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High-Resolution Spectroscopy of Jet-Cooled 1,1'-Diphenylethylene: Electronically Excited and Ionic States of a Prototypical Cross-Conjugated System

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S Supporting Information

ABSTRACT: The photophysics of a prototypical cross-conjugated π -system, 1,1'-diphenylethylene, have been studied using high-resolution resonance enhanced multiphoton ionization excitation spectroscopy and zero kinetic energy photoelectron spectroscopy, in combination with advanced ab initio calculations. We find that the excitation spectrum of S_1 displays extensive vibrational progressions that we identify to arise from large changes in the torsional angles of the phenyl rings upon electronic excitation. The extensive activity of the antisymmetric inter-ring torsional vibration provides conclusive evidence for a loss of symmetry upon excitation, leading to an inequivalence of the two phenyl rings. Nonresonant zero kinetic energy photoelectron spectroscopy from the ground state of the neutral molecule to the ground state of the radical cation, on the other hand, demonstrates that upon ionization symmetry is retained, and that the geometry changes are considerably smaller. Apart from elucidating how removal of an electron affects the structure of the molecule, these measurements provide an accurate value for the adiabatic ionization energy ($65274 \pm 1 \text{ cm}^{-1}$ (8.093 eV)). Zero kinetic energy photoelectron spectra obtained after excitation of vibronic levels in S_1 confirm these conclusions and provide us with an extensive atlas of ionic vibronic energy levels. For higher excitation energies the excitation spectrum of S_1 becomes quite congested and shows unexpected large intensities. Ab initio calculations strongly suggest that this is caused by a conical intersection between S_1 and S_2 .

I. INTRODUCTION

Although silicon and other inorganic semiconductors are playing a dominant role in the development of modern electronics, organic materials increasingly prove to be competitive by providing adequate solutions with simpler, more widely available, and cheaper technologies like spin-casting,¹ screen printing,² doctor-blading,³ or inkjet printing.⁴ Examples include conducting polymers, organic light emitting diodes^{5–7} scaled up to entire display matrices,⁸ organic lasers,^{9,10} organic photovoltaic cells^{11–14} providing a reasonable efficiency at low production costs, molecular wires,^{15–18} a large variety of optical^{19,20} and chemical detectors,^{21–23} organic transistors,^{24–26} and even large-scale integrated organic circuits.²⁷ Organic π -conjugated polymers, materials with alternating single and double bonds, have in this respect attracted attention from the very start. These molecular systems exhibit delocalization of electrons along their π -conjugated chains leading to the formation of band structure and making them intrinsic semiconductors. The gap between the valence and the

conduction band can be varied over a large energy range by choosing appropriate polymers^{28,29} that thus provide an excellent material base for generating organic light emitting diodes at various wavelengths, organic P–N junctions, and multilayer photovoltaic cells constructed to harvest light efficiently from the solar spectrum.

In view of their application potential, it will not come as much of a surprise that linear π -conjugated polymers have been the subject of a vast number of studies. Surprisingly, branched π -systems have attracted considerably less attention.^{30–33} These systems feature multiple conjugation paths that are not present in their linear counterparts. This can be a key in trying to fix one of the major drawbacks of linear conjugated polymers. Since charge carriers are slowed down when they hop between chains,

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Chart 1. Representation of the Structure of 1,1'-Diphenylethylene with Definition of Employed Angles^a

^aThe torsional angles φ_1 and φ_2 are defined as the dihedral angles $C_2-C_1-C_0-C_1'$ and $C_2'-C_1'-C_0-C_1$, respectively; θ is defined as the $C_1-C_0-C_1'$ bond angle; δ_1 and δ_2 are the dihedral angles $C_8-C_7-C_0-C_1$ and $C_8'-C_7'-C_0-C_1'$, respectively.

materials based upon these polymers can exhibit a strong anisotropy of their optical and charge-transfer properties. Controlling these properties thus implies control over the organization of the material on a molecular scale during device production. Furthermore, the presence of multiple conjugation paths could in principle also lead to enhanced carrier mobility,^{34,35} many other unique phenomena³⁶ and the design of intelligent materials in which the energy flow can be controlled at the molecular level. This perspective is nowadays especially appealing—and also realistic—with the rapid progress in the development of coherent control techniques that enable excited state dynamics to be steered as was, for example, demonstrated for the laser-controlled energy flow in natural and artificial light-harvesting antennas^{37,38} and other π -conjugated molecular systems.^{39,40}

1,1'-Diphenylethylene (DPE) (Chart 1) is a prototypical example of a branched π -system.⁴¹ Since the phenyl groups provide excellent chromophores, and because it is relatively easy to seed into supersonic expansions, DPE has favorable characteristics for high-resolution spectroscopic studies. An additional advantage of the system is that in recent years extensive studies have been performed on its nonconjugated analog diphenylmethane^{42,43} and simple derivatives^{44,45} that enable one to elucidate which properties of DPE are directly linked to its branched π -conjugation character, and which properties are associated with other effects such as, for example, excitonic coupling. Furthermore, studies on other nonconjugated, bridged biphenylic molecules like diphenylamine,^{46,47} and diphenyl ether⁴⁸ as well as heterocross-conjugated benzophenone^{49,50} provide an additional reference framework from which the effects of cross-conjugation can be assessed.

