Pyrene, a Test Case for Deep-Ultraviolet Molecular Photophysics

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ABSTRACT: We determined the complete relaxation dynamics of pyrene in ethanol from the second bright state, employing experimental and theoretical broadband heterodyne detected transient grating and two-dimensional photon echo (2DPE) spectroscopy, using pulses with duration of 6 fs and covering a spectral range spanning from 250 to 300 nm. Multiple lifetimes are assigned to conical intersections through a cascade of electronic states, eventually leading to a rapid population of the lowest long-living excited state and subsequent slow vibrational cooling. The lineshapes in the 2DPE spectra indicate that the efficiency of the population transfer depends on the kinetic energy deposited into modes required to reach a sloped conical intersection, which mediates the decay to the lowest electronic state. The presented experimental— theoretical protocol paves the way for studies on deep-ultraviolet-absorbing biochromophores ubiquitous in genomic and proteic systems.
Theoretical computations. The theoretical spectra provide similar spectra, in agreement with the gas-phase resonance Raman. The peaks at 272 nm (36.7 kcm−1) are responsible for the shoulder of the 272 nm band. Other symmetric carbon–carbon stretch vibrations form the Raman-active modes (Table 1 and Figure S7), which agree well with earlier Raman data.26,27 The solvent has little effect on the ES dynamics, as different solvents and environments—ethanol, polycrystalline powder acetonitrile,26 benzene27—provide similar spectra, in agreement with the gas-phase computations. The theoretical 1336 cm−1 band is the only intense band in the experimental Raman spectra; however, depolarization ratios suggest its existence.26 The 1242 cm−1 band is the only intense mode not appearing in the experimental laser spectrum (green dashed line). Figure 1 shows TA spectra up to 200 ps. Because of the extremely strong contribution of the nonlinear solvent response around zero delay and undesirable scattering effects of the solvent in the UV,26 the early time dynamics cannot be resolved. We observe an intense positive band at 272 nm associated with the bleach of the fundamental, together with two negative ESA signatures at 255 and 265 nm. A weak bleaching at 261 nm matching the first overtone of the 2B3u state in the LA spectrum is also present in the experimental TA spectrum, although very faintly because of overlap with the ESA.

The 2B3u absorption band is similar to that of the lowest bright state which absorbs around 320 nm, labeled 1B2u.26,27 Resonance Raman spectroscopy of the 1B2u26,27 as well as previously reported vibrationally resolved LA simulations,28 reveal that the same high-frequency (1456 cm−1) and low-frequency (405 cm−1) modes are responsible for the 2B3u band vibrational progression and broadening.

Table 1. Frequencies (ω, cm−1) and Huang–Rhys (HR) Factors of the Fundamental Raman Modes in Our Simulated Gradient Projection (grad. proj.) Approach and Adiabatic Molecular Dynamics

<table>
<thead>
<tr>
<th>simulation</th>
<th>experiment</th>
<th>mol. dynamics</th>
</tr>
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<tbody>
<tr>
<td>grad. proj.</td>
<td>HTG</td>
<td>Raman</td>
</tr>
<tr>
<td>v1</td>
<td>405</td>
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</tr>
<tr>
<td>v2</td>
<td>592</td>
<td>0.26</td>
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<tr>
<td>v3</td>
<td>888</td>
<td>(\omega)</td>
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<tr>
<td>v4</td>
<td>1079</td>
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<tr>
<td>v5</td>
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</tr>
<tr>
<td>v8</td>
<td>1574</td>
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</tr>
<tr>
<td>v9</td>
<td>1668</td>
<td>0.05</td>
</tr>
<tr>
<td>v10</td>
<td>2942</td>
<td>0.29</td>
</tr>
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</table>

“See section 3.2.1 in the Supporting Information. Frequencies (\(\omega\), cm−1) and intensity (int) of the vibrational modes obtained in ethanol by heterodyne transient grating (HTG, this work), from crystalline powder by Raman spectroscopy,70 and in acetonitrile by resonance Raman.26”
resolving vibrational coherences in the ground state. However, we note that the 2942 and 888 cm$^{-1}$ modes are absent in Raman experiments, the former being associated only with the 255 nm ESA.

