Revisiting the benzene excimer using [2,2] paracyclopophane model system: Experiment and theory

Omer Haggag; Roi Baer; Sanford Ruhman; Anna I. Krylov

https://doi.org/10.1063/5.0196641
Revisiting the benzene excimer using [2,2] paracyclophane model system: Experiment and theory

Omer Haggag,1 Roi Baer,2 Sanford Ruhman,1,a) and Anna I. Krylov3,a)

AFFILIATIONS
1 Institute of Chemistry, The Hebrew University of Jerusalem, Givat Ram, Jerusalem 9190401, Israel
2 Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, Givat Ram, Jerusalem 9190401, Israel
3 Department of Chemistry, University of Southern California, Los Angeles, California 90089, USA

a) Authors to whom correspondence should be addressed: sandy@mail.huji.ac.il and krylov@usc.edu

ABSTRACT
We report high-level calculations of the excited states of [2,2]-paracyclophane (PCP), which was recently investigated experimentally by ultrafast pump–probe experiments on oriented single crystals [Haggag et al., ChemPhotoChem 6 e202200181 (2022)]. PCP, in which the orientation of the two benzene rings and their range of motion are constrained, serves as a model for studying benzene excimer formation. The character of the excimer state and the state responsible for the brightest transition are similar to those of the benzene dimer. The constrained structure of PCP allows one to focus on the most important degree of freedom, the inter-ring distance. The calculations explain the main features of the transient absorption spectral evolution. This brightest transition of the excimer is polarized along the inter-fragment axis. The absorption of the light polarized in the plane of the rings reveals the presence of other absorbing states of Rydberg character, with much weaker intensities. We also report new transient absorption data obtained by a broadband 8 fs pump, which time-resolve strong modulations of the excimer absorption. The combination of theory and experiment provides a detailed picture of the evolution of the electronic structure of the PCP excimer in the course of a single molecular vibration.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0196641

I. INTRODUCTION
Excimers and exciplexes are important players in many photochemical processes. They are complexes of two molecular fragments that interact weakly in the ground electronic state but form much stronger bonds upon electronic excitation. Excimers are formed by two identical fragments, whereas exciplexes are formed by two different fragments.

The driving force for excimer formation is explained by the molecular orbital theory, as illustrated in Fig. 1 for the helium dimer. In the ground electronic state, interaction between the two He atoms is very weak because the formal bond order is zero. However, upon electronic excitation (or ionization), the bond order increases, giving rise to a strongly bound dimer. To highlight the similarity with the quantum-mechanical picture of covalent bonding, we refer to this description as the DMO-LCFMO (dimer molecular orbitals–linear combination of fragment molecular orbitals) framework.1 DMO-LCFMO explains trends in the ionization energies of π-stacked nucleic acid bases and other aromatic dimers1–3 as well as excimer formation in liquid helium4,5 and benzene.6,7

Excimers were first observed in mercury8 and helium9,10 dimers. The first observation of aromatic excimers (formed by pyrene) was reported in 1954 by Förster and Kasper.11 As a prototypical aromatic molecule, benzene has been the subject of numerous experimental and theoretical studies. The formation of excimers in benzene was first observed experimentally by Birks in 1968.12,13 It manifests in a strong and broad absorption band at 2.4–2.5 eV, located below the benzene monomer’s lowest excited singlet state. The nature of the transition has been somewhat unclear—because of symmetry considerations, Birks’ initial assignment of this transition to B1g → E1u was questioned. Later, theoretical analyses and high-level calculations confirmed1 that the strong excimer absorption
The Journal
of Chemical Physics
ARTICLE
pubs.aip.org/aip/jcp

Published under an exclusive license by AIP Publishing

of Chemical Physics

15–17
bulk to the rings plane.

between the absorption components polarized along and perpendicular to each other, and their long axes (the x axes) are parallel and coincide with the crystal’s unique direction (c). Accordingly, light propagating perpendicularly to the crystal plane measures the absorption component along the x axis (in-plane) if its polarization is set to coincide with this direction. Setting the light polarization perpendicular to the x axis measures the combined absorption along the y (inter-ring) and z (in-plane short axis) axes.

Recently, some of us reported the results of time-resolved experiments on PCP single crystals.18 The two benzene rings in PCP are already parallel, and the excitation induces structural relaxation along the inter-ring coordinate, leading to a large-amplitude breathing motion. The polarization data suggested that several absorbing states contribute to the signal and revealed absorbing components

FIG. 1. Molecular orbital diagram explaining excimer formation in He₂. In the ground electronic state, \( \sigma^*(1s) \rightarrow \sigma^*(1s) \), the formal bond order is zero, giving rise to a very shallow potential energy curve (bonding energy of 11 K). However, upon electron promotion from \( \sigma^*(1s) \) to \( \sigma^*(2s) \), the bond order becomes one, resulting in the formation of strongly bound He². This diagram also suggests the existence of a bright excimer transition, \( \sigma^*(2s) \rightarrow \sigma^*(2s) \), polarized along the He–He axis and resulting in a repulsive electronic state.

