

Insights into the lowest excited state of anthracene: Kerr-gated tuneable UV resonance Raman spectroscopy ($S_1 \leftarrow S_0$) and DFT analysis

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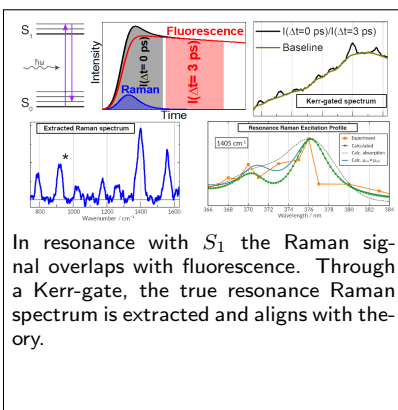
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Abstract

In this work, we present the first, well-resolved Raman spectrum of anthracene, a model system of polycyclic aromatic hydrocarbons, in resonance with the first electronic state. Until now, the auto-fluorescence associated with the $S_1 \leftarrow S_0$ transition had impeded the characterization of anthracene's S_1 state through resonance Raman. To overcome this limitation, we employ state-of-the-art Kerr-gated tunable UVR spectroscopy for effectively suppressing the UV-excited auto-fluorescence. Experimental RR excitation profiles with laser excitation wavelengths in the 366–383 nm range, covering the first fundamental vibronic transitions were recorded. With the exception of the first overtone of mode 59 (A_g symmetry) observed at 785 cm^{-1} , the experimental Raman excitation profiles (REPs) broadly follow the experimental absorption spectrum. Notably this overtone gains maximum intensity when excited with an excitation blue shifted to the absorption maximum (376 nm), in resonance with the $|59^1\rangle \leftarrow |0\rangle$ transition. These REP excitation profiles highlight the central influence of vibronic coupling on resonance Raman intensities and emphasize that, under the Franck–Condon assumption, truly predictive quantum-chemical simulations require sum-over-states treatments with explicit inclusion of the vibrational manifold of the intermediate electronic excited state.

TOC Graphic



Polycyclic aromatic hydrocarbons (PAHs) are an important class of compounds due to their relevance in a wide range of research fields, including the characterization of the organic fraction in the interstellar medium,¹⁻⁵ the study of combustion products and associated environmental issues,^{6,7} and the exploration of green materials in analytical chemistry for surface-assisted extractions^{8,9} and surface-mediated enhanced spectroscopy.^{10,11} Like graphene-based materials, PAHs consist of condensed aromatic systems, rendering them stable and rigid. These extended and delocalized π -electron systems give rise to strong dispersion-based interactions¹² but, above all, play a critical role in defining their electronic properties. Typically, PAHs exhibit lower electronic excitation energies than common organic molecules, and these energies decrease further as the conjugated system extends, eventually reaching conductive or semiconductive behavior in extended graphene layers and graphene-based nanorods.¹³⁻¹⁵

A comprehensive understanding of the structural and electronic properties of these compounds is therefore crucial for optimizing their applications, designing new graphene-based substrates, and predicting their chemical and photochemical reactivity.¹⁴ Rigorous investigations of PAHs also provide a foundation for more extensive studies of complex graphene-modified systems such as graphene oxide or specifically functionalized PAHs, which exhibit an even broader range of possible applications than PAHs themselves.¹⁶ In this context, anthracene not only exhibits specific applications when functionalized,^{17,18} but also serves as a standard prototype whose dimensions capture many features of larger polycyclic aromatic hydrocarbons while still remaining relatively compact for extensive computational studies.¹⁹

In this work, we focus on the spectroscopic characterization of the lowest excited state of anthracene as a model compound for this class, integrating both theoretical and experimental approaches. Notably, the symmetry of PAHs play a significant role on their spectroscopic responses; indeed, the number of non-forbidden transitions is governed by symmetry rules, while their rigidity produces narrower spectral features, typically yielding higher-quality spectra. While standard optical spectroscopic techniques (e.g., fluorescence and UV-vis absorption) provide information on excited states primarily through electric dipole transition

moments, scattering methods directly probe complementary vibrational features, which is particularly informative for symmetric systems.

