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Franck–Condon/Herzberg–Teller interferences in the ^1L_b transitions of pyrene and chrysene

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Abstract

In an extension of an earlier study, we present experimental evidence for pronounced Franck–Condon/Herzberg–Teller interferences in the first singlet transition (^1L_b) of pyrene and chrysene. The experimental observations are compared with the results of calculations based on first-order Herzberg–Teller theory and the floating orbital approximation. The calculations succeed for chrysene but not for pyrene. Possible reasons for this failure are discussed. © 1997 Elsevier Science S.A.

Keywords: Chrysene; Franck–Condon/Herzberg–Teller interferences; ^1L_b transitions; Pyrene

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1. Introduction

Weak electronic transitions, such as the ^1L_b transition in aromatic hydrocarbons, often exhibit considerable vibronic activity. To understand this activity, it is necessary to go beyond the Born–Oppenheimer approximation [1] and consider the dependence of the electronic transition moment $\mathcal{M}_{if}$ on the nuclear coordinates (i and f denote the initial and final electronic states respectively). In many cases, first-order Herzberg–Teller (HT) theory [2] is sufficient to describe the experimentally observed phenomena [3]. In this approximation, we obtain the transition moment for a single vibronic transition iv → fw as

$$\mathcal{M}_{iv\to fw} = \underbrace{\mathcal{M}^0_{if}\langle\chi_{iv}|\chi_{fw}\rangle}_{FC} + \underbrace{\sum_{k=1}^{3N-6}\left(\frac{\partial \mathcal{M}_{if}}{\partial Q_{f,k}}\right)\langle\chi_{iv}|Q_{f,k}|\chi_{fw}\rangle}_{HT} + O(Q^2)$$

where v and w denote the vibrations in the initial and final electronic states respectively, $|\chi\rangle$ is the vibrational wavefunction and Q represents a set of appropriate normal coordinates.

The Franck–Condon (FC) term vanishes for non-totally symmetric vibrations when we start from the vibrational ground state of the initial electronic state. For totally symmetric vibrations, both terms (HT and FC) can contribute to $\mathcal{M}$ either constructively or destructively. The resulting interference effects become strong if the two contributions are of similar magnitude [4–6]. This is only possible in weak electronic transitions where $\mathcal{M}^0_{if}$ is small. Such a situation is often met in aromatic hydrocarbons in which the lowest excited singlet state is a ^1L_b state. These states result from two one-electron excitations which combine in such a way that their individual transition moments nearly cancel (for this reason they are also called minus states) [7]. The vibronic structure of strong transitions is usually dominated by the FC term.

A verification of FC/HT interferences seems to require very high quality calculations which provide reliable intensities for single vibronic transitions. Fortunately, this is not true. The nuclear integral $\langle\chi_{i0}|Q_{f,k}|\chi_{fw}\rangle$ usually changes its sign between absorption and emission [3,8,9]. An interference that is constructive in absorption becomes destructive in emission and vice versa. Such a change is fairly easy to detect experimentally, especially when we are able to use transitions to non-totally symmetric vibrations as an internal standard. Because of the vanishing FC term, these transitions do not show FC/HT interferences in first order.

In an earlier publication [9], we investigated the FC/HT interferences in the ^1L_b bands of naphthalene and phenanthrene. A semiempirical treatment of the electronic structure of these molecules led to the correct prediction of all major interference effects in phenanthrene, but failed to predict the correct sign of the strong interference observed for $8a_g$ in naphthalene. The failure did not result from deficiencies in the applied force fields, but from an incorrect description of the relative weight of the two leading configurations in the ^1L_b wavefunction as predicted by semiempirical methods. Ab

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initio results from MCSCF [10] or CASSCF [11] calculations led to the correct sign of the interference [9]. The work on naphthalene has been extended by Negri and Zgierski [12] who treated the emission from single vibronic levels and compared it with the experimental spectra of Stockburger et al. [8] and Beck et al. [13]. It was shown that the correct sign of the interference can be obtained from a perturbation treatment which starts from ab initio geometries and force fields.

In an extension of our earlier work, we now present results on pyrene and chrysene, two other molecules with an allowed but weak first singlet transition (^1L_b in Platt's nomenclature [14]). Pyrene ($f(^1L_b) \approx 0.002$) belongs to point group D_{2h} as does naphthalene. Chrysene ($f(^1L_b) \approx 0.005$) is an example of a molecule with C_{2h} symmetry, a case not yet studied.