can indeed be assigned to this transition—a small distortion lowering symmetry from \( D_{ld} \) to \( D_{2d} \) splits the optically forbidden \( E_{hu} \) state into dark and bright components, with the bright component being polarized along the inter-fragment axis, as expected for the excimer transition.14 In the DMO-LCFMO framework, this transition is similar to the \( \sigma^*(2s) \rightarrow \sigma^*(2s) \) transition in the helium dimer (Fig. 1). This study also noted a mixed valence–Rydberg character (Fig. 1). This diagram also suggests the existence of a bright excimer transition, \( \sigma^*(2s) \rightarrow \sigma^*(2s) \), polarized along the He–He axis and resulting in a repulsive electronic state.

In a previous study,17 we used ultrafast time-resolved pump–probe spectroscopy to interrogate the dynamics of excimer formation in liquid benzene. We found that the characteristic excimer absorption appears within 50 fs following the excitation and then increases fourfold in the course of 100 ps. While the rearrangement of the benzene molecules to form an excimer structure (tight sandwich) explains the slow rise, the fast appearance was puzzling. The calculations attributed it to the delocalized excitations supported by suitably oriented pairs of molecules, which are present in liquid benzene in sufficient amounts due to its disordered structure and thermal fluctuations.

The highly disordered structure of the liquid, the presence of multiple configurations, and significant structural rearrangements involved in the formation of the excimer complicate the interpretation of time-resolved spectroscopic data.

These issues have motivated us to revisit the electronic states of benzene dimer and excimer formation using a model system in which benzene moieties are constrained to the sandwich configuration by covalent bridges. Here, \( [2,2] \)-paracyclophane (PCP) is such a model system (see Fig. 2). In addition to the constrained molecular structure, the crystal packing of PCP allows one to distinguish between the absorption components polarized along and perpendicular to the rings plane.15–17 Figure 3 shows the crystal structure of PCP. The unit cell of this tetragonal crystal contains two molecules of PCP. The benzene rings of the molecules are parallel to each other, and their long axes (the x axes) are parallel and coincide with the crystal’s unique direction (c). Accordingly, light propagating perpendicularly to the crystal plane measures the

FIG. 2. PCP structure, definitions of the axes, key distances (\( d_1 - d_3 \)), and dihedral angle \( \alpha_1 \) defined by highlighted atoms.

FIG. 3. Crystal structure of PCP. a–c is the crystal plane. Black axes show the internal coordinate frames (see Fig. 2) of the two molecular orientations present in the unit cell. Light polarized along the a direction probes transitions along the y and z axes, and light polarized along the c direction probes transitions along the x axis.
polarized along all three molecular axes, with the inter-ring component \((y + z)\) nearly twice as intense as the in-plane component \((x)\). However, the nature of the absorbing states was not characterized.

Here, we present a detailed theoretical analysis of the excimer formation in PCP and its absorption using state-of-the-art quantum chemical calculations. As in our previous studies,\(^6,7\) we employ the equation-of-motion coupled-cluster method for excitation energies with single and double substitutions (EOM-EE-CCSD or EOM-CCSD for short),\(^5,21\) which is capable of describing states of mixed character (here, valence and Rydberg states). In contrast to the previous studies, we use a larger basis set with additional sets of diffuse functions, 6-311(2\(d^\ast\),2\(p^\ast\))G(d,p).

We also present new experimental results. Our previous study\(^18\) has shown that excimer absorption polarized along the inter-ring axis features several bands with intensities that are strongly dependent on the inter-ring distance. Using the narrow bandwidth UV pump (FWHM = 4 nm),\(^19\) we were able to resolve the vibrational period of the inter-ring breathing mode but were not able to achieve sub-period resolution because the excitation pulse duration was insufficient for achieving perfect localization of the reactive wavepacket in the excited state. Here, we use a broadband UV pump (FWHM = 30 nm), which significantly improves the localization of the wave-packet, affording precise mapping of the energy differences between the PESs in the course of a vibrational period (more on this in Sec. III). This mapping enables a quantitative comparison between theory and experiment.

Figure 2 shows the structure of PCP in the standard Q-Chem orientation,\(^22\) along with the definitions of the key structural parameters. The calculations show that the system has a \(D_2h\) symmetry both in the ground state and in the lowest excited state (excimer state). In a perfect sandwich configuration, the symmetry is \(D_{2h}\). The deviation from \(D_{2h}\) can be explained by the structural strain, which results in slight twisting of the benzene rings (shown in Fig. S1 in the supplementary material). The strain is also responsible for the warping of the benzene rings. The distances \(d_1\) and \(d_2\) represent the distance between the two benzene moieties. In a perfect sandwich arrangement, \(d_1 = d_2\); however, the structure of PCP is strained and benzene rings are puckered. The difference between \(d_1\) and \(d_2\) can characterize the extent of the deformation. Another important parameter is the dihedral angle \(\alpha_1\). In a perfect sandwich configuration of \(D_{2h}\) symmetry, this dihedral angle is zero; hence, the value of \(\alpha_1\) quantifies the deviation from \(D_{2h}\). In the excited state, the excimer formation results in a shorter distance between the rings, as discussed in detail below. This inter-ring breathing motion, activated by electronic excitation, modulates excimer absorption. Quantitative understanding of these modulations is the main focus of this paper.