In this context, resonance Raman (RR) spectroscopy is a valuable tool for investigating excited states, even indirectly, and has demonstrated its effectiveness in vibrational studies of excited states and their dynamics.²⁰⁻²² From an experimental perspective, RR spectroscopy is also a highly sensitive technique for studying compounds in solution. By tuning the excitation frequency to an electronic transition of the target compound, an intense Raman signal can typically be achieved in the micromolar range, enabling selective and sensitive detection of the analyte. Spontaneous RR measurements can, however, be challenging depending on the energy of the state chosen to be in resonance. RR spectroscopy is typically done probing higher excited states at wavelengths below 300 nm. In contrast, performing resonance Raman on the lowest excited singlet states, those most frequently involved in natural photochemical processes, presents a significant experimental challenge. In particular, the excitation of these states is accompanied by strong fluorescence interference, as almost all molecules preferentially undergo radiative decay from their lowest excited singlet states (Kasha’s rule).²³ Therefore, the main challenge in RR spectroscopy on the lowest energy excited singlet state is the difficulty to isolate the Raman signal. Even with resonance enhancement, the inelastic Raman cross-sections are 6-9 orders of magnitude smaller than those of absorption, resulting in overwhelming fluorescence that obscures the Raman signal.²⁴

For these reasons, the Kerr-gate technique, a time-domain-based filtering method, is used in this study of the first excited (S_1) state of anthracene reported for the first time, suppressing the masking effect of fluorescence. The approach leverages the optical Kerr effect whereby the scattered light of the sample is intersected by a picosecond gating pulse that induces birefringence in a Kerr medium between two crossed polarizers.²⁵ This allows mainly the temporally synchronized, significantly faster decaying Raman signal to transmit towards the detector. Initially, Kerr-gated Raman spectroscopy was developed in the visible region for providing access to the molecular fingerprint of visible chromophores²⁵ and later

extended to the UV range by some of us.²⁶ This methodology has demonstrated to be efficiently applicable in different research fields to improve the performance of enhanced Raman spectroscopies.^{27,28}

The major drawbacks of this approach are the need for a pulsed laser, which reduces the sample damage threshold, and the transmission losses by the Kerr gate. In the case of probing the lowest excited state, the potential for photochemical side reactions, as in the present work, is reduced. Furthermore, the sample solution was circulated in a flow cell to mitigate the accumulation of photodimerized anthracene.^{29,30}

Another advantage in probing the lowest electronic state is that the re-absorption process of the inelastic scattered light can be safely neglected if it is shifted to the energy region below the absorption range of the sample.

Our experimental setup is shown in Fig. 1 and described in detail in section S1.1 of the Supplementary Information. Briefly, anthracene dissolved in acetonitrile is probed in the 386–366 nm wavelength range with a UV Raman beam generated as the second harmonic of a tunable optical parametric amplifier. Raman scattering was recorded in a Kerr-gated configuration designed to temporally distinguish the short-lived Raman signal from the longer-lived fluorescence background for our molecular system, more specifically, the ultrafast (~ 2.3 ps) Raman excitation with the 2.6 ps Kerr gate response and the ~ 6 ns fluorescence lifetime of anthracene. Scattered light is collected at different times to evaluate the fluorescence contribution: at $\Delta t = 0$ ps, where the Raman signal peaks, and complementary spectra at $\Delta t = 3$ ps, which are dominated by fluorescence. Due to the complexity of the spectral acquisition, a robust data analysis strategy was essential. To this end, the Raman signal was first calibrated using the Rayleigh scattering peak and then isolated by combining spectra recorded at the two different time delays between the Raman pump and the gating pulse. The recorded UVR spectra, shown in Fig. 1D and used for the subsequent in-depth vibrational analysis, were obtained by applying a baseline correction for the residual fluorescence, a data smoothing filter, and normalization with the acetonitrile non-resonant enhanced solvent peak

102 at 920 cm^{-1} (indicated by an asterisk in Fig. 1D), which served as an internal standard to
103 normalize the Raman intensities. Finally the Raman excitation profiles (REP) were deduced
104 by extracting the peak height as a measure of oscillator strength of each Raman peak by
105 applying a Gaussian fit and normalizing the values for each mode to the maximum measured
106 intensity in the wavelength tuning series (see Fig. S2 in the Supplementary Information for
107 a list of all resulting spectra). Further technical details on the data analysis are available in
108 section S1.2 of the Supplementary Information.