All the same, DPE has been the subject of surprisingly few studies up until now. Experimentally, IR absorption and Raman spectroscopy has been used to investigate the ground state vibrational structure,^{51,42} while the lower ionic manifold has been studied with He I photoelectron spectroscopy as part of studies on the effects of steric inhibition of resonance.⁵³ Studies on the spectroscopy and dynamics of electronically excited states are limited to a series of reports by Gustav and Bölke more than 25 years ago.^{54–57}

In the present work we have used mass-resolved, high-resolution spectroscopic techniques to study the spectroscopic and dynamic properties of DPE under isolated and internally cooled molecule

conditions. Electronic excitation spectra of the lower excited singlet states obtained by resonance enhanced two photon ionization (R2PI) spectroscopy display a vast amount of vibronic activity that nevertheless can be assigned confidently using the results of quantum chemical calculations. Interestingly, we find that when the molecule is excited to S_1 the two phenyl rings become inequivalent. Moreover, strong indications are found that some 800 cm^{-1} above the S_1 minimum excitation a conical intersection of S_1 and S_2 is present. Zero kinetic energy (ZEKE) photoelectron spectroscopy similarly enables us to determine the adiabatic ionization energy and study the properties of the lowest ionic state. Contrary to excitation of the lowest excited singlet state, symmetry is retained upon ionization.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Experimental Details. Resonant two-photon ionization (R2PI) spectroscopy, UV–UV depletion (UVD) spectroscopy, and one- and two-color zero-kinetic-energy pulsed field ionization (ZEKE-PFI) photoelectron spectroscopy have been used to study the spectroscopy and dynamics of ground and excited states of DPE. All experiments have been performed in a setup designed to perform laser spectroscopy on molecules cooled in a supersonic free jet expansion. In this setup the molecular beam is created with an injector assembly that consists of a stainless-steel oven in which a glass container with the sample is placed and kept at a temperature of 95 °C. The oven is connected to a pulsed valve (General Valve) equipped with a 0.5 mm diameter nozzle that is typically kept 10 °C above the oven temperature to prevent clogging of the nozzle. Typically, a pulse duration of 220 μs is used. In the present experiments neon at a backing pressure of 1.5–2.5 bar is led through the oven and expanded through the nozzle into the vacuum chamber. After passing through a skimmer with a diameter of 1 mm, the molecular beam is introduced into the ion source region. Here either mass-resolved ion detection is performed using a reflectron type time-of-flight spectrometer (R. M. Jordan Co.) or electron detection is performed using a custom-built setup (R. M. Jordan Co.) similar to the one described in ref 58.

One-color R2PI spectroscopy has been performed with a dye laser system (Sirah Precision Scan) pumped by a 30 Hz Nd:YAG laser (Spectra Physics Lab 190) using an unfocused laser beam and typical pulse energies of 1–2 mJ. To investigate whether the recorded R2PI spectra contain contributions from more than one DPE conformation, we have used UVD spectroscopy.⁵⁹ UVD spectroscopy monitors the signal from a probe laser that is fixed at the frequency of one particular band in the excitation spectrum associated exclusively with a single conformation. Scanning the pump laser then leads to a depletion of this signal as a result of the depopulation of the ground state each time the pump laser is in resonance with a transition of the selected conformer. The probe beam in our UVD experiments is generated by an excimer-pumped (Lambda Physik CompexPro 205) dye laser (Lumonics HD500). Pump and probe beams are introduced in a counter-propagating fashion into the ionization region with a delay between the two beams of 100 ns. Typical pulse energies of 5.0 and 0.2–0.3 mJ are used for pump and probe beams, respectively. Both laser beams are focused by a lens with a focal length of 30 cm.

The same two laser systems have been employed to perform one- and two-color ZEKE PFI photoelectron spectroscopy. In

the one-color experiments high- n Rydberg states are excited by two-photon excitation from the electronic ground state using pulse energies of ~ 6 mJ and a laser beam that is focused by a lens with a focal length of 30 cm. In the two-color experiments high- n Rydberg states are excited in a $(1 + 1')$ pump–probe excitation scheme in which the first photon excites a particular vibronic level in the electronically excited state. Typically, we use pulse energies of 1 and 6 mJ for the pump and probe beam, respectively, and do not delay the two counterpropagating beams with respect to each other. The two beams are not focused, although both beam profiles are narrowed using telescopes to maximize the overlap with the molecular beam. The high- n Rydberg states are excited in the presence of a small electric field (0.22 V/cm). After a delay of 200 ns, these Rydberg states are subsequently field-ionized by a pulsed electric field of 4.5 V/cm, leading to a clear separation of prompt and PFI electrons in the time-of-flight spectrum of the electrons.

DPE (97% purity) has been purchased from Sigma-Aldrich and has been used without further purification.

B. Theoretical Details. Full geometry optimizations of the ground, first, and second electronically excited singlet states of the neutral molecule, and of the ground state of the cation have been performed at various levels of theory that include (i) density functional theory (DFT) and time-dependent DFT (TDDFT),⁶⁰ (ii) Hartree–Fock (HF) and configuration interaction with single excitations (CIS), and (iii) second-order approximate coupled-cluster approach with resolution-of-the-identity approximation (RI-CC2).^{61,62} The CC2 method is known to be more accurate for the description of the excited states of charge-transfer character compared to CIS and TDDFT, which can be of importance for the description of electronic interactions in bichromophoric DPE. For the DFT and TDDFT calculations the B3LYP hybrid functional⁶³ and a Gaussian basis set of triple- ζ valence quality with polarization functions (*def*-TZVP)⁶⁴ was employed. HF, CIS, and RI-CC2 calculations used a correlation-consistent valence polarized double- ζ basis set (*cc*-pVDZ).⁶⁵ For each optimized geometry a normal mode vibrational analysis was performed to check if the stationary point corresponds to a minimum or to a transition state on the potential energy surface. HF and CIS calculations have been performed with the Gaussian98A.11 package,⁶⁶ the other calculations with the TURBO-MOLE 5.9 suite of programs.⁶⁷

Franck–Condon calculations of intensities in the vibronic spectra of the $S_1 \leftarrow S_0$ transition and in ZEKE spectra upon two-photon threshold photoionization ($D_0 \leftarrow S_0$) were calculated under the harmonic approximation taking into account the Duschinsky effect using an in-house developed program⁶⁸ based on the recursion relations for Franck–Condon integrals.⁶⁹ The intensities in the ZEKE $D_0 \leftarrow S_1$ spectra for various intermediate excited levels in S_1 were simulated using the Momo-fcf program as this program allows us to account for very long progressions.⁷⁰ Even though it is found that calculations based on geometries and force fields of good quality can reproduce experimental spectra quite reasonably, generally there still remain differences between the two. If we assume that the S_0 equilibrium geometry and the S_0 and S_1 (D_0) force fields are “correct”, we can reconstruct the excited (or, in the present case as well, ionic) state equilibrium geometry from the experimental intensities of fundamental $(\nu)_0^1$ transitions using the procedures described by Doktorov.⁶⁹ It is obvious that this assumption is not completely valid, but it is justified because the ground state calculations for the neutral, closed shell molecule are usually the most accurate ones and the influence of changes in the

force fields on the spectrum is small compared to the influence of changes in the equilibrium geometries.

