B_2$ and stiffer in $^3B_1$. 

Table 6.4: Frequencies (cm$^{-1}$) for the $^{2}A_2$, $^{1}A_1$, $^{3}B_2$ and $^{3}B_1$ states calculated with the 6-31G* basis set. IR intensities are shown in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>Anion $^{2}A_2$</th>
<th>Singlet $^{1}A_1$ TS</th>
<th>Triplet $^{3}B_2$</th>
<th>Triplet $^{3}B_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CCSD</td>
<td>EOM-SF</td>
<td>CCSD</td>
<td>EOM-IP</td>
</tr>
<tr>
<td>Sym. CH$_2$ OP</td>
<td>$b_1$</td>
<td>411 (12)</td>
<td>-203</td>
<td>431 (1.5)</td>
</tr>
<tr>
<td>Sym. CH$_2$ OP</td>
<td>$b_1$</td>
<td>433 (90)</td>
<td>475 (19)</td>
<td>724 (83)</td>
</tr>
<tr>
<td>Asym. CH$_2$ OP</td>
<td>$a_2$</td>
<td>436 (0.0)</td>
<td>774 (0.0)</td>
<td>644 (0.0)</td>
</tr>
<tr>
<td>CCC bend.</td>
<td>$a_1$</td>
<td>449 (0.0)</td>
<td>398 (9.5)</td>
<td>409 (0.9)</td>
</tr>
<tr>
<td>CO tilt</td>
<td>$b_1$</td>
<td>468 (33)</td>
<td>500 (33)</td>
<td>524 (3.4)</td>
</tr>
<tr>
<td>CH stretch</td>
<td>$a_2$</td>
<td>561 (0.0)</td>
<td>473 (0.0)</td>
<td>321 (0.0)</td>
</tr>
<tr>
<td>CO bend. OP</td>
<td>$b_1$</td>
<td>692 (22)</td>
<td>771 (79)</td>
<td>540 (9.6)</td>
</tr>
<tr>
<td>Asym. CH$_2$ tilt</td>
<td>$b_2$</td>
<td>925 (115)</td>
<td>925 (12)</td>
<td>961 (1.3)</td>
</tr>
<tr>
<td>Sym. CC stretch</td>
<td>$a_1$</td>
<td>961 (1.2)</td>
<td>882 (21)</td>
<td>914 (2.0)</td>
</tr>
<tr>
<td>Sym. CH$_2$ tilt</td>
<td>$a_1$</td>
<td>1069 (28)</td>
<td>1090 (8.7)</td>
<td>1082 (4.3)</td>
</tr>
<tr>
<td>Asym. CC stretch</td>
<td>$b_2$</td>
<td>1079 (958)</td>
<td>1300 (53)</td>
<td>1356 (51)</td>
</tr>
<tr>
<td>Asym. HCH bend.</td>
<td>$b_2$</td>
<td>1480 (47)</td>
<td>1506 (37)</td>
<td>1519 (52)</td>
</tr>
<tr>
<td>Sym. HCH bend.</td>
<td>$a_1$</td>
<td>1494 (18)</td>
<td>1508 (7.9)</td>
<td>1503 (0.7)</td>
</tr>
<tr>
<td>CO stretch</td>
<td>$a_1$</td>
<td>1613 (331)</td>
<td>1902 (367)</td>
<td>1421 (0.1)</td>
</tr>
<tr>
<td>CH stretch</td>
<td>$b_2$</td>
<td>3131 (116)</td>
<td>3197 (0.2)</td>
<td>3197 (0.2)</td>
</tr>
<tr>
<td>CH stretch</td>
<td>$a_1$</td>
<td>3144 (20)</td>
<td>3203 (0.0)</td>
<td>3201 (6.7)</td>
</tr>
<tr>
<td>CH stretch</td>
<td>$b_2$</td>
<td>3221 (37)</td>
<td>3311 (0.8)</td>
<td>3309 (0.2)</td>
</tr>
<tr>
<td>CH stretch</td>
<td>$a_1$</td>
<td>3229 (88)</td>
<td>3316 (6.4)</td>
<td>3312 (4.6)</td>
</tr>
</tbody>
</table>