In our pump–probe experiment, we excite the PCP crystal (Fig. 3) with a broadband pump centered around 300 nm (4.13 eV) polarized along \(x\), and then monitor the excited-state dynamics using ultrafast probe pulses in the range of 400–750 nm (3.10–1.65 eV). The pump is always aligned along the \(x\) axis using birefringent properties of PCP crystals. We then control polarization of the probe relative to the pump and measure the transient absorption polarized along \(x\) (in-plane long axis) and along \(y + z\) (inter-ring and in-plane short axis). A detailed description of the experimental setup is given below.

### II. COMPUTATIONAL DETAILS

All calculations were done with the Q-Chem quantum chemistry program.\(^3,5\) We use Q-Chem’s symmetry convention\(^22\) throughout the manuscript, meaning that the \(b_1\) and \(b_2\) irreps are flipped relative to the standard Mulliken convention (see Table S1 in the supplementary material).

We optimized the ground-state (\(S_0\)) structure of PCP (shown in Fig. 2 and in Fig. S1 in the supplementary material) using two range-separated functionals augmented with dispersion correction, \(\omega B97X-D\) and CAMB3LYP-D. The excimer structure was obtained by optimizing the lowest excited state (\(1^1B_2\), \(S_1\)). EOM-CCSD, \(\omega B97X-D\), and CAMB3LYP-D were used for the excited-state geometry optimization. In CAMB3LYP-D calculations, \(D_3\_ZERO\) dispersion correction was used (both in the ground and excited states).

| Table I: Essential structural parameters of PCP in the ground and first excited states. Figure 2 shows the definition of structural parameters, \(\omega_{br}\) and \(\omega_{tw}\) are frequencies of the breathing and twisting modes, respectively. |
|-----------------|--------|--------|---------|---------|---------|---------|
| State/method    | \(d_1\) | \(d_2\) | \(d_3\) | \(\alpha_1\) | \(\omega_{br}\) | \(\omega_{tw}\) |
| \(S_0/\text{exp}\) | 3.099  | 2.784  | 1.593   | -12.83  | 241     | 72      |
| \(S_0/\omega B97X-D\) | 3.115  | 2.800  | 1.591   | -18.12  | 256.5   | 78.8    |
| \(S_0/\text{CAMB3LYP-D}\) | 3.106  | 2.796  | 1.593   | -14.80  | 251.0   | 60.5    |
| \(S_1/\text{exp}\) |        |        |         |         | 233     | 72\(^d\) |
| \(S_1/\omega B97X-D\) | 2.903  | 2.617  | 1.571   | -13.6   | 249.3   | 29.2    |
| \(S_1/\text{CAMB3LYP-D}\) | 2.903  | 2.622  | 1.571   | -11.0   | 249.3   | 29.2    |
| \(S_1/EOM-CCSD\) | 2.931  | 2.630  | 1.577   | -13.6   | 233.4\(^e\) |        |

\(^a\)All optimization and frequency calculations were performed with the 6-311+G(d,p) basis.

\(^b\)From Refs. 35–37, the experimental dihedral and bond lengths were taken at 15 K (Ref. 37). The vibrational frequencies were taken from Refs. 35 and 36.

\(^c\)From Ref. 18.

\(^d\)In solution.

\(^e\)Numeric estimate; see the supplementary material.
All geometry optimizations and frequency calculations were carried out with the 6-311+G(d,p) basis set. Because we could not resolve the persistent imaginary frequency in calculations using ωB97X-D, we modeled the potential energy surface (PES) scans using CAMB3LYP-D/6-311+G(d,p) structures and normal modes. Both CAMB3LYP-D and EOM-CCSD yield \( D_2 \) excimer structures. The essential structural parameters are collected in Table I. The Cartesian geometries of the optimized structures and vibrational frequencies are given in the supplementary material.

The excited states were computed using the EOM-CCSD and CAMB3LYP-D methods with the 6-311\((2+\),+\)G(d,p) basis set. Additional calculations were carried out with aug-cc-pVTZ. To reduce computational costs, we used single precision in EOM-CC calculations. Core electrons were frozen in correlated calculations. An example of an input file for these calculations is given in the supplementary material.