2. Experimental details

The experimental set-up for the measurement of site-selective fluorescence and fluorescence excitation spectra has been described elsewhere [15,16]. For excitation, we used a dye laser (FL 2002, Lambda Physik) pumped by an XeCl excimer laser (EMG 101 MSC, Lambda Physik). The fluorescence was dispersed by a 1 m monochromator (THR 1000, Yobin Ivon) equipped with a 2400 lines mm^{-1} grating (resolution, 3–4 cm^{-1}). The fluorescence was either detected by a photomultiplier tube (R 943-02, Hamamatsu) or a photodiode camera (IRY-512, Spectroscopy Instruments). The excitation spectra were normalized to the laser intensity. The spectra were usually measured using a step width of 0.01 nm.

Matrices were prepared from extra pure argon or nitrogen (99.9999%, Messer Griesheim) brought into contact with the substance (Aldrich) in a vacuum chamber maintained at a pressure of 2×10^{-1} mbar. The gas mixture was deposited on a sapphire window cooled to 27 K using a closed cycle He cryostat (RG-210, Leybold Heraeus). The base pressure during deposition was about 2×10^{-6} mbar. The deposition time was usually 1–3 h leading to matrices of 0.5–1 mm thick. After deposition, all matrices were cooled to about 12 K.

3. Theory

To calculate the intensity of a single vibronic transition, we applied first-order HT theory (Eq. (1)) combined with a floating orbital approximation of molecular electronic wavefunctions [17]. This scheme leads to the following formulae

$$\left.\frac{\partial \mathcal{M}^0_{\mathrm{if}}}{\partial Q_{\mathrm{f},k}}\right|_0 = A^k_{\mathrm{if}} + B^k_{\mathrm{if}} + W^k_{\mathrm{if}} \tag{2}$$

$$A^k_{\mathrm{if}} = \sum_{j\neq i}\frac{V^k_{ij}\mathcal{M}^k_{j\mathrm{f}}}{(E^0_i - E^0_j)};\quad B^k_{\mathrm{if}} = \sum_{j\neq i}\frac{\mathcal{M}^0_{ij}V^k_{j\mathrm{f}}}{(E^0_{\mathrm{f}} - E^0_j)} \tag{2a}$$

$$W^k_{\mathrm{if}} = \left.\frac{\partial\langle \mathrm{i}^{\#}|\hat{m}|\mathrm{f}^{\#}\rangle}{\partial Q_k}\right|_0;\quad V^k_{\mathrm{if}} = \left.\frac{\partial\langle \mathrm{i}^{\#}|\hat{H}|\mathrm{f}^{\#}\rangle}{\partial Q_k}\right|_0 \tag{2b}$$

The derivatives are taken at the equilibrium geometry of the initial electronic state. # denotes the electronic wavefunctions in the floating orbital approximation. For the nuclear integrals $\langle\chi_{\mathrm{i0}}|\chi_{\mathrm{fw}}\rangle$ and $\langle\chi_{\mathrm{i0}}|Q_{\mathrm{f},k}|\chi_{\mathrm{fw}}\rangle$, we applied the method of Sharp and Rosenstock [18] (there is a misprint in eq. (21) of the original publication). This method allows the inclusion of changes in the equilibrium geometry and also a change in the normal coordinates between initial and final electronic states (Duschinsky rotation [19]).

Geometries and force fields for the ground and first excited states were obtained with the QCFF/PI method including the polarizability derivatives [20]. The equilibrium geometries were further used to calculate the electronic wavefunctions and transition moments with CNDO/S-SDCI and/or INDO/S-SDCI methods [21–24]. The actual calculation of the vibronic intensities was performed with the program system VIBROLA [3] which uses the force field and electronic wavefunctions from the preceding steps as input.

4. Results and discussion

On the left side of Fig. 1, we show the site-selective fluorescence and fluorescence excitation spectra of the ^1L_b transition of pyrene. The 0–0 transition of the investigated site is at 27 133 ± 3 cm^{-1}. The transition is short axis ($y \equiv b_{2u}$) polarized. B_{3g} vibrations become vibronically active by coupling with long axis ($z \equiv b_{1u}$) polarized electronic transitions.

The theoretical results are shown on the right side of Fig. 1. We only discuss excess energies lower than 1200 cm^{-1}. For the region between 1200 and 1700 cm^{-1}, the force field calculation predicts massive Duschinsky effects which mask FC/HT interferences. The assignment of the low-lying a_g and b_{3g} fundamentals is well established for the electronic ground state [25]. The frequency changes between the ground and first excited singlet states do not exceed more than 40 cm^{-1}, a fact that allows a consistent assignment of the low-lying a_g and b_{3g} vibrations in the ^1L_b state. The frequencies predicted for both states by QCFF/PI (right part of Fig. 1) agree sufficiently well with the observed frequencies as long as the excess energy does not exceed 1200 cm^{-1}.