To explore the characters of the two lower electronically excited states with respect to the torsional flexibility of DPE, we have performed two-dimensional scans of their potential energy surface as a function of the dihedral angles φ_1 and φ_2 of the phenyl rings relative to the plane of ethylene moiety (Chart 1). For the ground electronic state the 10×10 points PES map was calculated at the DFT/B3LYP/*def*-TZVP level for φ_1 and φ_2 angles ranging from 0° to 90° in steps of 10° . For each point on the two-dimensional surface a geometry with the appropriate values of the torsional coordinates was constructed from the S_0 optimized geometry. At this (unrelaxed) geometry the energy of S_0 was calculated. For electronically excited states both unrelaxed geometry scans encompassing the range of torsional angles from 8° to 53° (10×10 points) and relaxed scans for a selected region of the S_1 potential energy surface were performed. Starting point for these scans was the optimized geometry of the S_1 state at the CC2/*cc*-pVDZ level. In unrelaxed scans the energies of S_1 and S_2 were calculated for geometries in which the phenyl rings were simply rotated to the required φ_1 and φ_2 values. For the relaxed scans the geometries with fixed values of φ_1 and φ_2 were optimized in S_1 with respect to the other structural parameters. At this—for S_1 optimized—geometry the energy of S_2 was calculated. The latter energy thus refers to an unrelaxed energy.

III. RESULTS AND DISCUSSION

A. Experimental Results. 1. Excitation Spectrum. Figure 1 displays the one-color R2PI excitation spectrum of DPE in the $35000\text{--}36400\text{ cm}^{-1}$ range. At low excitation energies well-separated bands can be observed. Careful scanning of this region leads to the conclusion that the lowest observable transition is located at $(35076.2 \pm 0.1)\text{ cm}^{-1}$ (see inset). In the following we will show that the assignment of this band to the $0\text{--}0$ transition to S_1 leads to vibrational frequencies in S_1 that are in good agreement with predictions from quantum chemical calculations. The full width at half-maximum (fwhm) of the band is found to be $(1.2 \pm 0.1)\text{ cm}^{-1}$ and is determined by the rotational

Figure 1. One-color R2PI excitation spectrum of 1,1'-diphenylethylene. The inset displays the expanded low-energy region of the spectrum. The arrow indicates the lowest observable band in the spectrum (35076 cm^{-1}) which is assigned to the $0\text{--}0$ transition to the S_1 state.

exhibit extensive vibrational progressions for which an unambiguous assignment is only possible with the information obtained from the $D_0 \leftarrow S_0$ ZEKE-PFI spectra.

Figure 3 shows the $D_0 \leftarrow S_0$ 0° ZEKE-PFI spectrum in the one-photon energy range 32475–33050 cm^{-1} . From this spectrum we determine the adiabatic ionization energy as $65271 \pm 1 \text{ cm}^{-1}$, which, corrected for the electric field,⁷¹ extrapolates to $65274 \pm 1 \text{ cm}^{-1}$ (8.093 eV) under field-free conditions. This value is in qualitative agreement with the previously reported, albeit less accurate, value of 8.00 eV.⁵³ Also in this spectrum low-frequency modes play a prominent role though still considerably less than what is observed in the excitation spectrum. Assignment

Figure 3. (a) One-color ZEKE-PFI spectrum of 1,1'-diphenylethylene obtained after excitation from vibrationless level of S_0 . (b) Franck–Condon simulation of $D_0 \leftarrow S_0$ 0° ZEKE-PFI spectrum. The simulation uses the CC2 optimized geometry of S_0 , the CC2 harmonic force fields of S_0 and D_0 , and the reconstructed geometry of D_0 , which shows, however, only small deviations from the CC2 optimized geometry of D_0 . Energy is taken with respect to vibrationless level of D_0 .

of the various bands leads to the conclusion that the majority of the activity is associated with vibrational progressions involving modes with fundamental frequencies of 74.6 and 86.4 cm^{-1} . Based on quantum chemical calculations (vide infra) these modes are more or less the equivalent of modes 2 and 3 observed in the R2PI excitation spectrum discussed above. Interestingly, we thus find in the $D_0 \leftarrow S_0$ 0° ZEKE-PFI spectrum predominant activity of two low-frequency modes while in the $S_1 \leftarrow S_0$ 0° excitation spectrum three low-frequency modes are active. Below we will show that this provides direct evidence for the loss of symmetry of the molecule upon excitation to S_1 while symmetry is retained upon ionization.

Figures 4 and 5 display ZEKE-PFI spectra obtained after excitation of selected vibronic levels in S_1 . The spectrum associated with excitation of the S_1 0° level would of course be of particular interest, but the intensity of the 35076 cm^{-1} band precluded ZEKE-PFI spectroscopy via this transition. In Figure 4 ionization occurs after excitation of vibrational levels assigned to the progression of mode ν_1 in the excited state, while Figure 5 displays spectra obtained after excitation of members of the progression in mode ν_2 . In both cases, the dominant vibrational activity is associated with a 58.3 cm^{-1} vibrational mode in the ion. This mode can also be observed in the $D_0 \leftarrow S_0$ 0° ZEKE-PFI spectrum but shows in that case hardly any activity.