The deactivation mechanism was followed through energy minimization techniques (Figure 4). The FC point exhibits two dark electronic states near the bright 2B$_{3u}$ state, denoted as 1B$_{1g}$ and 2B$_{1g}$ (Table S4). The near degeneracy allows ultrafast nonadiabatic population transfer to 1B$_{1g}$. Because of missing stimulated emission (SE) signatures in the TA spectrum, we assume that 2B$_{3u}$ decays to 1B$_{1g}$ before probing is initiated (i.e., before 200 fs). This assumption has been recently confirmed experimentally in a two-color (deep-UV pump visible-probe) TA experiment.$^{22}$

According to our computations, the lowest bright state 1B$_{2u}$ is not involved in the immediate relaxation after 2B$_{3u}$ excitation. A nearly constant 0.5 eV 2B$_{3u}$/1B$_{2u}$ gap is observed in both static and dynamic calculations on the 2B$_{3u}$ state, rationalized by the identical vibrational modes (1456 and 405 cm$^{-1}$) characterizing both states (sec. 3.2.3 of the Supporting Information).

The 1B$_{1g}$ state exhibits a considerable energetic stabilization with a minimum 0.4 eV below the 2B$_{3u}$ minimum. Molecular orbital analysis at the 1B$_{1g}$ minimum demonstrates that geometrical deformations leading toward a CI with the state...
1B2u destabilize more substantially the dark state 1B3u, so that CI optimization encounters a three-state CI(1B1g/1B3u/1B2u) about 0.08 eV above the 1B1g minimum. D2h symmetry is reduced at the CI to C2v. This is realized along with a 350 cm\(^{-1}\) in-plane bending mode of 1B2u symmetry, which creates a coupling between the 1B1g and 1B3u states. In fact, while the gradient difference vector at the CI is of Ag symmetry (having large overlap with the 1668 cm\(^{-1}\) mode), the derivative coupling vector exhibits a large overlap with the 350 cm\(^{-1}\) mode of 1B2u symmetry. These observations indicate that at the three-state CI the wave packet populates the 1B3u state. The nonadiabatic transfer is facilitated by the same set of 12 modes of B2u symmetry, enabling the 2B3u \(\rightarrow\) 1B1g decay. We assign the 0.75 ps lifetime to the decay through the CI. The relatively long excited-state lifetime with respect to the sub-100 fs lifetimes of the bright states 1B2u and 2B3u\(^{30,31}\) could be rationalized by the time required to distribute energy in the decay-determining 1668 cm\(^{-1}\) mode, which has a small Huang–Rhys factor of 0.05 in the 2B3u state, as required in order to overcome the 0.1 eV barrier to reach the CI. Static fluorescence spectra collected after 260 nm excitation (Figure 5) show a small shoulder between 350 and 368 nm associated with 1B2u emission.\(^{32}\) Nevertheless, the short lifetime of the 1B2u state strongly suggests that no significant population could accumulate that could be the source of a measurable spectroscopic signal from 1B2u.\(^{30,31}\)

Upon transfer to the 1B3u state, pyrene encounters a steep potential toward equilibrium. A weak feature between 300 and 350 nm in the static fluorescence spectrum is tentatively assigned to the vibrational dynamics in the hot 1B3u state. According to simulations, half of the potential energy is stored in two modes: the 350 cm\(^{-1}\) in-plane bending (B2u symmetry) and a 1668 cm\(^{-1}\) carbon–carbon stretching (Ag symmetry, Figure S8). In support of our mechanism, we draw the reader’s attention to a recently reported two-color (deep-UV pump visible-probe) TA experiment by Borrego-Varillas et al.\(^{22}\) Therein, the authors report a quantum beat with a frequency of 390 cm\(^{-1}\) shown unambiguously to arise from the wavepacket on S1 after pumping the 2B3u state at 270 nm.\(^{22}\) The quantum beat can be attributed to dynamics along a symmetric mode (a 410 cm\(^{-1}\) mode has been observed in Raman experiments, see Table 1), which unexpectedly gains in intensity after decay to S1 in contrast to other Raman modes (e.g., 590 cm\(^{-1}\), not observed by Borrego-Varillas et al.). We note however that the frequency of 390 cm\(^{-1}\) matches closely that of the 350 cm\(^{-1}\) in-plane bending mode, predicted by our calculations to dominate the vibrational dynamics on the S1 state after passage through the three-state CI. The temporal resolution of the experiment of Borrego-Varillas et al. (~16 fs) does not allow the detection of the other dominant mode (1668 cm\(^{-1}\)) predicted by our model. Studies on azobenzene and rhodopsin have shown that large amounts of energy into a few modes could induce intensity beats in the TA lasting for picoseconds.\(^{8,12}\) Thus, the 8 and 24 ps lifetimes can be associated with vibrational cooling of photoactive vibrational modes.