ZPE, eV

6-31G* 1.53 1.58 1.57 1.60
6-311+(+++)G** 1.49 1.55 1.55 1.57

*OP: out-of-plane vibrations, the rest are in plane vibrations.*

6.3.3 The transient singlet OXA structure and its spectroscopic signatures

The true equilibrium geometry of the singlet $^{1}A_1$ state is the cyclic structure with the CCC angle of 64.6 degrees, CC bond 1.474 Å, and CO bond 1.197 Å; adiabatically it is 1.75 eV below the triplet $^{3}B_2$ state. The cyclic equilibrium geometry is derived from
the TS $^1A_1$ structure by closing the CCC angle and rotating the CH$_2$ groups out of the molecular plane. Fig. 6.5 shows the PES scan of the $^1A_1$ state in these two coordinates. As one can see, there is no barrier separating the Franck-Condon region (which is close to the planar OXA TS) and the cyclic cyclopropanone structure. The potential along the reaction coordinate is extremely shallow near the planar OXA geometries (small CH$_2$ out of plane rotation angles). Thus, the singlet OXA diradical is not a stable species in the gas phase. However, the flat shape of PES suggests finite lifetime of the wave packet in the Franck-Condon region (or, in other words, trapping in a vibrational resonance), which can give rise to a band in the photoelectron spectrum. We observed such behavior in our recent study of the photoelectron spectrum of water dimer cation, where the wave packet calculations showed that the wave packet lingers on the shelf in the Franck-Condon region despite large structural differences between the neutral and the ionized equilibrium geometries$^{56}$.

To evaluate the lifetime of the wave packet in the Franck-Condon region, we performed 2D wave packet propagation on the singlet PES. Fig. 6.6 and show wave packet snapshots and the autocorrelation function.

We observe that the wave packet spends about 100 fs in the Franck-Condon region. At about 250 fs, the autocorrelation function approaches zero and the OXA structure can be described as a closed-ring one. The expectation values of CCC and CH$_2$ are equal to 97° and 50°, respectively, however, the wave packet is rather delocalized, as shown in Fig. 6.6(d). Since energy redistribution between the vibrational modes (IVR) cannot be correctly described by this two-dimensional model, the autocorrelation function exhibit multiple recurrences up to about 2 ps. One can expect that coupling with 16 remaining degrees of freedom will efficiently dissipate the vibrational energy from the reaction coordinate making the return of the wave packet from the bottom of the
well back to the Franck-Condon region unlikely. Thus, we estimate the lifetime in the Franck-Condon region as 170 fs. This corresponds to 10 CO vibrations (the frequency of the CO/CC stretch is 1902 cm\(^{-1}\), which corresponds to 17.5 fs for one vibrational period) and approximately 200 cm\(^{-1}\) line broadening. Thus, CO/CC progression of the singlet PES might be observed in the experimental spectrum.

The photoelectron spectrum of the OXA anion

Fig. 6.7 shows the experimental\(^{13,37}\) and theoretical photoelectron spectra of the OXA anion. The theoretical spectrum was computed using the double harmonic approximation with Duschinskii rotations, as described in Sec. 6.2. As follows from Fig. 6.4, the anion-triplet (\(^2\)A\(_2\) \rightarrow \(^3\)B\(_2\)) photodetachment transition activates the CCC-bending normal mode, leading to an extended vibrational progression with the peak spacing of 409.2 cm\(^{-1}\) [computed at the CCSD/6-311(+,+)+G\(^**\) level]. Fig. 6.7(a) shows the photoelectron spectrum of the OXA anion computed considering the \(^3\)B\(_2\) neutral state only. In this case, the origin of the \(^2\)A\(_2\) \rightarrow \(^3\)B\(_2\) transition is set at eBE = 1.95 eV, coinciding with the position of the first peak in the experimental spectrum. For comparison, the best theoretical value (including the ZPE correction) for the \(^2\)A\(_2\) \rightarrow \(^3\)B\(_2\) origin transition is 1.94 eV. The calculated peak positions in Fig. 6.7(a) agree very well with the experimental progression; however, the relative intensities (calculated as Franck-Condon factors squared) of the second and third peak are reversed. This discrepancy suggests that the computed spectrum does not take into account all active transitions. Moreover, the polarization measurements and observed peak broadening have suggested that the first peak belongs to the singlet state\(^{13,37}\). As discussed above, the very flat potential energy surface of the \(^1\)A\(_1\) state along the reaction coordinate towards ring closure (which corresponds to the symmetric out-of-plane rotation of the two CH2 groups) gives rise to a
relatively long lifetime (170 fs) of the initial wave packet in the Franck-Condon region. Thus, the singlet state is expected to contribute well-defined vibrational lines to the photoelectron spectrum. The most active normal mode in photoexcitation from the anion to the $^1A_1$ transition state is the CO/CC stretching normal mode, with the frequency 1902 cm$^{-1}$ (at the EOM-SF-CCSD/6-31G* level).