As is clear from Figures 3–5, the information in a single ZEKE-PFI spectrum would normally not be sufficient to come to an unambiguous assignment of the bands in the spectrum. However, the measurement of ZEKE spectra via 20 different vibronic levels in the excited state provided us with an extensive set of ionic vibrational levels, which, in combination with theoretical predictions, enabled us to perform a reliable global assignment. The complete set of experimental ZEKE spectra is available in the Supporting Information (Figures S1–S3) where also Table S2 gives the energies of the most important vibronic levels in the D_0 ground state of the ion. The anharmonicity of modes 1 and 2 in D_0 has been evaluated by fitting 30 bands with standard deviation of 0.7 cm^{-1} to the same expression as employed for S_1 . In this case we find harmonic frequencies

Figure 4. Left side: experimental ZEKE-PFI spectra obtained after excitation of (a) the S_1 1¹ level (35120 cm^{-1}), (b) the S_1 1² level (35162 cm^{-1}), and (c) the S_1 1³ level (35203 cm^{-1}). Right side: Franck–Condon simulation of respective ZEKE-PFI spectra. The simulation uses the CC2 harmonic force fields of S_1 and D_0 , and the reconstructed geometries of S_1 and D_0 . Energy is taken with respect to vibrationless level of D_0 .

Figure 5. Left side: experimental ZEKE-PFI spectra obtained after excitation of (a) the S_1 2^1 level (35141 cm^{-1}), (b) the S_1 2^2 level (35205 cm^{-1}), and (c) the S_1 2^3 level (35270 cm^{-1}). Right side: Franck–Condon simulation of respective ZEKE-PFI spectra. The simulation uses the CC2 harmonic force fields of S_1 and D_0 , and the reconstructed geometries of S_1 and D_0 . Energy is taken with respect to vibrationless level of D_0 .

$\tilde{\nu}_1 = 58.6\text{ cm}^{-1}$ and $\tilde{\nu}_2 = 72.9\text{ cm}^{-1}$, while for the anharmonicities values of $\tilde{\chi}_{11} = -0.29\text{ cm}^{-1}$, $\tilde{\chi}_{22} = -0.25\text{ cm}^{-1}$, and $\tilde{\chi}_{12} = -0.42\text{ cm}^{-1}$ are obtained.

B. Theoretical Results. 1. *Electronic Structure Calculations.* Optimization of the geometry of DPE in its electronic ground state leads to a geometry of which the relevant parameters are given in Table 1. These include the dihedral torsional angles φ_1 and φ_2 of the two phenyl rings, the bending angle θ around the central carbon atom, and the dihedral torsional angles δ_1 and δ_2 of the ethylene group (see Chart 1). At all levels considered the molecule is predicted to have C_2 symmetry, the two phenyl rings being twisted by ca. 41° . In agreement with our experimental results no other stable conformations have been found.

Figure 6a shows the unrelaxed potential energy surface of the S_0 state as a function of the two torsional angles φ_1 and φ_2 . Apart from the stable C_2 structure, the potential energy surface shows the presence of two transition states. One of these has C_2 symmetry and corresponds to a structure in which the planes of both phenyl rings are perpendicular to the plane of the ethylene group. Optimization of this structure leads to a barrier height of 1540 cm^{-1} . The other transition state occurs for $(\varphi_1, \varphi_2) = (0^\circ, 90^\circ)$. In this structure of C_s symmetry one phenyl ring lies in the plane of the ethylene group while the other one is in the perpendicular plane. The optimized barrier height associated with this structure is 690 cm^{-1} . The all-planar structure in which both dihedral angles are equal to zero is highly destabilized due to steric interactions between the hydrogen atoms of the phenyl rings.

Calculation of the vertical excitation energies from the ground state S_0 predicts two close-lying electronically excited singlet states (Table 2). TDDFT and CIS calculations predict the 2^1A state to be the lowest excited singlet state S_1 . The second excited singlet state S_2 is the 1^1B state, which is calculated to be only about 800 cm^{-1} higher in energy. The transition to the 2^1A state has the largest oscillator strength, the oscillator strength to the 1^1B state is at least 1 order of magnitude smaller. At the CC2 level of theory, however, the order of excited states is reversed. Now we find that the 1^1B state is the state of lowest energy, and the energy separation with

Table 1. Geometrical Parameters of DPE in Various Electronic States Calculated with DFT and Ab Initio Methods and Parameters of Geometries as Reconstructed from Experimental Spectra

state/method	φ_1	φ_2	θ	δ_1/δ_2
S_0 /DFT	42.3		118.4	2.9
S_0 /HF	45.8		118.1	2.5
S_0 /CC2	40.7		117.7	3.4
S_1 /TDDFT	27.2		123.1	1.3
S_1 /CIS	51.1	14.2	122.2	7.0/12.6
S_1 /CC2	48.3	21.7	118.6	3.0/5.4
S_1 /exp ^a	50.8	20.1	119.9	3.9/5.4
S_2 /TDDFT		32.8	118.1	0.6
S_2 /CIS	55.3	26.4	118.5	2.6/3.1
D_0 /DFT		34.6	120.8	1.7
D_0 /CC2		32.8	119.2	1.8
D_0 /exp ^b		33.5	120.1	0.8

^a Reconstructed from intensities of vibronic transitions in experimental $S_1 \leftarrow S_0$ 0° R2PI spectrum. ^b Reconstructed from intensities of vibronic transitions in experimental $D_0 \leftarrow S_0$ 0° ZEKE-PFI spectrum.

the 2^1A state is reduced to a mere 300 cm^{-1} . The oscillator strengths for both electronic transitions are significantly lower, although the transition to the 2^1A state is still the more intense one.