We used natural transition orbitals (NTOs) and corresponding exciton descriptors\(^{26–30}\) to characterize electronic transitions. In particular, we used hole and particle sizes to quantify the extent of the Rydberg character and the participation ratio (PR\(_{\text{NTO}}\)) to quantify the essential number of configurations contributing to transitions, similar to our previous work.\(^ {31}\) We note that these descriptors can also help distinguish between excimers and excitons, as was shown by Plasser and Lischka.\(^ {14,32}\) This analysis was carried out using the libwfa package.\(^ {33}\)

To identify Franck–Condon active modes, we used the ezPCF program.\(^ {34}\) We then generated displacements along the Franck–Condon active mode and used them to compute excimer’s absorption spectra at different geometries. The computed stick spectra were convoluted with Gaussians (\(σ = 0.1\) eV).

To model transient absorption spectra, we mapped the structures to the probe times using the classic harmonic oscillator model; more details are given below.
Supercontinuum probe pulses in the range of 400–750 nm were generated by focusing the 800 nm seed on a 2 mm plate of CaF\(_2\). A \(\lambda/2\) wave plate was introduced into the probe path to control polarization of the probe pulse relative to the pump.

To align the pump polarization with the molecular \(x\) axis, we used the birefringent properties of the uni-axial PCP crystal. Following full blockage of the pump by a UV polarizer, the crystal sample was introduced into the optical path. Then, the crystal film was rotated to fully darken the pump transmission.

As mentioned in the Introduction, in the present experiments, we improved time resolution using the broadband pump. In the previous study, \(^\text{13}\) we used a narrow bandwidth UV pump (FWHM = 4 nm) with a 30 fs duration assuming a transform-limited Gaussian centered at 300 nm, which was sufficient to probe the vibrational period of the inter-ring breathing mode. However, the vibrational wave-packet induced on \(S_1\) was too broad. Figure S2 in the supplementary material shows a simulated wave-packet induced on the \(S_1\) PES under these conditions. During the period of vibration, the probability density of the wave-packet shifts from side to side, while maintaining a notable density throughout the entire allowed coordinate space. Due to this delocalization of the wave-packet, we could only partially resolve the evolution of the transient absorption within the vibrational period. Figure S3 in the supplementary material shows the simulations corresponding to the current experiment, a broadband UV pump pulse (FWHM = 30 nm) with a duration of \(\sim 8\) fs. As one can see, the localization of the wave-packet induced on \(S_1\) is significantly improved, allowing us to resolve instantaneous energy gaps between the electronic states of the excimer.

**IV. RESULTS AND DISCUSSION**

Figure 5 shows the sketch of the present experiment, highlighting the differences between the frequency-domain and time-domain approaches. The excimer state (\(S_1\) state) is characterized by increased bonding interactions between the two benzene rings relative to the ground state. The characteristic strong excimer absorption is dominated by the transition to the repulsive state (red curve), polarized along the inter-fragment axis. Because this state is strongly repulsive, excimer’s absorption spectrum is broad and featureless—as expected from the reflection principle. The information about the states responsible for excimer absorption (e.g., if there is more than one state involved) and the exact shape of the corresponding PES is hidden in the frequency-domain spectrum. In contrast, the time-resolved measurements can reveal these details. Briefly, the pump excites the PCP to the \(S_1\) state (excimer state), creating a vibrational wave-packet at the Franck-Condon (FC) point. This is an endpoint of the ensuing vibrational motion along the breathing mode. The wave-packet moves toward the \(S_1\) minimum but due to the acquired momentum, overshoots to an inner turning point along the breathing normal mode (inverted geometry, which corresponds to the compressed structure). As the wave-packet evolves on \(S_1\), the broadband probe pulses produce spectra corresponding to the specific positions of the wave-packet and reporting on the instantaneous energy gaps between the \(S_1\) and absorbing states as well as respective oscillator strengths. The precision of this report depends on the degree of localization of the wave-packet, which is very tight in the present experiment owing to the extreme shortness of the pump. Analysis of the spectral modulations as a function of the probe wavelength and polarization can reveal whether the modulations are due to a coordinate dependence of the vertical energy gaps between the PESs or due to a coordinate dependence of the transition dipole moments (non-Condon effects). Finally, the large frequency range of the probe allows observing the transitions to several absorbing states.

In the discussion below, we focus on the three structures—Franck-Condon point, the \(S_0\) minimum, and the inner turning point corresponding to the compressed geometry. Polarization measurements allow disentangling contributions from different absorbing states (e.g., blue vs red).

**A. Molecular orbital framework and symmetry**

The \(D_2\) character table is given in the supplementary material. Using the molecular orientation\(^\text{22}\) shown in Fig. 2, the \(z\) axis belongs to the \(b_1\) irreps, the \(x\) axis belongs to the \(b_2\) irreps, and the \(y\) axis belongs to the \(b_3\) irreps. Hence, transitions polarized along \(y + z\), which correspond to the inter-ring and short in-pane axes, belong to the \(b_1\) and \(b_2\) irreps, and transitions polarized along \(x\), which corresponds to the in-plane long axis, belong to the \(b_3\) irreps.

