Ab Initio Calculation of the Photoelectron Spectra of the Hydroxycarbene Diradicals

Lucas Koziol,† Vadim A. Mozhayksiy,‡ Bastiaan J. Braams,§ Joel M. Bowman,‡ and Anna I. Krylov*,†
Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482,
C. L. Emerson Center for Scientific Computation, Department of Chemistry, Emory University,
Atlanta, Georgia 30322

Received: April 15, 2009; Revised Manuscript Received: May 19, 2009

Photoelectron spectra of the cis and trans isomers of HCOH were computed using vibrational wave functions calculated by diagonalizing the Watson Hamiltonian, including up to four mode couplings. The full-dimensional CCSD(T)/cc-pVTZ potential energy surfaces were employed in the calculation. Photoionization induces significant changes in equilibrium structures, which results in long progressions in the ν5, ν4, and ν3 modes. The two isomers show progressions in different modes, which leads to qualitatively distinguishable spectra. The spectra were also calculated in the double harmonic parallel-mode (i.e., neglecting Duschinsky rotation) approximation. Calculating displacements along the normal coordinates of the cation state was found to give a better approximation to the vibrational configuration interaction spectrum; this is due to the effects of Duschinsky rotations on the vibrational wave functions.

I. 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.1−5 HCOH production is a major channel in the photodissociation of hydroxymethyl radical, CH2OH, in the 3p Rydberg state.6 Reisler and co-workers determined the heat of formation of the deuterated isotope HCOD to be 24 ± 2 kcal/mol.7 Recently, its synthesis and spectroscopic characterization were reported by Schreiner et al.,8 who isolated the trans-HCOH and HCOD in argon matrix at 11 K 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 cis- and trans-HCOH were reported.9 The calculated lines and intensities matched the experimental data of Schreiner 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 it overestimated the stretching modes by approximately 200 cm−1 in both isomers. Several combination/ overtone bands acquired intensity in the low-energy region (0−3000 cm−1) and complicated the spectrum. The cation HCOH+ has also been studied. Berkowitz10 and also Burgers11 observed the species by mass spectroscopy in the dissociative photoionization of methanol. Near the dissociation threshold of hydrogen elimination, HCOH+, rather than H2CO+, was the dominant product.10 Radom and co-workers 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, McLaugherty and co-workers13 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 co-workers.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, Wiest15 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 H2CO+ is much smaller (1811 cm−1; see Figure 1). Thus, it might be easier to observe HCOH isomer in the ionized rather than neutral state.

From the electronic structure point of view, HCOH is an example of substituted carbenes, diradical species playing an important role in organic chemistry.17 Spectroscopically, prototypical substituted carbenes have been studied by Reid and co-workers.18−21 Using high-resolution spectroscopy, they characterized the singlet−triplet gaps, spin−orbit couplings, and mode-specific dynamics of several triatomic carbenes.18−21 Halogen substitution reduces diradical character, resulting in the singlet ground state. The OH group has a similar effect: the ground state of hydroxycarbene is a singlet, and the singlet−triplet gap is about 1 eV.2−5,22,23

In this work, we calculate the vibrational levels of ground-state HCOH+ and the associated photoelectron spectra from ground vibrational states of cis- and 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 neglects electron correlation and orbital relaxation effects, it provides useful qualitative guidelines 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.

Vibrational progressions give frequencies and anharmonicities on the upper state and information about structural differences between the two states. This is the focus of this paper, which is organized as follows. Section II 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 III discusses the molecular orbitals and structural changes upon ionization, as well as barriers on the potential energy surface (PES). Section IV discusses the vibrational levels of HCOH and presents the photoelectron spectra, and Section V does the same for the deuterated isomers HCOD. Section VI 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 VII presents our conclusions.

II. Theory and Computational Details

The calculations employed PESs for the neutral and cation ground states. The neutral PES is described in our early publication. The new cation surface covers the cis and trans wells and the space connecting them. Both PESs are available for download along with precompiled ezPES software.

The PES is a 9th 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: \( y(i, j) = e^{-\alpha r(i, j)} \), \( r(i, j) \) is the internuclear distance between atoms \( i \) and \( j \), and on the basis of previous optimization studies, the value of \( \alpha \) is set to 2 bohr. Any value in the range 1.5 to 2.5 bohr will yield similar fitting precision, on the basis of our extensive experience using Morse variables in fitting PESs. The polynomial contains 2649 terms fitted by weighted data to 26,221 ab initio single point energies, calculated by the CCSD(T) method with the cc-pVTZ basis set. The restricted open-shell Hartree–Fock 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 (\( trans-\text{HCOH}^+ \) equilibrium structure), 1903 points in the range \([0.1, 0.2]\) a.u., and 1894 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 au were included to enforce asymptotes for fragmentation and small internuclear distances. The calculations were performed using MOLPRO.