The excitation spectrum of DPE depicted in Figure 1 shows a large amount of vibrational activity. Below we will show that for low excitation energies calculations can reproduce this activity quite well with respect to both the frequency and the intensity. However, a coarse inspection of Figures 1 and 2 already indicates that the intensities of the bands at higher excitation energies are significantly larger than what one might expect on the basis of the initial part of the excitation spectrum. The experimental spectrum thus supports the presence of two close-lying electronic states with the upper one having a larger oscillator strength than the lower one, in agreement with the predictions at the CC2 level.

Figure 6. Two-dimensional maps of parts of potential energy surfaces of S_0 , S_1 , and S_2 as a function of the two phenyl torsional coordinates φ_1 and φ_2 . (a) Unrelaxed (no geometry optimization) S_0 energies starting from B3LYP/def-TZVP optimized equilibrium geometry of S_0 ; (b) Unrelaxed CC2/cc-pVDZ energies of S_1 starting from CC2/cc-pVDZ optimized S_1 equilibrium geometry; (c) CC2/cc-pVDZ energies of S_2 at S_1 geometries from (b); (d) Relaxed CC2/cc-pVDZ energies of S_1 starting from CC2/cc-pVDZ optimized S_1 equilibrium geometry; (e) CC2/cc-pVDZ energies of S_2 at S_1 geometries from (d). Energies of S_1 and S_2 are given relative to the CC2/cc-pVDZ energy of the S_1 minimum. The blue dots indicate the equilibrium geometry of S_0 , the red dots the equilibrium geometry of D_0 , both calculated at the CC2/cc-pVDZ level.

Table 2. Excitation Energies (cm^{-1}) and Oscillator Strengths for the Two Lower Excited Singlet States of DPE for Various Geometries and Different Levels of Calculation^a

geometry	method	S_1		S_2	
		E	f	E	f
S_0	TDDFT	37930 (2^1A)	0.137	38700 (1^1B)	0.003
	CIS	47810 (2^1A)	0.185	48600 (1^1B)	0.008
	CC2	39940 (1^1B)	0.001	40280 (2^1A)	0.008
$S_1/\text{minimum}$	TDDFT	34420 (2^1A)	0.101	38940 (1^1B)	<0.001
	CIS	42900	0.369	50450	0.009
	CC2	38110	0.012	42040	0.059
S_1/C_2 TS	CIS	43100 (2^1A)	0.254	51210 (1^1B)	0.423
	CC2	39010 (2^1A)	0.045	39360 (1^1B)	0.001
$S_2/\text{minimum}$	TDDFT	36620 (2^1A)	0.159	36930 (1^1B)	0.005
	CIS	45470	0.261	47460	0.004
S_2/C_2 TS ^b	CIS	45390 (2^1A)	0.292	47800 (1^1B)	0.192
	CC2	39050 (1^1B)	0.001	39240 (2^1A)	0.017

^a State labels refer to symmetry of state at geometry with C_2 symmetry. Excitation energies are given with respect to the energy of the S_0 minimum calculated with the same method. ^b For the CC2 calculations the geometry of the 1^1B state has been optimized to the geometry of the transition state. At this geometry the 1^1B state has a lower energy than the 2^1A state and energetically thus has become S_1 .

Geometry optimization of the S_1 (2^1A) state at the TDDFT level leads to a structure that retains C_2 symmetry (Tables 1 and 2). Compared to the ground state, the phenyl out-of-plane torsional angles are significantly reduced from ca. 42° to 27.2° . At this geometry the S_2 (1^1B) state is predicted to be 4500 cm^{-1} higher in energy. Optimization of the 2^1A state at the CIS level and

imposing C_2 symmetry results in a transition state structure (Tables 1 and 2). Normal mode analysis reveals that the mode with an imaginary frequency is associated with the antisymmetric combination of two phenyl ring-breathing modes. When symmetry constraints are removed, both methods optimize to a nonsymmetrical geometry that is characterized by different values for the phenyl out-of-plane torsional angles (51.1° and 14.2°). Compared to the symmetric geometry, this nonsymmetrical geometry is stabilized by $\sim 300 \text{ cm}^{-1}$ (Table 2).

Optimization of the geometry of the molecule in S_2 leads at the TDDFT level to a structure with C_2 symmetry. This 1^1B state is predicted to lie 2500 cm^{-1} higher in energy than the 2^1A minimum. Such a symmetry conservation is not observed when the geometry optimization is performed at the CIS level of theory. In that case the C_2 geometry is predicted to be a transition state with the imaginary frequency mode having the same character as observed for C_2 geometry optimization of the 2^1A state (antisymmetric combination of the two phenyl ring-breathing modes). Optimization without symmetry restrictions results in a nonsymmetrical geometry that is characterized by phenyl torsional angles of 55.3° and 26.4° and an energy that is 340 cm^{-1} lower than that of the symmetric structure. The CIS calculations locate the S_2 minimum 4560 cm^{-1} above the minimum of the S_1 state. This energy difference would seem to be at odds with the experiment that suggests that more than one electronic state contributes to the excitation spectrum in Figure 1.

As mentioned previously, the ordering of the states is reversed at the CC2 level of calculation. At the S_0 equilibrium geometry S_1 is the 1^1B state, while the 2^1A state is S_2 . Geometry optimization under the restriction of C_2 symmetry leads for both states to geometries with a similar excitation energies ($\sim 39000 \text{ cm}^{-1}$). However, in both cases the optimized geometry does not correspond to a minimum on the potential energy surface, but

Figure 7. Molecular orbitals of DPE at the optimized geometry of the 2^1A state obtained at the CC2/cc-pVDZ level of theory.

to a transition state with an imaginary frequency mode that has the same character as found in the CIS calculations. Interestingly, we find that the ordering of the 1^1B and 2^1A states is reversed for C_2 symmetric structures with torsional angles between 31.8° and 35.3° . Optimization of S_1 without symmetry constraints leads to a nonsymmetrical geometry with phenyl out-of-plane torsional angles (48.3° and 21.7°) and a stabilization energy ($\sim 900\text{ cm}^{-1}$) that nicely matches values found with calculations at the CIS level (Table 2). After correction for the zero-point vibrational energy, an adiabatic excitation energy of 36850 cm^{-1} is obtained for S_1 which compares well with the experimentally observed value of 35076.2 cm^{-1} .