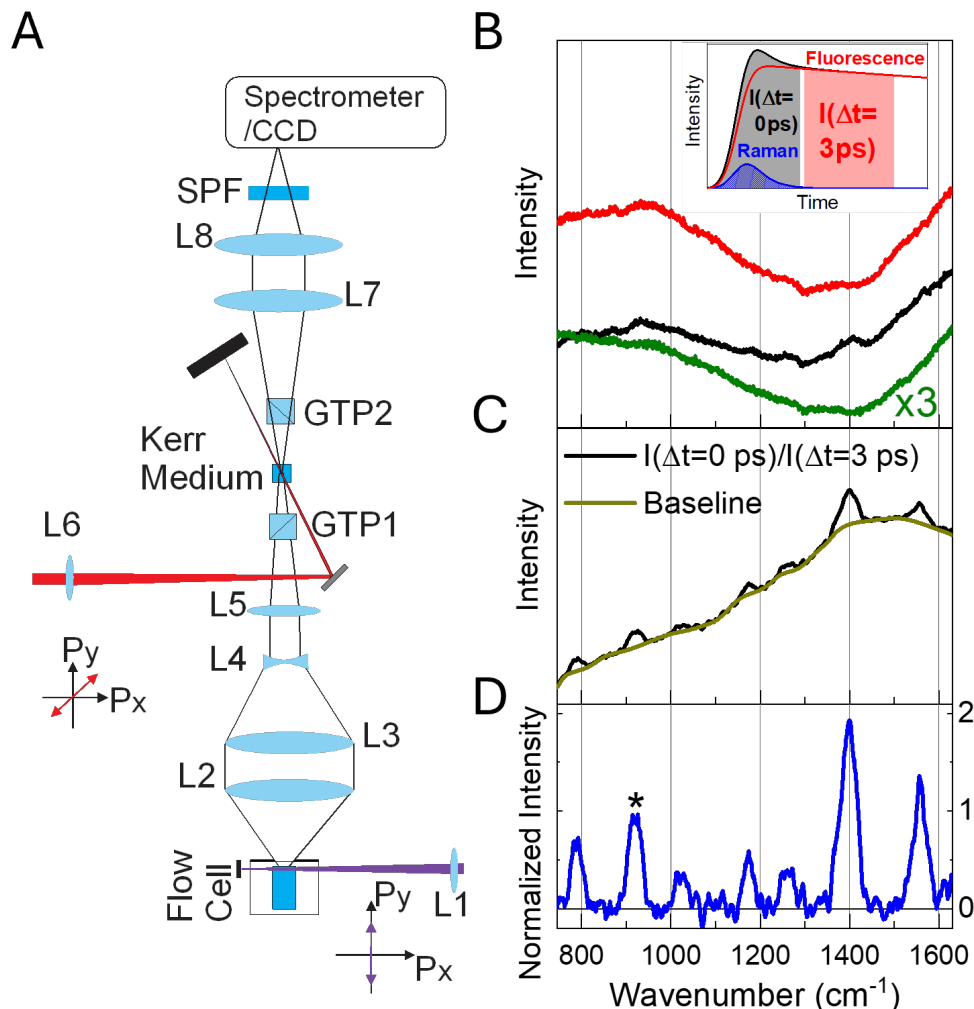


Figure 1: (A) Schematic representation of the Kerr gate for Raman measurements of anthracene in resonance with its first excited state. (B) Kerr-gated Raman spectrum (black), Kerr-gated fluorescence spectrum (red), and polarizer leakage measurement (green, performed without the Kerr pulse). The inset provides a schematic representation of the Raman and fluorescence signals in the time domain, with the shaded area indicating the portion of the signals transmitted through the Kerr gate. (C) Divided Kerr-gated Raman spectra (black) with the spline baseline for background-subtraction (brown). (D) Final normalized Raman spectrum after background subtraction (blue); the asterisk marks the solvent peak used as internal standard, as discussed in the main text.

109 As mentioned before, this work represents, to the best of our knowledge, the first sys-
 110 tematic experimental probing of the S_1 state of anthracene using Kerr-gated tunable UVR
 111 spectroscopy to suppress the massive auto-fluorescence emission associated with the $S_1 \leftarrow S_0$
 112 transition. The acquired experimental data provide a solid basis for critically evaluating and

refining commonly used theoretical models for the interpretation of molecular electronic enhancement phenomena in Raman scattering.

From a theoretical standpoint, the Placzek approximation is insufficient to describe RR spectroscopy, since it typically ignores the vibrational contributions in the definition of the transition polarizability. As a result, it is necessary to go beyond standard computational protocols, designed for far-from-resonance regimes, and to include a more complete description of the intermediate electronic states and their interaction with the ground state. In this work, to evaluate the theoretical REP, we employ the approach proposed by some of us³¹ to compute the Raman response under the time-independent (TI) Adiabatic Hessian (AH) Franck-Condon (FC) scheme at the B3LYP/jun-cc-pVTZ level of theory for different excitation energies. For more details on the computational protocol see section S2 of the Supplementary Information.