Fig. 6.7(b) shows the photoelectron spectrum in the same energy range as before, computed with the contributions of both the $^3B_2$ and $^1A_1$ neutral states. Compared to Fig. 6.7(a), the origin of the $^3B_2$ band is now shifted to 2.01 eV, to coincide with the position of the second peak in the experimental spectrum, while the first peak, at eBE = 1.95 eV, is assigned as the origin of the $^1A_1$ band. For comparison, the best theoretical estimate (including the ZPE correction) for the singlet 0-0 transition is 1.88 eV. The $^1A_1$ band intensities in the theoretical spectrum are multiplied by 0.3 relative to the $^3B_2$ state. Due to accidental degeneracy between the $^1A_1 \rightarrow ^3B_2$ energy gap and the CO/CC progression in the triplet state, the calculated peak positions in Fig. 6.7(b) agree with the experiment just as well as in Fig. 6.7(a). In addition, the relative intensities of the second and third peak in the combined $^3B_2$ and $^1A_1$ spectrum also agree with the experiment. It is troublesome that the second peak in the singlet state progression in Fig. 6.7(b) (at eBE = 2.19 eV) is not as prominent as expected in the experimental spectrum, but the resonance character of the $^1A_1$ state may be responsible for this behavior. Indeed, the experimental spectrum reported in Ref.13 exhibits a broadened peak corresponding to the fundamental level of the CO stretching mode. Thus, the overall agreement between the experimental and calculated spectra, combined with the polarization dependence of the relative peak intensities and observed broadening of the singlet lines13 make the reported assignment convincing. Fig. 6.7(c) shows the theoretical and experimental photoelectron spectra of OXA$^-$ up to eBE = 3.5 eV. The origin of the $^3B_1$ band is shifted
to 2.77 eV, compared to the computed value of 2.73 eV, based on the ZPE corrected adiabatic \( ^3B_2 \rightarrow ^3B_1 \) gap of 0.80 eV. The \( ^2A_2 \rightarrow ^3B_1 \) band intensities in Fig. 6.7(c) are multiplied by 0.6 relative to the \( ^3B_2 \) band. The individual vibrational lines correspond to the CO/CC stretch and CCC bend progressions in the \( ^3B_1 \) state. The overall shape of the \( ^3B_1 \) band agrees well, however, the experimental resolution is not sufficient to assign the individual peaks of these progressions. We also note that there is a resonance excited state of the anion at 2.5 eV (\( f_l=0.013 \)), and the excitation to this autodetaching state may contribute to the signal above 2.5 eV.