The spectra in Fig. 1 are drawn in such a way that the sum of the band heights of $9b_{3g}$ to $12b_{3g}$ is the same in both spectra. These vibronic transitions should not exhibit any interferences in first-order HT theory. Their intensity results solely from the HT term. The only effect that can modify their intensity is the Duschinsky rotation. The small changes in the relative intensity among the four bands are an indication of the weakness of such effects. The fact that the intensity ratio between $12a_g$ and $10a_g$ is somewhat higher in absorption than in emission is reproduced by the calculations, but not the ratio itself. The strong vibronic activity of $9b_{3g}$ is also not described properly.

The use of non-totally symmetric vibrations as internal standard immediately reveals FC/HT interferences among the totally symmetric vibrations. $12a_g$ is strong in absorption, but nearly undetectable in emission. The FC and HT contributions must be of similar magnitude so that they nearly

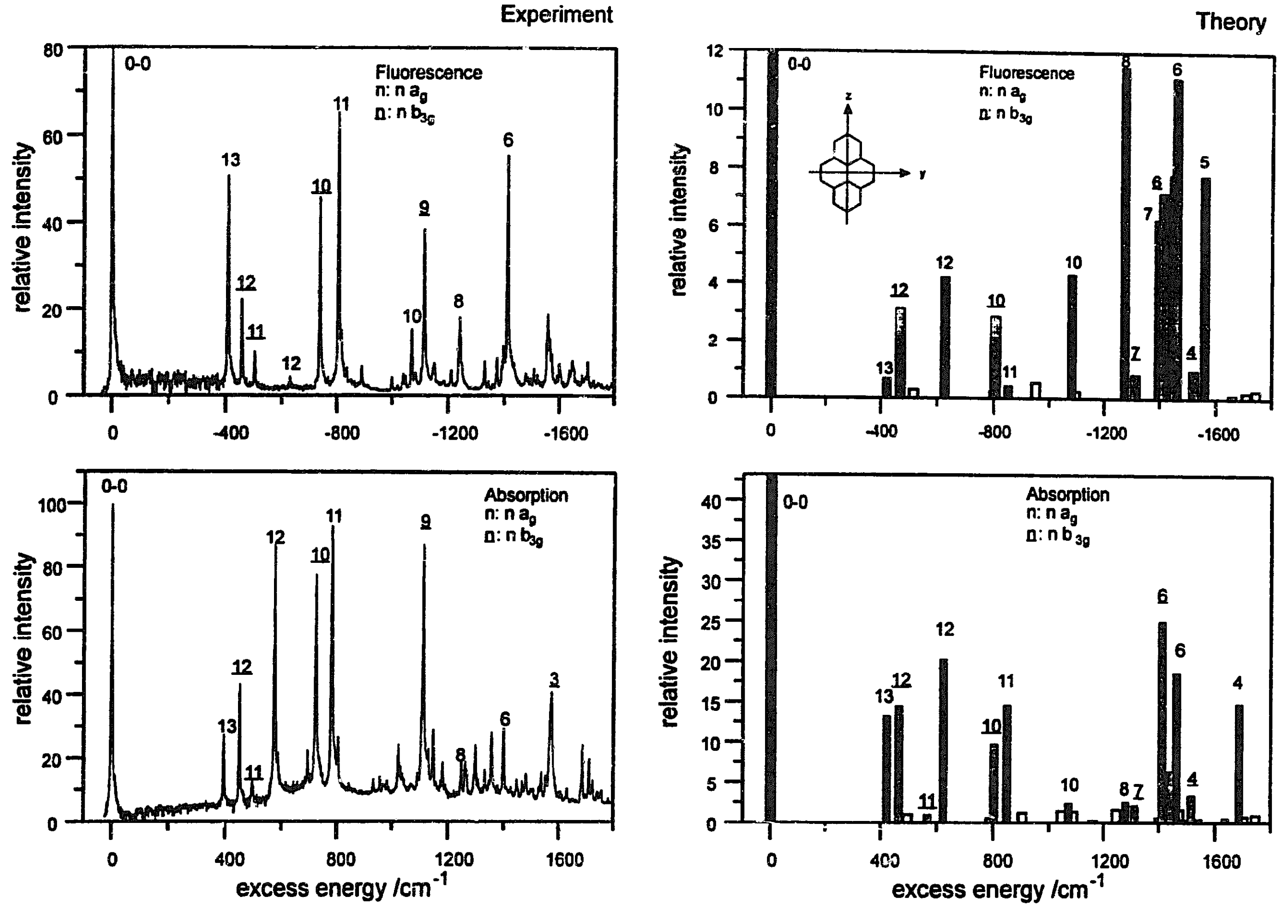

Fig. 1. Left: site-selective fluorescence and fluorescence excitation spectrum of pyrene in a nitrogen matrix ($T \approx 12$ K). The spectra cover the range from the 0–0 transition of ^1L_b (27 133 cm^{-1}) to an excess energy of ± 1700 cm^{-1}. Right: calculated intensity for single vibronic transitions in the ^1L_b band of pyrene. The intensities are shown relative to the intensity of the 0–0 transition which was set to 100. Empty columns belong to overtones, combination bands or fundamentals of a different symmetry.