Following the proposed mechanism, we simulated the TA spectrum up to 1 ps. After the pump pulse, we observe SE out of 2B3u which enhances the signal intensity in the GSB region (270–275 nm) and reaches down to 290 nm. The 2B3u state shows a weak ESA band around 250–260 nm which partially cancels the second vibronic band at 262 nm. Our calculations predict further characteristic fingerprints around 360 and 540 nm, observed recently experimentally.\(^{22}\) The 2B3u fingerprint

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**Figure 5.** Static fluorescence emission spectrum of pyrene in ethanol. Excitation wavelength, 260 nm; excitation slid, 20 mm; emission slid, 1.5 mm. Average time of acquisition for each wavelength is 5 s.

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**Figure 6.** Experimental (a) and simulated (b) 2D maps of pyrene at waiting time of 1000 fs. Experimental (c) and simulated (d) intensity fluctuations of selected peaks in the 2DPE. Photoinduced absorption signal PA1, which gives rise to peak 2 in panel a appears red-shifted below the diagonal bleach signal in the simulated spectrum (b). A Fourier transform of the oscillations in panel c is shown in the Supporting Information (Figure S27).
signals decay on a 100 fs time scale. (A phenomenological 100 fs lifetime was adopted for the 2B_{3u} \rightarrow 1B_{1g} population transfer in agreement with recent findings by Borrego-Varillas et al.) At later times new signatures appear: a strong ESA between 250 and 260 nm (labeled PA_{2}) and a weaker ESA around 280 nm (labeled PA_{3}). Both peaks are fingerprints of the 1B_{3u} state populated with the 0.75 ps lifetime. The 1B_{3u} state exhibits further characteristic ESA in the near-UV at 370 nm and in the visible at 475 nm, potentially accessible through a two-color pump–probe setup. PA_{3} overlaps strongly with the GSB and is responsible for the intensity beat pattern in the 270 nm region. Simulated TA shows intensity beating due to the vibrational dynamics in the pair of 1B_{3u}-specific modes 350 and 1668 cm^{-1}. The experimental TA also shows an intensity beat pattern, with weak contributions from the pair of 1B_{3u}-specific modes. However, the 1413, 1238, and 597 cm^{-1} modes dominate the modulation of the ESA signatures, previously assigned to the 2B_{3u} state. A progression of 1450 cm^{-1} is visible at 300–350 nm in the static fluorescence spectrum, indicating memory conservation upon departure from the 2B_{3u} state, a mechanism not implemented in our simulations, leading to overemphasizing 1B_{3u}-specific modes. The 1B_{3g} state immediately populated in the relaxation has no characteristic ESA in the probed spectral window, but our calculations show that it exhibits absorption features in the visible which could be addressed to scrutinize the proposed model. Two close-lying states absorbing 3.6–3.8 eV above the S_{1} equilibrium would lead to an intense signal in the transient spectra around 330 nm. Thus, we propose a two-color, deep-UV pump near-UV probe, experiment with pulses centered at 290 and 330 nm, respectively, for validating the 1B_{3g} involvement.

Figure 6 shows experimental and simulated 2DPE spectra at a 1000 fs waiting time. Spectra at further waiting times are provided in section 4.1 (simulation) and section 11 (experiment) of the Supporting Information. A checkerboard pattern of positive and negative contributions along two stripes at \omega_{f} = 36.7 \text{ km}^{-1} and \omega_{i} = 38.2 \text{ km}^{-1} corresponding respectively to the fundamental and the first overtone of the 2B_{3u} band is shown. Diagonal bleach contributions (positive, red color) are detected at (36.7, 36.6) \text{ km}^{-1} and (38.0, 38.2) \text{ km}^{-1} in the experiment, while off-diagonal bleach contributions are encountered at (38.0, 36.7) \text{ km}^{-1} (intense, above diagonal) and at (37.0, 38.2) \text{ km}^{-1} (weak, below diagonal). The pattern arises from strong coupling of the electronic transition to the high-frequency carbon–carbon stretching. The signals are characterized by an oscillatory intensity. Theoretical simulations reproduce the experimental bleach pattern and its dynamics, allowing for the separation of individual contributions to the PE. The intensity oscillations (period of approximately 22 fs) are associated with the dynamics of an interstate coherence created by the pump–pulse pair between the fundamental and first overtone in the potential of the carbon–carbon stretch. At early times (first 100 fs), for which only simulations are available, the spectra resolve additional peaks below 36.0 \text{ km}^{-1} resulting from the strong SE out of the 2B_{3u} state (sec. 4.2 in the Supporting Information). Their absence in the experimental PE spectra supports that 2B_{3u} decays on a sub-200 fs time scale. There are several 2B_{3u} fingerprints contributing to the ESA at early times, but their transition dipole moments are orthogonal to the dipole moment of the GS-2B_{3u} transition, consequently appearing weak when all pulses have identical polarizations (Figure S11).