Within the framework of the Franck-Condon approximation, only Albrecht’s A term needs to be computed to predict the resonance Raman intensities, since the perturbation responsible for the higher-order B, C, and D terms (related to the Herzberg-Teller effects)—which couple multiple vibrational contributions to each band—is neglected.²⁴ Within this model, the Raman intensity is primarily driven by the overlap integrals between vibrational states, so it is possible to decompose the contributions to the Raman signal by examining separately the roles of the relevant molecular transitions from the initial (in our case the vibrational ground state $|0\rangle$) to the intermediate ($m \leftarrow i$) and from the intermediate to the final state ($f \leftarrow m$).

For our analysis of the Raman enhancement in the resonance regime, we concentrate on two vibrational peaks, observed at 785 and 1405 cm^{-1} in the experimental RR spectrum of anthracene with 376 nm Raman excitation (see Fig. 1, panel D).

The corresponding theoretical wavenumber values, computed at the anharmonic level, specifically with the generalized vibrational perturbation theory at the second-order (GVPT2),^{32,33} using density functional theory (DFT), are 785 and 1388 cm^{-1} , respectively. The 785 cm^{-1}

band can be assigned to the first overtone of mode 59, whose fundamental is predicted at 393 cm^{-1} and corresponds to an in-plane totally symmetric mode of the central ring breathing, depicted in Fig. 2.

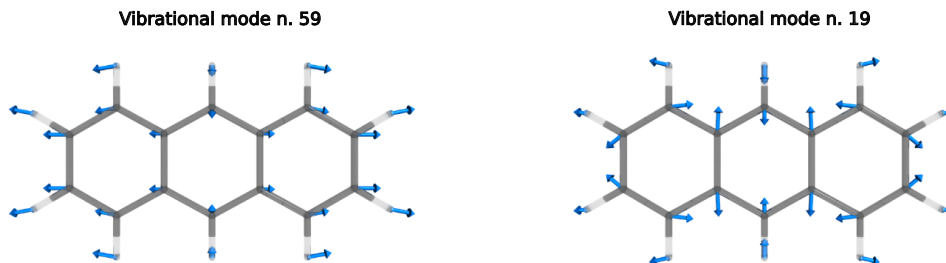


Figure 2: Graphical representation of the vibrational modes of interest, computed at the B3LYP/jun-cc-pVTZ level including PCM effects. Vibrational energies were computed at the anharmonic GVPT2 level.

The most intense signal recorded at 1405 cm^{-1} (Fig. 1, panel C) is associated to the fundamental transition 19¹, involving C=C stretching motions, particularly of the tertiary carbons. It is noteworthy that previously reported resonance Raman (RR) experiments targeting the strongly absorbing higher-energy electronic state, using laser excitations at 229 nm (post-resonance), 244 nm (in resonance), and 251 nm (pre-resonance) (Gooije et al.³⁴), consistently reveal a prominent 1400 cm^{-1} band.^{19,35} By contrast, the 785 cm^{-1} band emerged only as a minor feature under electronic resonance at 244 nm and otherwise remained indistinguishable from the background noise. Therefore, our observation of a prominent signal of the band at 785 cm^{-1} underscores how Raman features can exhibit intensity patterns that depend strongly on both the resonance regime and the molecular nature of the probed vibrational transition. Indeed it is well known that weak or “dark” transitions can be enhanced through direct interaction with the excited electronic state, making vibrational Raman signals that would otherwise be inaccessible experimentally observable and thus rendering data interpretation non-trivial. This highlights the importance of conducting an in-depth analysis of not only the fundamental transitions but also the first overtones to predict the intensity pattern in the fingerprint region recorded in the electronic resonance

regime.

Valuable experimental and theoretical information can be obtained by UV-visible absorption spectroscopy, commonly referred to as one-photon absorption (OPA), which gives an overview of the electronic properties of a chromophore. From an experimental standpoint it is necessary to accurately determine the excitation energies where resonance Raman can occur. For the computational approach, OPA serves to verify and fine-tune the computational protocol, which includes the determination of the exact experimental resonance conditions to reproduce them correctly. The OPA spectrum of anthracene in acetonitrile at 1 mM concentration is shown in Fig. 3.