Inspection of the molecular orbitals at the CC2 optimized S_1 geometry shows a preferential localization of the electronic density on the phenyl ring that has the lowest dihedral angle with respect to the ethylene plane (Figure 7). At this geometry S_1 is described by multiple excitations with a dominant contribution of the $\text{HOMO}-1 \rightarrow \text{LUMO}$ (0.32) and $\text{HOMO} \rightarrow \text{LUMO}+1$ (0.26) configurations. Upon excitation the degree of π -conjugation between the ethylene and one of the phenyl groups increases, thus tending to a more planar configuration. On the other hand, the conjugation with the other phenyl ring decreases and leads to a larger torsional angle.

Attempts to optimize the geometry of the S_2 state at the CC2 level theory without symmetry restrictions have not been successful. Inspection of the molecular orbitals during optimization indicates that a strong mixing occurs between the two lower electronically excited states that are built up from the same excitations. To assess the region where a possible minimum of the S_2 state might be located, we have investigated the excitation energies to the unrelaxed S_2 state for a range of S_1 geometries. The search was done on the two-dimensional map of the two phenyl torsional angles that were varied in the range from 8° to

53° (Figure 6). Parts b and c of Figure 6 display such maps for unrelaxed geometries of the S_1 and S_2 states that start from the (nonsymmetric) CC2/cc-pVDZ optimized S_1 equilibrium geometry. In this case we find an energy minimum 2670 cm^{-1} above the minimum of the S_1 state that corresponds to a structure with torsional angles of 42° and 23° .

In the electronic ground state the two phenyl rings of DPE are equivalent. Localization of the excitation on one of the rings in S_1 implies the existence of another isoenergetic state in which the excitation is localized on the other ring. The maps in Figure 6, however, do not show this second symmetric minimum for the excited states. This is due to the fact that the energy at each point of the potential energy surface is calculated starting from an initial guess for the orbitals for the asymmetric S_1 global minimum structure localized on one particular ring. To have a more reliable picture of the potential energy surface of S_1 and S_2 , we have performed a two-dimensional scan of their potential energy surfaces using S_1 relaxed geometries for the range of coordinates indicated in Figure 6d, which includes possible regions of S_1 and S_2 energy minima. Qualitatively, similar results are found as for the unrelaxed potential energy maps. For S_2 (Figure 6e) the minimum is located approximately at (46° , 19°). The coordinates of this minimum are very similar to that of S_1 (48.3° , 21.7°). The energy of the S_2 state at this (unrelaxed) geometry is 2650 cm^{-1} above the S_1 minimum. This is significantly higher than the energy of the C_2 symmetry transition state of S_2 (Table 2), which is $\sim 900\text{ cm}^{-1}$ above the S_1 minimum and only a few tens of cm^{-1} above the energy of the S_1 transition state. The single minimum for each electronically excited state, located only on one side with respect to diagonal of the map, and the lack of transition states on the relaxed two-dimensional potential energy surface indicate that relaxation along coordinates other than the phenyl torsions is necessary for delocalization of the orbitals. These degrees of freedom could also be important for lowering the energy of S_2 .

As yet, we have considered the potential energy surfaces of S_1 and S_2 in terms of stable minima and transition states. In view of the close proximity of S_1 and S_2 one might expect the two states to have a conical intersection not too far away from the S_1 minimum. Such a conical intersection is found indeed about 970 cm^{-1} above the S_1 minimum. In contrast to the S_1 optimized geometry, the molecule retains approximate C_2 symmetry at this conical intersection with torsional angles of about 34° . The energies of the S_1 and S_2 states at this point are within 20 cm^{-1} difference as they do an avoided crossing.

The geometry of the ground state D_0 of the DPE cation has been optimized using both DFT and CC2 methods. In both cases the molecule has been found to retain C_2 symmetry with very similar equilibrium torsional angles ($\sim 33^\circ$) (Table 1). The adiabatic ionization energy of the X^2B state corrected for zero-point vibrational energies is predicted to be 7.597 eV at the DFT level and 8.347 eV at the CC2 level of theory. These values are in reasonable agreement with the experimental value of 8.093 eV determined in the present study.

2. Harmonic Force Fields. Table 3 reports the frequencies of vibrational modes as calculated from the harmonic force fields of S_0 , S_1 , and D_0 . In a subsequent section, in which we compare the experimental and theoretical results, we will come to the conclusion that the results obtained at the CC2 level of theory lead to the best match with the experiment. In Table 3 we therefore only report CC2 results. Similarly, we restrict Table 3 to modes with frequencies below $\sim 450\text{ cm}^{-1}$ because for the $S_1 \leftarrow S_0$ excitation

Table 3. Theoretical and Experimental Vibrational Frequencies (cm^{-1}) for S_0 , S_1 , and D_0 States of DPE in the Range up to $\sim 450 \text{ cm}^{-1}$ ^a

		S ₀		S ₁		D ₀		
		frequency		frequency		frequency		
mode	sym	theo	exp	theo	exp	sym	theo	exp
1	b	44		48	44.2	b	64	58.3
2	a	60		66	64.4	a	72	74.6
3	a	77	90	75	77.1	a	88	86.4
4	b	138	150	118		b	137	129.2
5	a	215	224	193		a	224	214.5
6	b	224	240	229		b	251	
7	a	292	294	267		a	307	296.5
8	b	326	340	291		b	337	
9	b	402	404	317		b	417	
10	a	406	408	357		a	430	
11	a	433	440	402		b	438	
12	b	446	449	404		a	447	423.5

^aTheoretical frequencies have been calculated at the CC2/cc-pVDZ level from harmonic force fields. Experimental frequencies for S_0 have been taken from ref 52; frequencies for S_1 and D_0 have been determined in the present study.

and $D_0 \leftarrow S_1 \leftarrow S_0$ ZEKE spectra we are only able to assign reliably the region up to $\sim 450 \text{ cm}^{-1}$ above the 0–0 transition, while for $D_0 \leftarrow S_0$ ZEKE spectra the highest identifiable fundamental mode was found at 424 cm^{-1} . In the electronic ground state of the neutral and the radical cation the molecule retains C_2 symmetry. In the reported energy region most vibrations thus come in pairs as symmetric and antisymmetric combinations of displacements of the phenyl groups. For the S_1 state this is not the case, although one can still make a reasonable correlation of atomic displacements to approximate normal modes in the S_0 and D_0 states.