The lowest excited state of PCP is \(B_2\) (using the molecular orientation shown in Fig. 2). At the \(S_0\) geometry, this state is located 4.41 eV above the ground state [at the EOM-CCSD/6-311G(d,p) level of theory] and is weakly allowed (\(\epsilon_1 = 0.001\), polarized along the \(x\)-axis). Figure 6 shows the NTOs for the \(S_0 \rightarrow S_1\) transition. They are very similar to the NTOs of the analogous transition in the benzene dimer,\(^\text{6,7}\) confirming that PCP is a good model of the benzene dimer. Hole NTOs can be described as anti-bonding (with respect to the two benzene rings) combinations of the \(\pi^*\)-type HOMOs, and particle NTOs can be described as bonding combination of the \(\pi\)-type LUMOs. Thus, similar to the \(\text{H}_2\) example (Fig. 1), the transition results in bonding interactions between the two rings so that the excitation to \(S_1\) leads to significant...
The S$_1$ vibrational analysis yields an inter-ring breathing frequency of 249 cm$^{-1}$ and twisting frequency of 29 cm$^{-1}$, in-line with the experimental values obtained from the excitation spectrum of cold PCP crystals$^{35,36}$ and transient absorption data of the PCP excimer.$^{37}$

Within the double-harmonic parallel-mode approximation (a displaced harmonic oscillator model), $ezPCF$ calculation$^{34}$ shows that the most active Frank–Condon mode for the S$_0$ → S$_1$ excitation corresponds to the inter-ring breathing vibration with a 1.1772 Å/amu displacement (calculated using the normal modes of the S$_1$ state). We also computed the Huang–Rys factors (i.e., the number of vibrational levels for a given mode accessible upon vertical transition) for this transition using the following equation:

$$s_k = \frac{1}{2} \left( \frac{\omega_k \cdot |\Delta \tilde{q}_k|^2}{\hbar} - 1 \right),$$

where $s_k$, $\omega_k$, and $|\Delta \tilde{q}_k|$ denote the Huang–Rys factor, frequency, and mass-weighted displacement along the $k$th normal mode, respectively. Given the ground-state ($\tilde{r}_0$) and excited-state ($\tilde{r}_1$) Cartesian geometries, the mass-weighted displacement along the $k$th normal mode is calculated according to the following equation:

$$|\Delta \tilde{r}_k| = \tilde{q}_k \cdot M^1 \cdot (\tilde{r}_1 - \tilde{r}_0),$$

where $\tilde{q}_k^1$ represents the $k$th mass-weighted normal mode and $M^1$ is a diagonal matrix containing the square-roots of masses ordered according to their positions in the displacement vectors. The computed Huang–Rys factors yield $s = 5$ for the inter-ring breathing mode (see Fig. S4 in the supplementary material) and $s = 0$ for the rest.

Accordingly, we generated 21 Cartesian geometries, $\tilde{R}(n)$, for displacements along the breathing mode centered around the S$_1$ minimum (zero displacement, $n = 0$),

$$\tilde{R}(n) = \tilde{r}_1 \pm \frac{n}{10} \cdot |\Delta \tilde{r}_0| \cdot \tilde{r}_0, \quad n = 0, 1, \ldots, 10,$$

where $\tilde{r}_0$ represents the breathing mode and $|\Delta \tilde{r}_0|$ represents the total displacement along this mode, both in the Cartesian units (Å),

$$|\Delta \tilde{r}_0| = \tilde{r}_0 \cdot (\tilde{r}_1 - \tilde{r}_0).$$

The displacements range from −0.474 to 0.474 Å in Cartesian coordinates and from −1.2 to 1.2 Å/amu in mass-weighted coordinates, with 0.474 corresponding to the Franck–Condon point, zero corresponding to the the S$_1$ minimum, and −0.474 corresponding to the inner turning point of the breathing mode (the most compressed structure).

To validate the displacements and to estimate anharmonicity, we numerically solved the vibrational problem using the computed PES scans (see Fig. S4 in the supplementary material). The numerically computed harmonic frequencies are very close to the analytic CAMB3LYP-D value for the CAMB3LYP-D curve (249.9 vs 249.3 cm$^{-1}$), whereas the EOM-CCSD curve yielded a smaller value (233.4 cm$^{-1}$). The anharmonicities for both curves were negligible. We note that the EOM-CCSD frequency of the breathing mode of the excimer is in remarkably good agreement with the experimental value.
C. Excited states of PCP