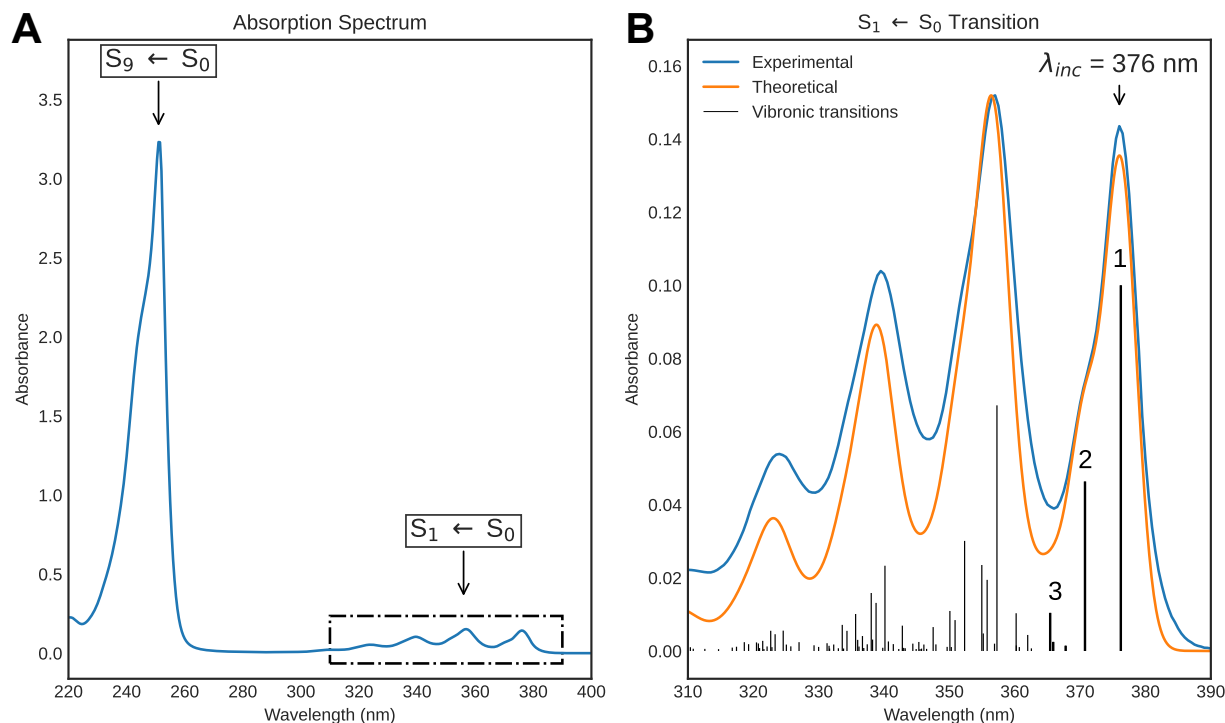


Figure 3: Panel A: experimental absorption spectrum of anthracene in acetonitrile (1 mM). Panel B: Experimental and theoretical absorption spectrum of anthracene in acetonitrile in the region of the first electronic transition (rectangular area in the left panel). Computations were done at the B3LYP/jun-cc-pVTZ level with vibronic transitions predicted within the TI AH|FC framework. A shift of 4221 cm^{-1} was applied to the predicted transition energies, and the intensities were scaled to match the maximum of the experimental absorption. The transitions contributing predominantly to the first band with a maximum at 376 are highlighted. The numbers refer to the vibronic transitions discussed in detail in the main text: (1) $|0\rangle \leftarrow |0\rangle$, (2) $|59^1\rangle \leftarrow |0\rangle$, (3) $|52^1\rangle \leftarrow |0\rangle$, $|46^1\rangle \leftarrow |0\rangle$ and $|59^2\rangle \leftarrow |0\rangle$.

As well-documented in the literature, the bands associated to the first allowed electronic transition ($S_1 \leftarrow S_0$) are approximately 30 times less intense than the band associated to the second contributing transition ($S_9 \leftarrow S_0$ in Fig. 3).³⁶ The experimental band-shape shows a clear vibronic progression of four well-resolved peaks at 376, 357, 339, and 321 nm. The lowest-energy peak shows a distinct shoulder at about 370 nm.

A comparison of the 310–390 nm experimental region with the theoretical prediction (Fig. 3) shows an excellent agreement, thereby confirming the reliability of the vibronic model (TI AH|FC) and the chosen level of theory (B3LYP) combined with the jun-cc-pVTZ basis set in a polarizable continuum model (PCM) to simulate the effects of the solvent, acetonitrile. It also confirms that the observed peaks are primarily driven by Franck–Condon overlap factors, dictated by symmetry selection rules.

Indeed, the computational modeling of the one-photon absorption in acetonitrile reveals a small number of distinct transitions within the energy range probed experimentally. These transitions are indicated by vertical dark lines in Fig.3 (panel B) and, for clarity, have been grouped into three numbered energy regions (a comprehensive table of vibronic transitions is available in table S1 of the Supplementary Information).