The core electrons were frozen in all PES calculations. Similarly constructed PESs have been used in several dynamics, and spectroscopy studies details of constructing the symmetrized polynomial basis are given elsewhere.

Basis set effects were considered by examining equilibrium structures and frequencies with the aug-cc-pVTZ and cc-pVQZ bases (Figure 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 H–O–C 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 \( cis-\text{HCOH}^+ \) (Figure 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 1, 2). To emphasize the character of the motion, we refer to some bending motions as “in-plane” and “out-of-plane” and “wag” terms used to describe planar and nonplanar motions, respectively.

Vibrational energies and wave functions were calculated by diagonalizing the Watson Hamiltonian\(^{40}\) for \(J = 0\) (pure vibration) in a basis of vibrational self-consistent field (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 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 the 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 because these are most likely to be of relevance to future experiments.

Nonzero Franck–Condon factors were calculated for levels up to 7000 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 4000 cm\(^{-1}\), with the exception of four combination/overtones of \(\nu_b\), which are converged to about 2 cm\(^{-1}\). This mode leads toward 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 4000 cm\(^{-1}\), convergence in these states is about 5–10 cm\(^{-1}\). \(\nu_b\) 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 7000 cm\(^{-1}\).

Single-point energies for the PES fitting were calculated using MOLPRO.\(^{30}\) Harmonic frequencies were calculated using MOLPRO and ACES II\(^{41}\) 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 a finite differences procedure. MOLPRO harmonic vibrational frequencies were computed by finite differences using total energies, whereas ACES II calculations employed first analytic derivatives.\(^{45}\)

All vibrational wave functions and energy levels were computed using the 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 6000 cm\(^{-1}\) (approximately 160 states) and within 2 cm\(^{-1}\) below about 7300 cm\(^{-1}\) (300 states).

### III. 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.\(^{48,49}\) Substituted carbones have diverse properties; for example, in the stereospecificity of their reactions.\(^{17,50–52}\) 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;\(^{53,54}\) substituent groups with \(\pi\)

### TABLE 1: Comparison of Harmonic Frequencies (cm\(^{-1}\)) and IR Intensities (km/mol, in parentheses) for cis-HCOH\(^+\)

<table>
<thead>
<tr>
<th>mode</th>
<th>symmetry</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>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_6)</td>
<td>op wag</td>
<td>(a'')</td>
<td>935 (32)</td>
<td>931</td>
<td>921</td>
<td>924</td>
</tr>
<tr>
<td>(\nu_5)</td>
<td>ip bend</td>
<td>(a')</td>
<td>988 (65)</td>
<td>996</td>
<td>984</td>
<td>984</td>
</tr>
<tr>
<td>(\nu_4)</td>
<td>ip bend</td>
<td>(a'')</td>
<td>1177 (176)</td>
<td>1119</td>
<td>1116</td>
<td>1169</td>
</tr>
<tr>
<td>(\nu_3)</td>
<td>CO stretch</td>
<td>(a')</td>
<td>1733 (73)</td>
<td>1711</td>
<td>1710</td>
<td>1724</td>
</tr>
<tr>
<td>(\nu_2)</td>
<td>CH stretch</td>
<td>(a')</td>
<td>3085 (45)</td>
<td>3055</td>
<td>3047</td>
<td>3054</td>
</tr>
<tr>
<td>(\nu_1)</td>
<td>OH stretch</td>
<td>(a')</td>
<td>3464 (339)</td>
<td>3448</td>
<td>3428</td>
<td>3446</td>
</tr>
</tbody>
</table>

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

### TABLE 2: Comparison of Harmonic Frequencies (cm\(^{-1}\)) and IR Intensities (km/mol, in parentheses) for trans-HCOH\(^+\)

<table>
<thead>
<tr>
<th>mode</th>
<th>symmetry</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>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_6)</td>
<td>op wag</td>
<td>(a'')</td>
<td>966 (157)</td>
<td>965</td>
<td>965</td>
<td>958</td>
</tr>
<tr>
<td>(\nu_5)</td>
<td>ip bend</td>
<td>(a')</td>
<td>999 (213)</td>
<td>997</td>
<td>994</td>
<td>987</td>
</tr>
<tr>
<td>(\nu_4)</td>
<td>ip bend</td>
<td>(a'')</td>
<td>1257 (33)</td>
<td>1255</td>
<td>1249</td>
<td>1246</td>
</tr>
<tr>
<td>(\nu_3)</td>
<td>CO stretch</td>
<td>(a')</td>
<td>1706 (87)</td>
<td>1692</td>
<td>1685</td>
<td>1699</td>
</tr>
<tr>
<td>(\nu_2)</td>
<td>CH stretch</td>
<td>(a')</td>
<td>3097 (58)</td>
<td>3073</td>
<td>3066</td>
<td>3073</td>
</tr>
<tr>
<td>(\nu_1)</td>
<td>OH stretch</td>
<td>(a')</td>
<td>3529 (413)</td>
<td>3511</td>
<td>3499</td>
<td>3511</td>
</tr>
</tbody>
</table>