Instead, a cross-polarized pump–probe pair of pulses would enhance the intensity ESA signatures (Figure S12).

The bleach pattern is typical for vibrational coherences in a coupled two-level system. Further negative contributions appear in the PE spectrum at approximately \omega_{f} = 36.0 \text{ km}^{-1}, \omega_{i} = 37.5 \text{ km}^{-1}, and \omega_{i} = 39 \text{ km}^{-1}, associated with the mentioned ESA signatures PA_{1} and PA_{2} observed also in the TA spectrum. PA_{3} spreads from \omega_{i} = 35.5 to \omega_{i} = 37.5 \text{ km}^{-1} and falls under the bleach of the fundamental. PA_{2} exhibits a vibrational progression from \omega_{i} = 37.0 \text{ km}^{-1} to \omega_{i} = 40.0 \text{ km}^{-1} with absorptive and dispersive features associated with the dynamics in the 1660 \text{ cm}^{-1} mode connecting the CI with the 1B_{3u} minimum. It covers completely the bleach of the second overtone. Both PA_{1} and PA_{2} lead to the ESA feature at \omega_{i} = 37.5 \text{ km}^{-1} which interferes with the bleach of the first overtone (see sec. 4.3 in the Supporting Information). The bleach–ESA interference, although complicating the analysis of the spectral dynamics, is essential for interpreting the spectra.

The experimental 2D spectrum shows a very intense ESA contribution along the trace of the overtone at (\omega_{i}, \omega_{f}) = (38.2 \text{ km}^{-1}, 39.0 \text{ km}^{-1}) in disagreement with theory. This feature is observable only with broad-band UV-ES 2D spectroscopy. Tentatively, this pronounced ESA intensity could be assigned to the weak bleach contribution at the “overtone” pump frequency (whereas it is stronger at the “fundamental” pump frequency, canceling the ESA more effectively). This interpretation does not hold for long delay times when the system has relaxed in the lowest S_{1} vibrational level and the probe signal is no longer correlated with the pump frequency. Consequently, at longer delay times, the signal at a certain probe frequency \omega_{i} should be understood as a convolution of the electronic probe spectrum of the lowest vibrational level with the pump (i.e., linear absorption) spectrum. The most intense band in the LA spectrum is that of the “fundamental” frequency and so should be signals along the “fundamental” pump frequency in the 2DES spectrum at longer delay times. However, the intense ESA along the “overtone” pump frequency survives for tens of ps. A more plausible interpretation of this long-lasting feature is that the population transfer to 1B_{3u} is more efficient when the overtone of the 2B_{3u} band is excited, because of additional kinetic energy in the carbon–carbon stretch at disposal for reaching the sloped CI(1B_{1g}/1B_{3u}/1B_{3u}), whereas part of the population excited in the fundamental remains trapped in the 1B_{1g} state.

A combination of experimental and theoretical advances has been applied for the first time to record and interpret the pyrene time-resolved broadband spectroscopy in the deep-UV (250–300 nm). On the basis of TA, HTG, and 2D PE experiments and state-of-the-art electronic-structure computations, we propose a model for the deactivation following excitation of the second bright 2B_{3g} state. Computations reveal an ultrafast sub-200 fs depopulation of the bright state into a dark state 1B_{1g} which has neither emissive nor absorptive features in the probed spectral region. The emergence of a prominent ESA band at 250 nm in the TA and HTG spectra with a build-up time of 0.75 ps is shown to match the population time of the lowest dark state 1B_{3u} that acts as a bottleneck and is accessed via a sloped three-state conical intersection. The process exhibits characteristic ESA signatures, reproduced in the simulations.

While the first bright 1B_{3u} state decays within \sim 100 fs, the second bright state 2B_{3u} lives 1 order of magnitude longer.
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jp-lett.9b01325.

Sample preparation, experimental setup, data analysis, more experimental and simulated results, simulation protocols for nonlinear spectroscopy and molecular dynamics, simulation parameters, simulated spectra, molecular orbitals, and Cartesian coordinates (PDF)

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Notes
The authors declare no competing financial interest.

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REFERENCES