Figure 7 shows excited-state PESs along the inter-ring breathing mode computed with EOM-CCSD/6-311(2+,+)+G(d,p) (the CAMB3LYP-D results are shown in the supplementary material). The lowest state is the excimer state (1B2). We computed 12 excited states of A symmetry, 17 excited states of B1 symmetry, one excited state of B2 symmetry (excimer state), and 12 excited states of B3 symmetry. At zero displacement (excimer structure), this covers energy ranges up to 7.09, 7.00, and 7.13 eV in the A, B1, and B3 symmetries relative to the ground state or, equivalently, up to 3.19, 3.10, and 3.23 eV relative to the excimer state (located at 3.90 eV). As one can see, the manifold of electronic states is very dense. Hence, it is not surprising that the transient absorption cannot be modeled by assuming a single absorbing state with fixed oscillator strength. According to the NTO analysis, the states can be described as valence-like and Rydberg-like excitations, as well as states of mixed character.21 Importantly, different states show different dependences on the inter-ring distance, which can be rationalized by the shape of the corresponding NTOs. In the discussion below, we focus our analysis on the states relevant to excimer absorption.

To recall the transient-absorption setup and the definitions of the relevant structures, we refer readers to Fig. 5. After the discussion of the computed PESs, one can now appreciate the additional complexity of PCP in which multiple electronic states are contributing to the excimer absorption.

Figure 8 shows the computed excimer absorption spectrum at zero displacement (i.e., at the S1 minimum). The brightest peak in the excimer absorption spectrum corresponds to the 1B2 → 9B1 transition at 2.4 eV (f = 0.1237, polarized along y). NTOs for the S0 → 9B1 transition are shown in Fig. S6 in the supplementary material. Based on the orbital shapes and exciton descriptors, this state has mixed valence/Rydberg character—compare the particle sizes of the S0 → S1 and S0 → 9B1 transitions (2.6 vs 3.7 Å). Figure 9 shows NTOs for the 1B2 → 9B1 transition, which visualizes the changes in electron density for the excimer absorption. The valence NTOs for the 1B2 → 9B1 transition correspond to the transition from bonding to anti-bonding (with respect to the fragments) orbitals, leading to the strongly repulsive PES. This orbital picture is similar to the bright excimer state characterized in Ref. 6, but with a larger Rydberg contribution, in part, because here we use a larger basis with more diffuse functions. The computed transition energy (2.36 eV) is lower than the computed transition energy in the benzene excimer reported in Ref. 6 (3.04 eV). Larger contributions of Rydberg configurations in PCP explain the lower oscillator strength of the transition (0.12 here vs 0.3 in Ref. 6). The next bright state in the z + y polarization is 16B1 at about 3.1 eV (f = 0.0220), i.e., 0.7 eV above 9B1. The rest of the states have very low oscillator strengths.

For the transitions polarized along x (A states), the brightest one is the 2A state at 1.89 eV (f = 0.0176). Its oscillator strength is 6.8 times smaller than that of the 9B1 state. The next brightest state is 5A at 2.61 eV (f = 0.0059). NTOs for these two transitions are shown in Fig. 10. The particle sizes for these transitions are 6.2 and 7.0 Å, respectively, revealing their predominantly Rydberg character.
Figure 10. NTOs for the transition from the ground state to the 2A and 5A states (the brightest transitions in excimer absorption for polarization along the x axis) at the optimized geometry of the excimer. EOM-CCSD/6-311(2+)+G(d,p). Renormalized squares of singular values. 2A state: \( \Omega = 0.83, PR_{\text{NTO}} = 1.0 \), particle size = 6.2 Å. 5A state: \( \Omega = 0.84, PR_{\text{NTO}} = 1.02 \), particle size = 7.0 Å.

Figure 11 shows the PESs corresponding to the brightest transitions in each polarization. As anticipated, the energy of the brightest B\(_1\) state (purple-then-orange curve) strongly depends on the inter-ring distance. We also observe interaction of this bright state with another state from the B\(_1\) manifold, leading to the diabatic-like interchange of the orange and purple curves shown in Fig. 11, which indicates the changes in the character due to the varying weights of valence and Rydberg excitations. This change in the character of the states leads to change in the respective oscillator strengths of the two adiabatic states (orange and purple), as illustrated in Fig. S7 in the supplementary material. From these plots, one can anticipate large variations in the transient absorption polarized along the \( z + y \), with the most blue-shifted absorption corresponding to the inner turning point (compressed geometry)—the difference in the excitation energy of the brightest B\(_1\) state at the two turning points is 0.6 eV. The PES of the bright A states are flat (i.e., the difference in the excitation energy of the brightest A state at the two turning points is 0.1 eV), consistent with their Rydberg character. Hence, one can anticipate much smaller spectral modulations in the \( x \)-polarized transient absorption in the course of excited-state vibrations. We note that A states also show significant non-Condon effects (Fig. 11, bottom panel, and S7, right panel).

