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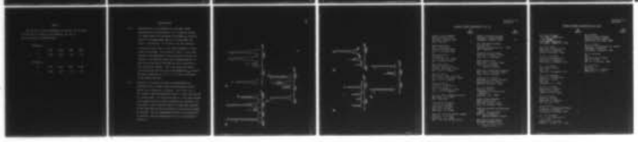

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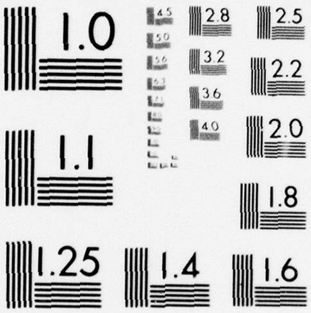

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Spectroscopic Investigation of the Origin of Distortion of Guest Coronene in Various Sites of n-Heptane Shpol'skii Matrix,

by

⑩ William M. Pitts, Anne-Marie Merle [redacted] M. A. El-Sayed

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Spectroscopic Investigation of the Origin of Distortion of Guest Coronene in Various Sites of n-Heptane Shpol'skii Matrix

by

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Abstract

We report the high resolution emission ($S_1 \rightarrow S_0$, $T_1 \rightarrow S_0$) and laser single site singlet excitation ($S_1 \leftarrow S_0$) spectra for the various insertion sites of coronene in n-heptane cooled to 1.5 K. The observation of site splitting of doubly degenerate vibrations and weak electric dipole forbidden 0,0 bands in the $S_1 \leftrightarrow S_0$ and $T_1 \rightarrow S_0$ spectra indicates that the ground state, the first excited singlet and lowest triplet states are all distorted. In these spectra, the intensity distribution of the various sites in the 0,0 bands suggests that the distortion is different from site to site but similar in S_0, S_1 and T_1. Identical ordering of the sites in $S_1 \rightarrow S_0$ and $S_1 \leftarrow S_0$ spectra as well as the observation of weak shifts in the vibrational frequencies in the two states implies the absence of strong pseudo Jahn-Teller forces in the first excited singlet state. We propose, further, that this is also true for the triplet state. This conclusion is supported by the similarity in zero-field splitting parameters of coronene and deuterated coronene. Taken together, these results indicate strongly that the distortion of coronene in n-heptane is primarily crystal field induced and is not greatly changed upon excitation of the molecule to its lowest excited states.

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1. Introduction:

The distortion of the electronic states of highly symmetric aromatics has been principally investigated for the case of benzene. The observation of site splittings of degenerate vibrations in the emission and excitation spectra(1,2) of benzene as a guest in C_6D_6 as well as in the pure crystal proved that not only are the first excited singlet and triplet states distorted, but that the ground state is distorted as well. The origin of this distortion in the triplet state has been extensively studied.(2-8) The large difference between the energy of the ν_8 vibration in the phosphorescence spectrum (1500 cm^{-1}) compared to its energy in the $S_0 \rightarrow T_1$ excitation spectrum (250 cm^{-1})(2) suggested that a strong Jahn-Teller effect was responsible for the distortion of the triplet state. This proposal has been supported by calculations of the stabilization of this vibration depending on the type of distortion involved.(9) The aim of this work is to extend this type of investigation to another highly symmetric aromatic: coronene. The distortion of the electronic states of this molecule embedded in n-heptane has been investigated.

n-Heptane was chosen as a matrix because the spectra are sharp (Shpol'skii effect) and because this lattice offers various modes of insertion to the aromatic as evidenced by a multiplet of at least five components, one of them occurring in polycrystals only. The measurement of the zero-field splitting parameters of the different sites which appear in the phosphorescence spectrum has shown that each site corresponds to a different distortion within the triplet state.~~(10)~~ When the sites (in single and polycrystals) were listed in order of decreasing $S_0 - T_1$ energy separation, it was found that the triplet state distortion varied in a monotonic manner from a very small quinoidal distortion to a non-negligible antiquinoidal one.(10) If the ratio $T = \frac{2E}{D}$ is taken to be a good indication of an absolute distortion of the molecule, it appears that coronene (T varies from +.02 to -.09 depending on the site) is less distorted than benzene in cyclohexane (T = +.11 in phase II and T = -.11 in the metastable phase III(11)) and has a distortion comparable to that of benzene in deuterated benzene (T = -.08).(12) This conclusion is in agreement with the fact that the ESR spectrum of coronene does not indicate a strong distortion from hexagonal symmetry.(13)