The three lower frequency modes involve the antisymmetric and symmetric torsions of the two phenyl groups designated as $\bar{T}$ and T , respectively, and the butterfly mode designated as β , which changes the bending angle between the two rings around the central carbon atom. While an assignment of the modes in terms of these descriptions is fairly straightforward for S_0 - $\bar{T}$ is the 44 cm^{-1} mode, T the 60 cm^{-1} mode and β the 77 cm^{-1} mode - such a description is more complicated for S_1 and D_0 . The atomic displacements calculated for the 66 cm^{-1} and 75 cm^{-1} modes in S_1 and 72 cm^{-1} and 88 cm^{-1} modes in D_0 are mixed and cannot be described as pure butterfly or symmetric phenyl torsion modes. On the basis of the dominant coefficients in the Duschinsky matrices for the S_0 - S_1 and S_0 - D_0 transitions, we assign the modes with the higher frequency in each pair to the butterfly mode β and the one with the lower frequency to the symmetric torsion mode T .

As yet, the amount of experimental and theoretical data available on the vibrational IR and Raman spectrum of DPE in its electronic ground state is rather limited. In Table 3 we have made tentative assignments of bands reported in the experimental studies.^{51,52} The $\bar{T}$ and T modes have not been identified in these studies, but for the other modes a nice agreement is observed between the experiment and theory with respect to both frequencies and mode symmetries.

C. Comparison Experiment and Theory. On the basis of the equilibrium geometries determined at the various levels of theory for the S_0 , S_1 , and D_0 states as well as the harmonic force fields, we have simulated excitation and ZEKE spectra within the Franck–Condon approximation (Figure 3). For the $D_0 \leftarrow S_0$ 0° ZEKE spectrum excellent agreement was obtained at the CC2 level, and to a lesser extent at the DFT level. Table 1 shows that a reconstruction of the geometry of the D_0 state on the basis of the CC2 geometry and the experimentally observed intensities of fundamental (ν)₀ transitions leads only to minor changes in structural parameters. The simulation predicts a strong dominance of mode 3 in the ion, and to a lesser extent of modes 2 and 7, a prediction that is perfectly reproduced by the experimental spectrum shown in Figure 3. We can thus conclude that the equilibrium geometry and normal modes calculated for S_0 and D_0 are to a very good approximation representative for the true geometries and normal modes.

For the spectra involving S_1 ($S_1 \leftarrow S_0$ excitation and $D_0 \leftarrow S_1 \leftarrow S_0$ ZEKE spectra) the predictions are more method dependent, in particular with respect to the activity of the antisymmetric $\bar{T}$ torsional mode. TDDFT calculations predict that C_2 symmetry is preserved upon excitation to S_1 and thereby do not show any activity of this mode. This is clearly at odds with the experimental results. We therefore have to conclude that this level of theory is not adequate to describe the first excited singlet state of DPE. CIS and CC2 calculations, on the other hand, do predict a strong activity of the antisymmetric $\bar{T}$ torsional mode. Comparison of the spectra predicted by both methods leads to the conclusion that the best match is obtained with the geometries and force field data calculated at the CC2 level of theory. Reconstruction of the geometry of the molecule in S_1 using experimentally observed intensities in the $S_1 \leftarrow S_0$ excitation spectrum does not give rise to large changes in the structural parameters (Table 1). Nevertheless, the agreement between experimental and predicted spectra (Figures 2, 4, and 5) remains worse than for the $D_0 \leftarrow S_0$ spectrum (Figure 3). In particular, the enhanced activity in the higher energy part of the $S_1 \leftarrow S_0$ excitation spectrum as compared to the simulated spectrum might indicate that the geometry changes upon excitation are larger than predicted by the calculations.

At the same time, one should also keep in mind that the CC2 calculations predict that for these excitation energies we approach a conical intersection with S_2 . As a result, one may expect enhanced mixing with vibronic levels of S_2 , which will undoubtedly influence the transition intensities and lead to an increase in vibronic activity. Moreover, closer to the conical intersection a reduction of the lifetime of vibronic levels, and concurrently broadening of resonances, can be anticipated, which could very well be the reason for the continuum appearance of the spectrum at these excitation energies. Also in this sense the CC2 calculations match the experiment better than the CIS calculations since the latter calculations, although qualitatively predicting correctly the loss of symmetry of the excited states, predict a large gap between S_1 and S_2 .

In case of the $D_0 \leftarrow S_1 \leftarrow S_0$ ZEKE spectra obtained by initial excitation of vibronic levels in S_1 involving the antisymmetric $\bar{T}$ torsional mode (Figure 4), both experiment and theory show the most pronounced progressions involving the same mode in D_0 . The measurements show that when higher members of the $\bar{T}$ progression in S_1 are pumped, progressively lower vibrational levels in D_0 are accessed. This indicates that excitation of this mode brings the vibrational wave function in the excited state

closer to the equilibrium geometry of D_0 . This observation is in excellent agreement with the theoretical predictions graphically represented in Figure 6, which shows that the path between the excited state geometries of S_1 and S_2 to the D_0 geometry is almost exclusively along the coordinates of the antisymmetric torsional mode.