\(^a\) ACES II using analytic gradients, all electrons are correlated. \(^b\) MOLPRO using finite differences, core electrons are frozen. \(^c\) Finite-differences calculations using PES fitted to the cc-pVTZ (frozen core) results.
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-pV6Z level (ZPE excluded). The highest occupied molecular orbital (HOMO) on HCOH is a lone pair on the carbon center. The ionized carbon atom presents a much higher energy level, and the oxygen’s electron density is brought closer to its original position. 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.

**TABLE 3: Comparison of Harmonic Frequencies (cm\(^{-1}\)) between the Neutral and the 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>1376</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 cis and trans wells, are 6190 and 7085 cm\(^{-1}\) above the trans minimum (Figure 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 6717 cm\(^{-1}\) for the linear, and by 3578 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.

**TABLE 4: The HCOH\(^+\) VCI Vibrational Levels below 3600 cm\(^{-1}\), and Corresponding Levels for HCOD\(^+\) (cm\(^{-1}\))**

<table>
<thead>
<tr>
<th>state</th>
<th>no.</th>
<th>label</th>
<th>cis-HCOH(^+)</th>
<th>cis-HCOD(^+)</th>
<th>trans-HCOH(^+)</th>
<th>trans-HCOD(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \nu_1 )</td>
<td>905</td>
<td>746</td>
<td>935</td>
<td>781</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( \nu_2 )</td>
<td>949</td>
<td>822</td>
<td>967</td>
<td>822</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( \nu_4 )</td>
<td>1126</td>
<td>1099</td>
<td>1211</td>
<td>1143</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( \nu_5 )</td>
<td>1684</td>
<td>1671</td>
<td>1664</td>
<td>1655</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2( \nu_5 )</td>
<td>1811</td>
<td>1475</td>
<td>1858</td>
<td>1547</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( \nu_6 + \nu_8 )</td>
<td>1874</td>
<td>1575</td>
<td>1915</td>
<td>1604</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2( \nu_6 )</td>
<td>1885</td>
<td>1641</td>
<td>1933</td>
<td>1644</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>( \nu_5 + \nu_8 )</td>
<td>2045</td>
<td>1835</td>
<td>2149</td>
<td>1912</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>( \nu_6 + \nu_8 )</td>
<td>2052</td>
<td>1947</td>
<td>2141</td>
<td>1982</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2( \nu_6 )</td>
<td>2224</td>
<td>2167</td>
<td>2405</td>
<td>2259</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>( \nu_1 + \nu_5 )</td>
<td>2582</td>
<td>2436</td>
<td>2597</td>
<td>2417</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>( \nu_1 + \nu_5 )</td>
<td>2624</td>
<td>2488</td>
<td>2626</td>
<td>2477</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>( \nu_3 )</td>
<td>2711</td>
<td>2193</td>
<td>2779</td>
<td>2301</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>( \nu_7 + \nu_8 )</td>
<td>2782</td>
<td>2306</td>
<td>2826</td>
<td>2365</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>( \nu_1 + \nu_5 )</td>
<td>2801</td>
<td>2753</td>
<td>2863</td>
<td>2785</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>( \nu_3 )</td>
<td>2823</td>
<td>2456</td>
<td>2908</td>
<td>2463</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>( \nu_7 + \nu_8 )</td>
<td>2825</td>
<td>2395</td>
<td>2903</td>
<td>2430</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>( \nu_7 )</td>
<td>2896</td>
<td>2384</td>
<td>2933</td>
<td>2478</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>( \nu_7 + \nu_8 )</td>
<td>2954</td>
<td>2784</td>
<td>3054</td>
<td>2818</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>( \nu_5 + \nu_8 )</td>
<td>2962</td>
<td>2557</td>
<td>3100</td>
<td>2671</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>( \nu_7 + \nu_8 )</td>
<td>2990</td>
<td>2691</td>
<td>3090</td>
<td>2751</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>( \nu_5 + \nu_8 )</td>
<td>3122</td>
<td>3038</td>
<td>3298</td>
<td>3109</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>( \nu_5 + \nu_8 )</td>
<td>3156</td>
<td>2877</td>
<td>3340</td>
<td>3016</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>( \nu_5 )</td>
<td>3248</td>
<td>2900</td>
<td>3328</td>
<td>2927</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>( \nu_3 )</td>
<td>3300</td>
<td>3191</td>
<td>3578</td>
<td>3347</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>( \nu_3 )</td>
<td>3347</td>
<td>3321</td>
<td>3306</td>
<td>3287</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>( \nu_1 + \nu_5 )</td>
<td>3481</td>
<td>3176</td>
<td>3519</td>
<td>3177</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>( \nu_5 + \nu_8 )</td>
<td>3542</td>
<td>3253</td>
<td>3574</td>
<td>3285</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>( \nu_5 + \nu_8 )</td>
<td>3560</td>
<td>3504</td>
<td>3589</td>
<td>3301</td>
<td></td>
</tr>
</tbody>
</table>