### 6.4 Chapter 6 conclusions

In this chapter we have report accurate electronic structure calculations of the low-lying electronic states of oxyallyl and oxyallyl anion. Our best estimates for the adiabatic electron binding energies (including ZPE) corresponding to the \( ^3B_2 \) and \( ^3B_1 \) neutral states are 1.94 and 2.73 eV, respectively, compared to the reported experimental values are 2.01 and 3.02 eV. The electron binding energy of the neutral \( ^1A_1 \) at the relaxed geometry of the anion is calculated to to be 1.88 eV, compared to the experimental value of 1.942 eV. However, the singlet PES does not have a minimum corresponding to an open-ring diradical structure. Thus, the singlet diradical is not a stable species in the gas phase and will undergo barrierless isomerization to the cyclopropanone. The flat shape of the PES suggests resonance trapping in the Franck-Condon region giving rise to a feature in the photoelectron spectrum. The estimated lifetime is 170 fs, which corresponds to 200 cm\(^{-1}\) linewidth. Thus, our calculation lend strong support to the reported assignment of the photodetachment spectra of the OXA anion.
Figure 6.5: (Color) Top panel: The PES scan of the singlet $^1A_1$ surface (EOM-SF-CCSD/6-31G*, UHF). Solid and dashed contour lines are every 0.25 eV and 0.05 eV, respectively. The red dashed line denotes the approximate reaction path from the $C_{2v}$ transition state (0,112) to the equilibrium cyclic geometry (90,64). Geometry of the “$C_s$ transition state” discussed in$^{13}$ is close to (35,108) point on this plot. Bottom panel: The PES scan along the reaction path from the top panel. Solid red circles – EOM-SF/6-31G*, UHF; Stars – EOM-SF/6-311(+,+)G(2df,2pd), UHF; Empty black circles – EOM-SF/6-311(,+G(2df,2pd), ROHF.
Figure 6.6: Evolution of the anion ground vibrational state wave function on the singlet $^1A_1$ PES. (a) Two-dimensional PES with contour lines every 0.27 eV. The cross marks the Franck-Condon region. (b) The initial wave function shown with contour interval 0.2. (c) and (d): The wave packet at time $t=55$ fs and $t=110$ fs, respectively. The autocorrelation function is shown in panel (e).
Figure 6.7: (Color) The calculated (see Sec. 6.2) and experimental\textsuperscript{13,37} photoelectron spectrum of the OXA anion. Solid red bars, dashed black, and solid blue bars denote the progressions in the triplet $^3\text{B}_2$, singlet $^1\text{A}_1$ and triplet $^3\text{B}_1$ bands, respectively. Solid black lines are the experimental photoelectron spectra\textsuperscript{13,57} measured with 532 nm (a,b) and 355 nm (c) lasers. (a): The calculated triplet state progression is superimposed with the experimental spectrum. (b) and (c): The calculated singlet and triplet state progressions are shifted such their respective 00 lines coincide with the positions of the first and the second peak.
6.5 Chapter 6 reference list


Chapter 7

Future work

Development of the computer hardware nowadays progress towards multi-core and multi-processor architecture. However to take the advantages of new hardware, the software should be rewritten to enable the parallel execution. Evaluation of the potential surfaces is trivial to parallelize as it is just a set of independent \textit{ab initio} calculations. However, the lack of standard automatic tools to create and analyze potential energy scans makes this otherwise relatively fast calculation (even with the currently available computational power) intractable. In multidimensional systems, only several coordinates are usually “active” or significantly anharmonic, and a PES scan in a subspace of a reduced dimensionality may help to understand/model nuclear dynamics in anharmonic cases: double wells, coupled coordinates, transition states and reaction coordinates, etc. Two dimensional PES scan for a molecule of the benzene size is no more expensive than a finite difference frequency calculation, and while the latter is readily available in any \textit{ab initio} package for any level of theory, there are no standard tools for PES generation, analysis and visualization in the molecular structure theory.

The cause and/or consequence of this PES unavailability is the lack of standard, automatic tools for solving nuclear Schrödinger equation and performing quantum nuclear dynamics. These tasks do not scale well, but perfectly feasible for several dimensions, which may provide an important insight into the dynamics of the full dimensional system.
A possible workaround is a molecular dynamics with on-the-fly evaluation of the PES in the region of interest. In this approach, one to avoid a full PES reconstruction, however it does not allow a complete quantum mechanical treatment of the problem—a nonlocal by its nature. Direct solution of the time dependent Schrödinger equation on a PES probably may be pushed beyond just few dimensions (a limitation of a discrete variable representation) if special basis sets are developed alongside with tools to help an automatic selection of the basis depending on the shape of the potential energy surface.

To conclude, virtually any easy to use and well documented tool to create, analyze and plot 2D projections of multidimensional surfaces based on *ab initio* calculations would be an extremely useful instrument for a molecular structure theory at the current level of computer hardware. It may as well stimulate a new wave of standard tools for quantum nuclear dynamics.
Bibliography


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