cancel in emission. $13a_g$, on the other hand, is considerably stronger in emission than in absorption. $6a_g$ may also exhibit a pronounced interference effect, but it lies in the region of strong Duschinsky rotation. Therefore this fundamental is not discussed any further.

As in the case of naphthalene, the calculated interferences do not agree with the experimentally observed interferences. The calculation predicts $13a_g$ to be stronger in absorption than in emission, opposite to that found in experiment. For $12a_g$, the calculations predict only a small interference effect in contrast with the pronounced interference observed in the spectra. 11_{ag}, on the other hand, shows a strong interference in the theoretical result, but in reality it is nearly unaffected. Bearing in mind what we observed for naphthalene, we suggest that all these deficiencies result from the inability of the semiempirical methods to describe properly the electronic wavefunction of the ^1L_b state of a D_{2h} molecule. This wavefunction contains two leading configurations of nearly equal weight which determine the relative sign of $\mathscr{M}^0_{if}$. We have already started a program to tackle this problem with ab initio calculations. Results will be reported in a separate publication.

Chrysene is somewhat different from the systems studied so far. It belongs to point group C_{2h}. The first excited state is again ^1L_b, but the symmetry is only C_{2h}. π–π^* transitions which connect the ^1A_g ground state to the ^1B_u excited state are symmetry allowed, but the transition moment is no longer confined to a certain direction within the molecular plane. Only a_g modes are expected to be vibronically active. Other modes can gain intensity only through coupling with out-of-plane polarized transitions and these transitions are of low intensity in planar π systems.

The experimental spectra are shown on the left side of Fig. 2. The fluorescence excitation spectrum exhibits some site contamination. The corresponding bands are marked with an asterisk. All vibrations which are vibronically active can be assigned to totally symmetric modes. In emission, we observe the a_g fundamentals 29 to 21 [26] with the exception of $25a_g$ and $22a_g$ (Fig. 2). The frequency shifts between the ground and excited states are again minor, a fact which allows an assignment of the a_g modes 29 to 23 of the first excited state with the exception of $28a_g$.

The analysis of the observed spectra is slightly more complicated than in the case of pyrene because of the lack of non-totally symmetric vibrations which can function as internal standard. All of the observed bands are prone to FC/HT interferences and, indeed, we observe some very pronounced deviation from mirror symmetry. The most obvious concerns