It should be noted that Figure 1 in our previous paper\(^6\) had a typographical error: energies of the two barriers connecting cis- and trans-HCOH were incorrectly labeled relative to the cis minimum, rather than to the trans, as indicated. 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 Web site.

**IV. Photoelectron Spectra of HCOH**

Vibrational levels of HCOH\(^+\) up to 3600 cm\(^{-1}\) are listed in Table 4. Considering the fundamental excitations, the first four levels (up to 1700 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 Figure 5, and positions and intensities are tabulated in Tables 5 and 6. The intensities are unitless; an intensity of 1 corresponds to full overlap between the neutral and cation wave functions. The cis-HCOH photoelectron spectrum is given in Figure 5 and Table 5. In the low-energy region (0–2000 cm\(^{-1}\)), the lowest-frequency mode, \( \nu_5 \), has no intensity. This is the only mode that is not fully symmetric. If this normal mode were separable in the PES, then transitions to odd levels would be forbidden by symmetry. The other four fundamentals in this range have appreciable intensity, with \( \nu_5 \) and 2\( \nu_5 \) being the strongest. In cis-HCOH\(^+\), \( \nu_5 \) is a scissoring of OH and CH, which moves the molecule toward linearity. From Figure 4, displacement along this mode brings the cation into the Franck–Condor region. \( \nu_5 \) increases one angle and decreases the other one. It is active because the difference in H–C–O angles in neutral and cation structures is much larger than the...
The qualitative differences in the two photoelectron spectra are due to the conformational 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 bond angle change.

V. Photoelectron Spectra of HCOH

The photoelectron spectra for cis- and trans-HCOH are depicted in Figure 6 and tabulated in Tables 5 and 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-HCOH.

VI. 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; that is, 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 the
equilibrium structures along that normal coordinate. Because
of the neglect of rotations, \( \Delta Q \) depends 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.

Figure 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 Figure 7) and the 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 (amu)\( ^{1/2} \) for neutral
and cation normal coordinates, respectively. The differences are
due to rotations (mixing); the CO bond is longer in the neutral;
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 H–O–C and H–C–O
angles (by 0.35 and 0.33 Å (amu)\( ^{1/2} \) in the neutral and the 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 Figure 7) and underestimates
the intensity of all states with quanta in this mode.

Figure 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 Figure 8). The displacements are 0.05 and 0.15 Å (amu)\( ^{1/2} \)
in the neutral and cation normal coordinates, respectively.

The effect of normal coordinate rotation on the wave function
overlap between states is shown in Figure 9. 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 Figure 9). 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 Figure 9). 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.

VII. Conclusions

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 neutral isomers are also presented. HCOH$^+$ is derived by removing an electron from a doubly occupied lone pair orbital on the carbon atom (Figure 3), with antibonding contribution along CO. This leads to large structural changes upon ionization, including shortening of the CO bond and an increase in the H–C–O 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 within 35 cm$^{-1}$ of the harmonic ones for the lowest four normal modes, whereas 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, nonzero Franck–Condon factors are calculated for energies up to 7000 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 from those 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 accurate only 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 2000 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.

**Acknowledgment.** This work is conducted under the auspices of the iOpenShell Center for Computational Studies of Electronic Structure and Spectroscopy of Open-Shell and Electronically Excited Species supported by the National Science Foundation through the CRIF:CRF CHE-0625419 + 0624602 + 0625237 grant. A.I.K. and J.M.B. also acknowledge support of the Department of Energy (DE-FG02-05ER15685 and DE-FG02-97ER14782, respectively).

**References and Notes**


**Figure 9.** The effect of rotations of normal coordinates on Franck—Condon factors with the parallel-mode approximation. (a) The correct overlap between wave functions on lower (q\(_{\alpha}\)) and upper (q\(_{\beta}\)) 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.

**References and Notes**