The presence within the same solute-solvent system of different solute distortions is a very favorable case for studying the origin of such distortion. As shown by the calculations of the pseudo Jahn-Teller stabilization for the triplet state of benzene,(9) it is expected that different spectroscopic characteristics (i.e., zero point energies and vibronic distributions) will be observed for each site (distortion) of the coronene triplet or singlet if such a stabilization is effective.

In order to study the distortions of coronene within the heptane lattice, we have recorded for each site moderately high resolution spectra of coronene fluorescence and phosphorescence as well as selectively determined the phosphorescence excitation spectrum of the first excited singlet state of each site. The results of this work have enabled us to ascertain the effect of distortions on the spectral properties of the different sites and to determine the importance of Jahn-Teller coupling on the spectra. Even though it is not the primary concern of this work, we will make some comment on the vibronic assignments for coronene and describe the effects of deuteration on the phosphorescence spectrum.

2. Experimental:

n-Heptane monocrystals doped with coronene were prepared as described elsewhere.(13) When polycrystals were used the solution was quickly frozen to liquid nitrogen temperatures. All samples were studied at 1.5 K.

Phosphorescence spectra were obtained by irradiating the sample continuously with the 3650 Å line of a high pressure mercury lamp. The emission was resolved with a 1 m Czerny Turner monochromator with 0.4 Å resolution and detected photoelectrically (EMI 9502S photomultiplier with photon counting detection).

Fluorescence spectra were obtained in two ways. In one case fluorescence was excited with the 2650 Å line of the mercury lamp and monitored in the way described above. Alternatively, the first excited singlet state was excited using a commercially available nitrogen pumped dye laser (Molectron UV 1000/DL 200) to selectively excite each site. Two dyes (Bis MSB and PBBO) were used to provide coverage of the region of interest. After passing through the monochromator the fluorescence was detected with a photomultiplier and Boxcar Integrator (PAR Model 162 with Model 163 plug-in).

The absorption of the first excited singlet state has been obtained by observing, as a function of exciting wavelength, the intensity of the phosphorescence induced by excitation with the dye laser. The one-meter spectrometer was used to isolate the phosphorescence emission of the 0,368 cm^{-1} band of each individual site.

Monochromator calibration was performed with an iron hallow cathode tube and the monochromator was used to check the calibration of the laser. Recorded energies and wavelengths are recorded in air. All recorded energies are believed to be accurate to within ± 3 cm^{-1}. Errors are due to a combination of instrumental error, determination of band center error, and difficulty in resolving and determining centers of vibronic bands showing site splitting.

3. Results

3.1 The multiplet structure

The emission spectra exhibit a multiplet structure which has been described previously.(13) The phosphorescence spectrum of single crystals is composed of three sites: a small component β followed by two intense components, γ and δ (γ is the larger), at lower energies. In polycrystals a fourth component (α) is observed to higher energy. The multiplet structure of the deuterated coronene phosphorescence is identical to the one of coronene-h_{12}. The fluorescence spectrum shows a very similar multiplet structure with an additional weak site ε lying at lower energy. Site ε was not considered in this study.

The multiplet structure of the $S_1 \leftarrow S_0$ excitation spectrum is found to be very similar to the one observed in emission and the energy ordering of the sites is identical in emission and excitation.

The phosphorescence, fluorescence, and singlet excitation spectra of the lowest energy e_{2g} vibration are shown in Fig. 1. This vibration is the only one which appears in all three types of spectra. The site structure can be clearly seen. Note that the energy ordering of the sites is the same for each of the spectra.