To illustrate variations of the absorption along the breathing mode, we compare the computed spectra at the excimer geometry and the two turning points—the Franck–Condon geometry and the inverted (compressed) structure (see Fig. 5). Figure 12 shows the three spectra for \( y + z \) polarization. As expected from the molecular orbital considerations (recall that this transition corresponds to the excitation from a bonding to an anti-bonding orbital), the most intense peak is red-shifted at the FC point relative to the excimer geometry. In addition, the second most intense peak gains intensity at FC geometry so the difference between the two most intense peaks becomes smaller. Passing the S\(_1\) minimum, as the rings come closer, the intensity and energy of the main peak continue to increase and a new peak appears (due to the 12B\(_1\) state).

The spectra for \( x \) polarization are shown in Fig. 13. The difference between the three spectra is much smaller, again, in agreement...
The increase in the intensity of the secondary peak at the two turning points.

D. DFT vs EOM-CCSD

Figures S8–S10 in the supplementary material show the PESs computed with CAMB3LYP-D. They also show the high density of excited states and capture different slopes of the valence and Rydberg states; however, closer comparison with the EOM-CCSD PES reveals important differences. The differences can be attributed to the residual self-interaction error (SIE), which affects the description of both Rydberg and charge-resonance valence states. For example, the state interaction of the bright $S_1$ states is not captured. Consequently, the computed spectra are notably different, as illustrated in Figs. S10 and S11 in the supplementary material. CAMB3LYP-D correctly identifies the brightest transition for excimer’s absorption as a $B_1$ state with a valence character similar to that of EOM-CCSD; however, its position is strongly red-shifted and its intensity is overestimated compared to that of EOM-CCSD. In the $A$ manifold, the intensity pattern also differs between CAMB3LYP-D and EOM-CCSD. Hence, although the CAMB3LYP-D excimer structures and frequencies agree reasonably well with EOM-CCSD, the excited-states characters and their energies are not accurate. Given its complicated electronic spectrum, PCP can serve as a challenging benchmark for the functional development of excited states.

E. Transient absorption spectra: Theory vs experiment

To connect theory and experiment, we use the computed excitation energies and oscillator strengths at different displacements along the breathing mode to compute the excimer absorption spectra and then compare them with the experimental absorption at the corresponding time delays (see Fig. 5).

We map the structures to the times as follows: Figure 14 shows a transient absorption time trace at the probe energy of 2.0 eV, polarized along $x+y$. Periodic modulation, which persists throughout the entire probing range, is due to the motion of the wave-packet on the $S_1$ PES. Fourier transform and decay analysis of the modulating residual yields a single frequency of $\omega = 233$ cm$^{-1}$ (vibrational period $T_{vib} = 144$ fs) and an exponential decay lifetime of 1.2 ps. The comparison with the experiment requires care because (i) the theoretical calculations are expected to have errors in the absolute values of excitation energies and (ii) experimental spectrum is measured in the 1.75–3.25 eV window. Figures 15 and 16 compare theoretical spectra at the three geometries with the respective experimental traces of the transient absorption. The three theoretical spectra for $y+z$ polarization are red-shifted by 0.57 eV to match the position of the highest peak at the excimer geometry. The theoretical spectra for $x$ polarization are blue-shifted by 0.28 eV to match the position of the highest peak at the excimer geometry. As one can see, once these shifts are applied, the theory and experiment agree reasonably well. The directions of the shifts are consistent with the character of the states—the valence-like $\pi \rightarrow \pi^*$ transitions, such as the bright excimer state, are known to be sensitive to dynamic
As a result, EOM-CCSD often overestimates their excitation energies. Hence, the Rydberg states, which are less sensitive to dynamic correlation, appear red-shifted relative to the excimer state.

We note that the ratio of the intensities of the dominant peaks in each polarization is 7:1 in the computed spectra and 3:1 in the experimental transient absorption (at the $S_1$ minimum). This discrepancy could be due to insufficient correlation treatment; however, it can also be explained by the differences in the radiative lifetimes of the respective states. In the simulations, we applied uniform broadening for all states; however, a simple estimate (see the supplementary material) shows that the radiative lifetime of the $9B_1$ state is 4–5 times shorter than the radiative lifetime of the $2A$ state. Applying broader Gaussians to the former would reduce the apparent intensities of the computed $y + z$ spectra, bringing the ratio closer to the experimental value.

Finally, Fig. 17 compares the time evolution of the excimer absorption for the two polarizations. As one can see, the trends are reproduced very well, both in terms of energy and intensity changes,
as well as appearance of isosbestic points. These large variations of absorption for the $y + z$ polarization reflect changes in the transition energies and in the character of the absorbing states (e.g., relative weight of Rydberg vs valence contributions) along the breathing coordinate, as anticipated from the molecular orbital picture and the scans of the PES and transition dipoles. The blue shift (relative to the FC point) of the main peak results from the combination of the Condon and non-Condon effects: as the vibrational wave-packet moves from the FC geometry toward the compressed structure, the $S_1 \rightarrow 9B_1$ energy gap increases by 0.2 eV, and the oscillator strength increases as well at the expense of the $S_1 \rightarrow 8B_1$ transition (see Fig. 11 and Fig. S7 in the supplementary material). The isosbestic points at 2.4 and 2.7 eV reflect the enhancement of the $S_1 \rightarrow 12B_1$ transition at the expense of the $S_1 \rightarrow 16B_1$ transition. Much smaller variations for the $x$ polarization reflect flatter PES of the absorbing Rydberg states. We note that such levels of detail would not be possible to obtain from the frequency-domain measurements.