Table 1: Vibrational modes, energy (anharmonic) and symmetry of ground and intermediate excited state involved in vibronic transitions relevant to RR and OPA processes, as discussed in the main text.

Energy (cm ⁻¹)	Vibr. state (GS)	Symmetry
1388.05	$ 19^1\rangle$	A_g
782.49	$ 59^2\rangle$	A_g
Energy (cm ⁻¹)	Vibr. state (ES)	Symmetry
751.09	$ 47^1\rangle$	A_g
609.99	$ 52^1\rangle$	A_g
393.01	$ 59^1\rangle$	A_g

The transition contributing predominantly to the first vibronic absorption band is the $|0\rangle \leftarrow |0\rangle$ transition (labeled as 1 in Fig.3, panel B), centered at 376 nm. Near the funda-

mental ground-state 0-0 transition, the $|59^1\rangle \leftarrow |0\rangle$ transition, responsible for the shoulder observed at 370 nm (labeled as 2 in Fig. 3, panel B), has a significant impact on the overall band-shape. Weaker transitions such as $|52^1\rangle \leftarrow |0\rangle$, $|46^1\rangle \leftarrow |0\rangle$ and $|59^2\rangle \leftarrow |0\rangle$ are less intense and modulate the absorption intensity in the region labeled as 3 in Fig. 3, panel B, overlapping with the tail of the primary 0-0 transition and its adjacent shoulder. Since the theoretical absorption spectrum had to be shifted by 4221 cm^{-1} to align with the first experimental vibronic transition at 376 nm, the same offset was then employed to adjust the theoretical incident energy for the RR intensity calculations, ensuring that the computational model reproduces the resonance conditions, involving the same intermediate vibronic states as those probed experimentally.

Resonance Raman spectroscopy was performed by carefully tuning the Raman excitation wavelength around the energy of the first vibronic band maximum of anthracene (centered at 376 nm), specifically, from 366 up to 386 nm. This ensures that the main first OPA peak, as well as its shoulder are fully encompassed. As mentioned above, the lower bound of 366 nm was also selected to avoid significant re-absorption of Raman scattered light inside the sample in particular for the lower wavenumber peak at 785 cm^{-1} (emitted at ca. 387 nm for the 366 nm excitation), which could impact the measured REP. The upper bound was set to avoid the pre-resonance regime, for which a fundamentally different computational approach is required for an accurate theoretical comparison.²⁴ The resulting Raman excitation profile for the two selected transitions are shown in Fig. 4, in orange. Notably, the Raman intensity for the 1405 cm^{-1} signal closely follows the OPA line shape, peaking at 376 nm and decreasing at both higher and lower excitation wavelengths. In contrast, the 785 cm^{-1} Raman signal exhibits a significant deviation from the OPA profile, with its peak shifted to a lower wavelength at 370 nm. From these experimental observations, it is clear that a common assumption that the resonance enhancement follows a pattern closely aligned to the one-photon absorption spectrum is invalid for the transition seen at 785 cm^{-1} . To understand the source of this discrepancy, we recall the standard sum-over-states expression for

the resonance Raman (RR) intensity within the FC approximation,

$$I_{if}^{\text{RR}} \propto \sum_m \frac{\langle i | \boldsymbol{\mu}_{im} | m \rangle \langle m | \boldsymbol{\mu}_{mf} | f \rangle}{\omega_{\text{inc}} - \omega_{im} - i\Gamma_m}. \quad (1)$$

with ω_{inc} the incident energies in wavenumbers, $\omega_{im} = \omega_m - \omega_i$, and Γ_m the damping constant. The true RR intensity I_{RR} is thus not proportional to $|\boldsymbol{\mu}_{im}^2|$, which corresponds to the one-photon absorption intensity, but depends on the product $\langle i | \boldsymbol{\mu}_{im} | m \rangle \langle m | \boldsymbol{\mu}_{mf} | f \rangle$. This term is thus governed by two overlaps involving either the initial or the final state with each intermediate vibrational state.

This can play a significant role especially with molecular systems exhibiting structural symmetries, and a more robust method to predict the Raman enhancement profile is required. To this end, we extended our tool to compute OPA spectra from any vibrational initial state. It should be noted that this is relatively straightforward to do for the sum-over-states formalism, but more complicated for time-dependent approaches. Consideration of a specific initial state requires the derivation of *ad hoc* formula³⁷ or special methods,³⁸ with algebraic complexity increasing with the number of quanta. Since convergence is not an issue here and the identification of the transitions contributing to the one-photon spectra is straightforward since the spectral band-shapes are mostly governed by vibrational progressions, only the time-independent formalism is considered here. We thus compute two OPA spectra to generate the Raman excitation profile, one from i , and one from the final vibrational state of interest, f . Then, we approximate the Raman intensity as $(I_{i \rightarrow m}^{\text{OPA}} \times I_{f \rightarrow m}^{\text{OPA}})^{1/2}$. To get the correct shape the band-shape for $m \leftarrow f$ needs to be shifted by $\Delta E = E_i - E_f$. For a system with high symmetry like anthracene, an alternative approach is to consider explicitly each non-null transition in the two spectra and do their product. To generate the REP, a computational tool was developed to combine automatically the OPA spectra and plot the results.