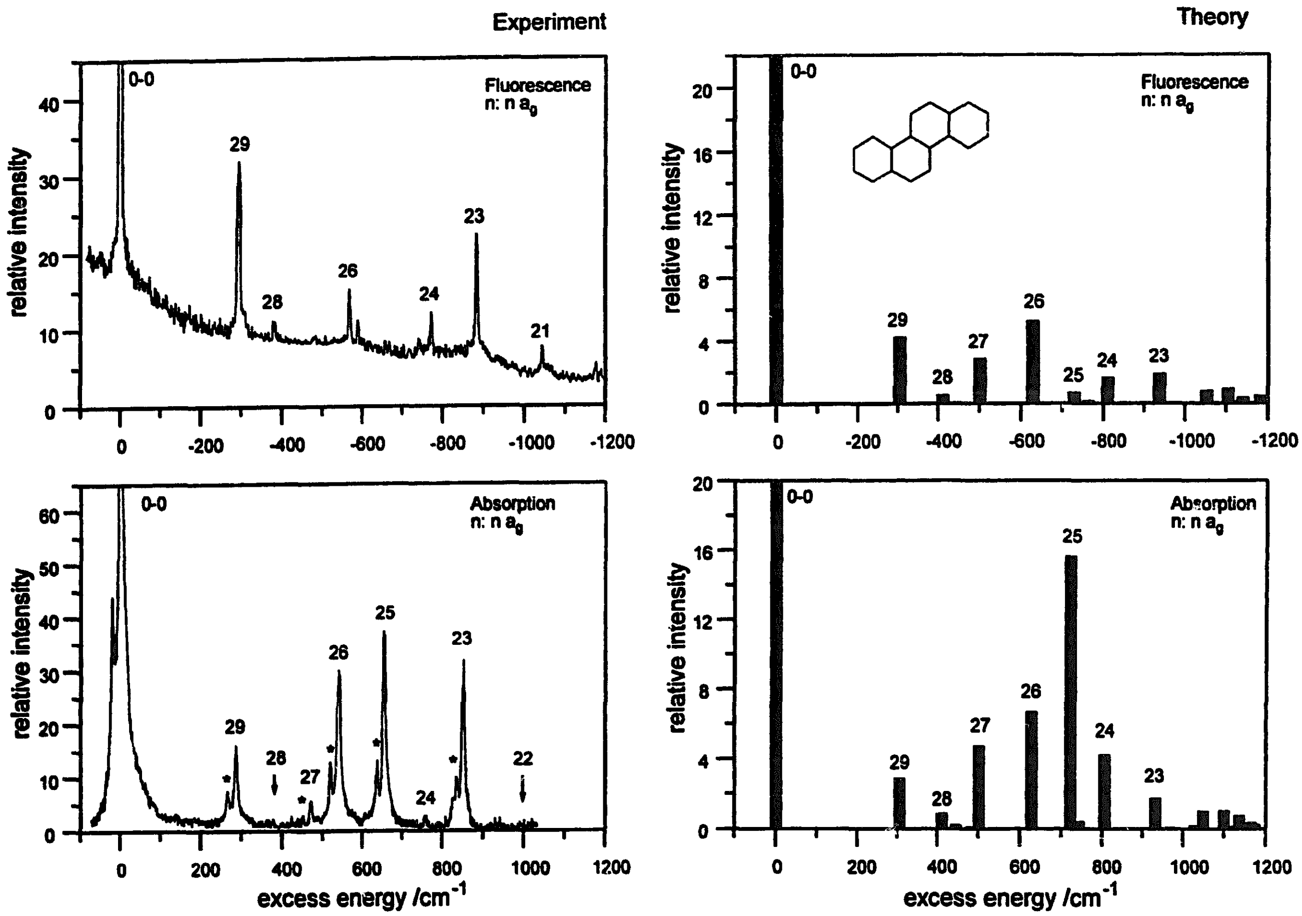

Fig. 2. Left: site-selective fluorescence and fluorescence excitation spectrum of chrysene in an argon matrix ($T \approx 12$ K). The spectra cover the range from the 0–0 transition of ^1L_b (27 911 and 27 953 cm^{-1} for the low- and high-energy site respectively) to an excess energy of ± 1200 cm^{-1}. Right: calculated intensity for single vibronic transitions in the ^1L_b band of chrysene. The intensities are shown relative to the intensity of the 0–0 transition which was set to 100.

$25a_g$, which is the strongest low-energy band in absorption, but not detectable in emission. Given the small frequency shift between absorption and emission and the well-separated vibrational levels in this energy region, this dramatic intensity change cannot be caused by Duschinsky rotation, a fact that is confirmed by the calculations. It must be the result of FC/HT interference. $29a_g$, another example of a mode with marked differences in the relative intensities, is more intense than $23a_g$ in emission, but only half as intense in absorption.

Comparison with theory shows that the most important features are reproduced by our calculations, i.e. the drastic change in the intensity of $25a_g$, the higher intensity of $29a_g$ in emission and the similar intensity of $23a_g$ in absorption and in emission. Therefore we drew the experimental spectra in Fig. 2 in such a way that $23a_g$ has about the same intensity in both spectra. The relative intensities predicted in the absorption and emission spectra are still not satisfactory. In absorption, for example, the calculated intensities of $24a_g$, $25a_g$ and $27a_g$ are too high and that of $23a_g$ is too low. It is probable that these deviations are not the result of badly balanced FC/HT interferences, but of the poor quality of the molecular force field obtained from QCFF/PI. That the force field is not as good as in the case of pyrene is obvious from the larger differences between the calculated and observed vibrational frequencies. High quality ab initio calculations are again very much needed.

5. Conclusions

Similar to the earlier studied examples of naphthalene and phenanthrene [9], we observe pronounced FC/HT interferences in the highly resolved absorption and emission spectra of pyrene and chrysene. In both cases, we encounter a weak first singlet transition, a situation in which first-order HT contributions can compete with the FC contribution.

Calculations based on semiempirical electronic wavefunctions provide a qualitative understanding of the observed interferences in the case of chrysene, but fail in the case of pyrene. This failure is most probably caused by the incorrect weights of the two leading configurations in the electronic wavefunction.

Acknowledgements

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