Figure 18 shows two-dimensional transient absorption maps for both polarizations. Here, we again see strong oscillations for the $y + z$ component and more shallow dynamics for the $x$ component (note the different scales used in the two panels). The higher-energy feature in the $x$ component is not accessible in the present experiment. The oscillations persist for several picoseconds, which is quite remarkable for a system with so many degrees of freedom. Such a long coherent motion is possible due to a constrained structure of PCP, which results in a perfectly harmonic potential of a single Franck–Condon active mode.

V. CONCLUSIONS

We presented new time-resolved pump–probe measurements and high-level quantum chemistry simulations of the time-dependent absorption of PCP. The electronic states of PCP are similar to the states of the benzene dimer, both in terms of state energies and molecular orbitals involved in the transitions. Hence, PCP represents a suitable and relevant model of the benzene excimer. With the improved resolution, we are able to resolve the changes in the electronic character of the excimer in the course of a single vibrational period. The simulations explain the main experimental findings and the observed trends in the evolution of the main spectral features in terms of the molecular orbital theory. The excimer spectrum in PCP is dominated by the bright transition polarized along
the inter-ring axis. The nature of the excimer state and the bright absorbing state in PCP is very similar to the corresponding states in benzene dimer. The excimer state can be described as the transition from the anti-bonding (with respect to the dimer) orbital formed by benzenes’ HOMOs to the bonding (with respect to the dimer) orbital formed by benzenes’ LUMOs. The bright absorbing excimer state, polarized along the interfragment axis, can be described as a mixture of valence and Rydberg excitations from the former orbital. Because of this character, the excitation energy for this transition is strongly modulated by the PCP breathing mode. The relative weights of Rydberg vs valence configurations also strongly depend on the structure. In addition to this transition, there are much weaker transitions, predominantly of the Rydberg character, polarized in the plane of the benzene rings. These transitions are dwarfed in the total spectrum but become visible when using a polarized probe.

This work illustrates the power of time-resolved spectroscopy. The strongly repulsive PES of the bright absorbing state and multiple absorbing states exhibiting strong vibronic interactions result in a featureless and not very informative absorption spectrum in the frequency domain. In the time domain, by following the evolution of a narrow vibrational wave-packet on S1, we were able to follow the PESs of absorbing states along the breathing coordinate and map the experimental spectral evolution into the computed electronic states.

We conclude by emphasizing the importance of the interplay between theory and experiment. Although the present simulations of the transient absorption spectra agree reasonably well with the experiment and explain the main trends, several aspects of the theory call for improvement: (i) improving correlation treatment to achieve quantitative agreement in transition energies (to eliminate the need of empirical shifts), (ii) building theoretical framework to estimate spectral broadening, (iii) extending the capabilities beyond a single Franck–Condon active mode, and (iv) incorporating the quantum nature of the vibrations in the calculation of the spectra.

SUPPLEMENTARY MATERIAL

The supplementary material contains computational details, structures and frequencies, wave-packet simulations, transition dipole moments and state mixing, EOM-CC data, TD-DFT PES, and spectra.

ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation (Grant No. CHE-2154482 to A. I. K.) and by the Binational Science Foundation (Grant Nos. 2016102 and 2020105 to S. R.). R. B. acknowledges support from the Israel Science Foundation (ISF 1153/23). O. S. H. was supported by an Azrieli Fellowship awarded by the Azrieli Foundation. We thank Mr. Goran Giudetti (USC) for his help with making orbital images. S. R. and O. S. H. thank Cristian Manzoni for his guidance in setting up the UV-SFG optics. O. S. H. thanks Dr. Hadassah Elgavi Sinai and Dr. Ester Livshits (Fritz Haber Center for Molecular Dynamics, Hebrew University of Jerusalem) for providing information about the BNL functional and its use in TD-DFT calculations. Their expertise and support were crucial in the successful completion of this work.

AUTHOR DECLARATIONS

Conflict of Interest

The authors declare the following competing financial interest(s): A. I. K. is the president and a part-owner of Q-Chem, Inc.

Author Contributions

Omer Haggag: Investigation (equal); Visualization (equal); Writing – original draft (equal). Roi Baer: Methodology (equal); Supervision (equal); Writing – review & editing (equal). Sanford Ruhman: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Supervision (equal); Writing – review & editing (equal). Anna I. Krylov: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (equal); Supervision (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and the associated supplementary material.

REFERENCES

The Journal of Chemical Physics