The approximated profile from $|\boldsymbol{\mu}_{0m}| \times |\boldsymbol{\mu}_{mf}|$ is shown in blue in Fig. 4 for the states responsible for the 785 and 1405 cm^{-1} signals. They are compared to the computed (green) and

238 experimental (orange) excitation profiles of the resonance Raman bands and the theoretical
 239 absorption spectrum from the ground state.

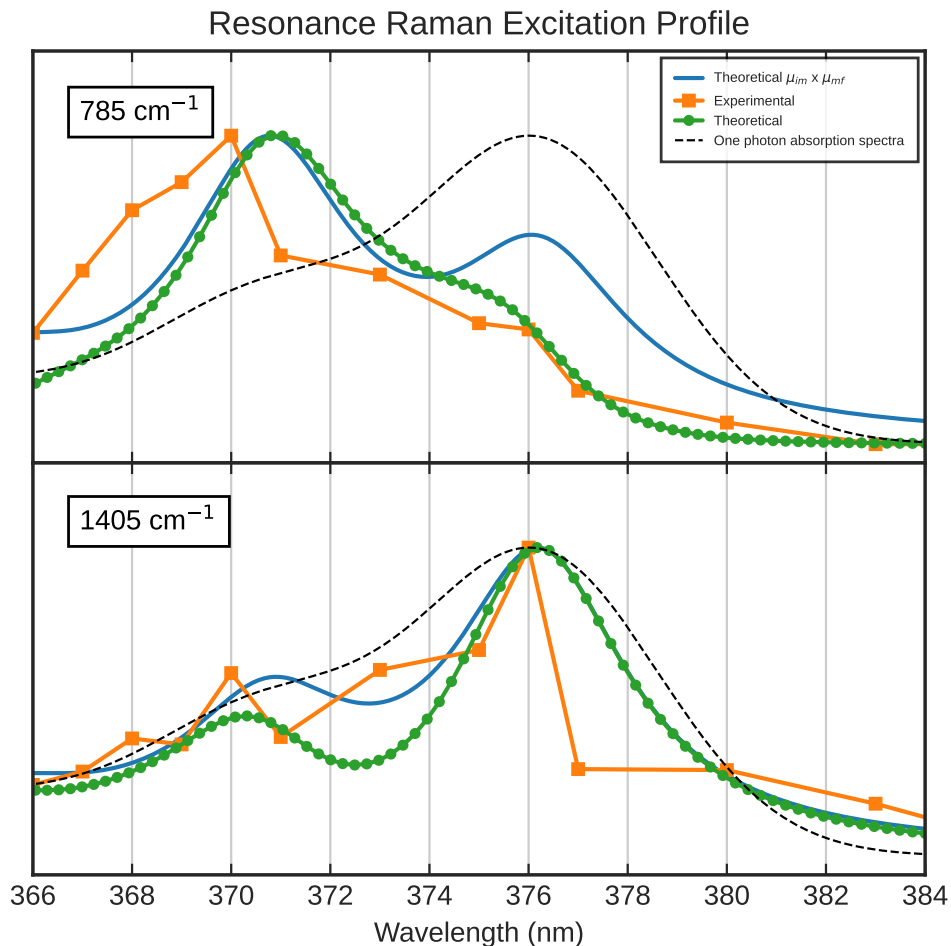


Figure 4: Experimental (orange) and theoretical (green) resonance Raman excitation profiles, theoretical one photon absorption spectrum (dotted black), and product of transition probabilities $|\mu_{0m}| \times |\mu_{mf}|$ (blue) involving final state $|59^2\rangle$ (upper panel) and final state $|19^1\rangle$ (lower panel).

240 The calculations show that the 1405 cm^{-1} transition is primarily driven by the transition
 241 dipole μ_{0m} , whereas the 785 cm^{-1} transition is governed by the vibronic overlap between the
 242 excited-state 59^1 and the ground-state 59^2 vibrational levels. In contrast, the other vibronic
 243 transitions involved in the absorption process display weak overlap with the 59^2 ground-state
 244 level and thus do not effectively drive the Raman transition to this final state. The computed
 245 vibronic transition energy $|59^1\rangle \leftarrow |0\rangle$ is predicted at 371 nm and is therefore in excellent

agreement with the experimental REP maximum observed at 370 nm.