Differences between the experimental and predicted Franck–Condon factors are found in the index of the most intense member of the $\bar{T}$ progression. In all cases the maximum of the progression envelope is shifted in the experimental ZEKE spectra toward higher energy by one or two quanta. When considered exclusively in terms of geometry changes, this would indicate that there is a larger difference between the S_1 and D_0 equilibrium geometries in the direction of the $\bar{T}$ vibrational mode than was calculated. A further difference between calculations and experiment is found in the activity of mixed progressions. The calculations predict a strong activity of 1^x progression and to a lesser extent of 1^x2^1 and 1^x7^1 progressions. However, in the experimental spectra we only identify 1^x , 1^x4^1 , and 1^x4^2 progressions. The calculated equilibrium geometry and normal coordinates of D_0 have been validated by the $D_0 \leftarrow S_0$ spectrum. We therefore have to conclude that the equilibrium geometry predicted for S_1 is less accurate. The absence of a strong 1^x2^1 progression indicates that this concerns in particular coordinate changes along the symmetric torsional (T) mode of the phenyl rings.

More information on the geometry changes along the T mode upon $D_0 \leftarrow S_1$ ionization can be derived from Figure 5. In contrast to the ZEKE spectra via $\bar{T}$ vibrational levels in the excited state, we observe here that the ZEKE spectrum is shifted toward higher vibrational energies when ionization occurs via higher members of the T mode. This holds both for the experimental and for the predicted spectra. It implies that displacements along this mode do not displace the vibrational wave function in the direction of the equilibrium geometry of D_0 . Theoretical confirmation of this conclusion is found in the calculated potential energy maps displayed in Figure 6. Figure 5 also confirms our previous conclusions on the uncertainty of calculated excited state geometry along the $\bar{T}$ and T modes. In both the calculations and the measurements we observe predominantly 1^x2^y progressions. However, in the experimental data the progressions have their highest intensity for higher x and lower y values than the calculations predict. This is once more an indication that the difference between the S_1 and D_0 geometries is larger in the direction of $\bar{T}$ coordinates and smaller in the direction of the T coordinates as compared to the calculation.

All of the above observations prove that the two phenyl rings become inequivalent in the first electronically excited state of DPE. The calculations show that this is directly related to the localization of electronic excitation on one of the phenyl rings and by this leads to a breaking of symmetry. Although the asymmetrical nature of S_1 is thereby firmly established, a more accurate determination of its equilibrium geometry requires further theoretical work.

IV. CONCLUSIONS

The present combined experimental and theoretical work has enabled us to elucidate the properties of the lower electronically excited singlet states of 1,1'-diphenylethylene as well as the ground state of its radical cation. The excitation spectrum of S_1 shows a rather complicated spectrum with an extremely weak

0–0 transition that nevertheless can be reliably assigned on the basis of the frequencies of subsequent vibrational bands. UV depletion spectroscopy has confirmed that the complexity of the spectrum does not arise from conformational heterogeneity but finds at least in part its origin in the large changes that occur in the structure of the molecule upon electronic excitation. One of the prominent changes in this respect is that the C_2 symmetry element that the molecule has in its neutral ground state is lost in the excited state. As a result, the two phenyl groups become inequivalent. A further question that the excitation spectrum gives rise to concerns the vibronic activity at higher excitation energies. High-quality ab initio calculations reproduce satisfactorily the observed Franck–Condon activity for low excitation energies but fail to reproduce that activity at higher excitation energies. Exploration of the potential energy surfaces of S_1 and S_2 leads to the conclusion that these two excited states have similar excitation energies. A conical intersection has been located that lies $\sim 1000\text{ cm}^{-1}$ above the minimum of the S_1 potential energy surface. We take the close correspondence of this energy with the energy region where we are no longer able to explain the observed vibronic activity as evidence that such a conical intersection is indeed the reason for the complexity in this part of the spectrum.

ZEKE experiments in which nonresonant two-photon excitation is employed to probe the ground state of the radical cation show convincingly that removal of an electron does not lead to inequivalent phenyl groups. The ZEKE spectrum shows vibrational activity due to relatively small changes in the geometry, but activity of nontotally symmetric modes that would indicate loss of symmetry is absent. The conclusions drawn on the basis of the $S_1 \leftarrow S_0$ REMPI excitation spectrum and the $D_0 \leftarrow S_0$ ZEKE spectrum have been confirmed by ZEKE spectra obtained after excitation of vibronic levels in S_1 . These spectra display extensive activity of the antisymmetric phenyl torsional mode, and of symmetric modes associated with the orientation of the phenyl rings with respect to the ethylene chromophore.

The 1,1'-diphenylethylene molecule thus presents itself as an interesting case in which localization of excitation energy occurs in spite of the inherent symmetry of the molecule in the ground state. One might speculate that molecular systems exhibiting similar characteristics could play in the future an important role as intelligent materials in which the energy flow can be controlled on the molecular level and in which properties can be altered by external stimuli. Put into a broader context, it is interesting to notice that structurally similar molecules such as diphenylmethane, diphenylamine, and benzophenone do not show as complicated excitation spectra as observed here for 1,1'-diphenylethylene. In this respect it is worth noticing that for diphenylmethane it has been concluded that the adiabatic excitation energies of S_1 and S_2 only differ by 123 cm^{-1} . Nevertheless, its excitation spectrum is rather straightforward to analyze. The present study has started to unveil the effects of cross-conjugation. It would be worthwhile to extend the theoretical analysis initiated here to obtain a more fundamental insight that would also be applicable to larger cross-conjugated systems.

■ ASSOCIATED CONTENT

S Supporting Information. All recorded ZEKE spectra and tables with full assignments of bands in R2PI excitation and $D_0 \leftarrow S_0$ as well as $D_0 \leftarrow S_1 \leftarrow S_0$ ZEKE spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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