This agreement between theoretical predictions and experimental results strongly suggests that the significant deviation of the REP for the 785 cm^{-1} transition from the shape of the OPA spectrum can be attributed to strong vibronic coupling involving the 59^1 vibrational state, which is blue-shifted respect to the 0-0 transition at 376 nm and selectively enhances the Raman signal.

As a conclusion, our combined experimental and theoretical findings reveals that the standard way of predicting Raman excitation profiles based purely on the zero-temperature OPA band-shape is inherently flawed, and in particular for conditions involving strictly symmetry rules, it can produce very poor results, since the overlap of distinct vibronic wavefunctions with unique resonance conditions can significantly alter the overall response across different normal modes. In particular, the transition dipole moment between the intermediate and final vibrational states μ_{mf} , explicitly computed in this work, is shown to be a key determinant in shaping the resonance Raman profiles of individual transitions within the fingerprint region. By employing the Kerr gate to measure both the Raman-rich spectrum ($\Delta t=0$ ps) and the pure fluorescence spectrum ($\Delta t=3$ ps) we effectively overcame the issue of strong fluorescence background in the first excited state which would otherwise obscure the Raman signal. Because of this, it was possible to obtain high-resolution spectra and precisely extract the Raman excitation profiles.

Our findings has thus confirmed that near-resonance conditions are highly sensitive to minute deviations in excitation wavelength: even nanometer-scale variations in the excitation light can shift the system away from perfect electronic resonance, yielding non-trivial interpretations of resonance Raman signals and large changes in intensity enhancement. This study underscores the need to consider factors beyond symmetry rules and absorption-like enhancement—even within the Franck–Condon approximation—and highlights how experimental techniques such as Kerr-gated UV resonance Raman can refine theoretical models to accurately account for subtle but significant excitation-energy variations.

We plan to extend our combined experimental-theoretical research on the higher-energy absorption peaks of the vibronic $S_1 \leftarrow S_0$ structure (< 360 nm, see Fig. 3, panel B). This could provide further evidence on the intriguing coupling properties between the vibrational ground and excited electronic states probed by resonance Raman spectroscopy. However it should be noted that resonance measurements at the highest absorption peak (357 nm), for example, would be particularly challenging due to the substantial Raman re-absorption, while strong spectral fluorescence overlap would continue to affect the signal-to-noise ratio. In contrast, fluorescence overlap is expected to be significantly reduced at 339 nm, making Raman re-absorption the primary challenge to accurately capture the REP.

To improve the quality of Kerr-gated UV resonance Raman, where the signal-to-noise ratio is significantly reduced because of a strong fluorescence background, a more powerful laser system could be used by increasing the pulse repetition rate of the Kerr gate. This would allow for faster and higher-quality detection and enable a broader study of the currently unknown resonance Raman responses of the first excited state in a wide range of building-block molecules with significant fluorescence quantum yields. The suppression ability of the Kerr gate naturally depends on the fluorescence lifetime. However, the approach should still be applicable to many faster-decaying molecules, as a short lifetime is strongly associated with non-radiative decay. This would reduce the fluorescence quantum yield and, in turn, reduce the background suppression required to detect RR in the first excited state. Alternatively, our approach could be used to measure the RR response in azulene’s second excited state, a unique molecule that does not adhere to Kasha’s rule.³⁹ Such measurements could provide deeper insights into their vibrational-electronic structure and contribute to the refinement of theoretical models.

Planned work on the theoretical side includes the explicit evaluation of the Herzberg-Teller effect, which could be critical to predict the REP of systems with weaker transition probabilities to the resonance state, as well as Raman optical activity in general. This would require at least the isolation and quantification of the B and C terms of the Raman po-

larizability expansion, which can generate non-negligible contributions of vibronic coupling from individual intermediate states. Moreover, it would be valuable to interpret spectral regions where multiple overlapping signals contribute simultaneously. By calculating the spectral integral of the experimental REP and convolving the theoretically computed transitions within the range of interest, one could directly correlate the experimentally observed and theoretically predicted intensities.

Supporting Information Available

Details on the experimental setup and data processing. Description of the computational protocol. List of the vibronic transitions contributing at least to 0.1% of the total intensity for the $S_1 \leftarrow S_0$ one-photon absorption spectrum from the ground vibrational state.

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