Table 1 lists the energies of the 0,0 bands for the sites of the various spectra as well as the separation in cm^{-1} between the sites. The single crystal sites have full width at half maxima (FWHM) which varies from 2 to 4 cm^{-1} (which, in some cases, may be limited by the experimental resolution). All of the sites are considerably broadened in the polycrystal with the exception of the α site which has a width of ~4 cm^{-1}.

The intensity distribution among the various sites is very similar for all the spectra and appears to remain constant for all the vibronic lines except the 0,0. This distribution is believed to reflect the relative number of molecules trapped in each site. The energy separations between the sites are constant for a given type of spectrum but vary for the singlet-singlet transitions ($S_1 \rightsquigarrow S_0$ and $S_1 \leftarrow S_0$) and triplet-singlet transitions ($T_1 \rightarrow S_0$) (see Table 1). On this basis, the vibrational analysis for each type of spectrum will be indicated for the multiplet as a whole.

3.2 The emission spectra of coronene and deuterated coronene

The phosphorescence and fluorescence spectra observed were similar to spectra previously recorded in the literature.(13,14) Much of the vibrational analysis of the fluorescence and phosphorescence spectra indicated in Tables 2 and 3 has been taken largely from previous work.(13-17) The principal ground state vibrations of the emission spectra have e_{2g} symmetry. The coronene molecule has twelve e_{2g} vibrations and of these nine have been assigned in either fluorescence or phosphorescence.

Both emission spectra are electric dipole forbidden and are induced by vibronic coupling. e_{2g} vibrations are expected to be the inducing vibrational modes. In the case of fluorescence, this coupling occurs between the first excited singlet ($^1B_{2u}$) and a higher excited singlet state ($^1E_{1u}$). The phosphorescence arises via the coupling of the lowest triplet ($^3B_{1u}$) and a higher triplet ($^3E_{1u}$) which is then spin orbit coupled to a higher energy $\sigma\pi^*(^1A_{2u})$ singlet state. These mechanisms have been established by comparison with benzene and support for them is found in the observation of in-plane emission in fluorescence and out-of-plane emission in phosphorescence. As is the case for benzene, the e_{2g} vibrations which are most active in phosphorescence and fluorescence are different. (The strongest vibronic band in phosphorescence is the 0,1639 cm^{-1} band while the strongest in fluorescence is the 0,995 cm^{-1} band.) As shown by Moffitt and Liehr for benzene,(18) this is due to the efficiency of different types of e_{2g} vibrations for mixing $^3B_{1u}$ with $^3E_{1u}$ states (C-C stretching modes are most effective) and $^1B_{2u}$ with $^1E_{1u}$ states (skeletal modes are most effective).

Some of the degenerate e_{2g} vibrations in the emission spectra show a site splitting which will be related to distortion of the coronene molecule. If the assumption is accepted that the molecule remains planar following the distortion, the lowering of symmetry will lead to a D_{2h} symmetry. An e_{2g} vibration is thus expected to be split into a_g and b_{3g} vibrational components.

The radiative properties of the spin levels of the triplet state and group theoretical arguments allow one to assign the vibrational symmetries of these split components in the phosphorescence. The totally symmetric a_g vibrations as well as the 0,0 transition are expected to originate from the τ_B triplet spin sublevel whereas the b_{3g} vibrations should originate within the τ_A triplet spin sublevel.* The observation of different zero-field transitions for each component of the site split e_{2g} vibrations confirms that the two sites are related to a symmetry lowering of the coronene and, by comparison with the observed zero-field transition of the 0,0 band, allows the assignment of the symmetry of the two vibrational components.

For all the split vibrations except the 0,485 cm^{-1}, the higher energy component in the phosphorescence spectrum has been assigned to a b_{3g} vibration as only the $\tau_A \rightarrow \tau_N$ zero-field transition is observed strongly. In contrast, for the vibration 0,485 cm^{-1}, the a_g component is the higher energy one. Note that the observation of site splitting for this vibration is in contradiction with its previous assignment(16,17) to an a_{1g} symmetry

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*τ_i (i = A, B and N) are the spin levels of the lowest excited triplet state. A, B and N refer to directions within the molecule. A passes through the atoms, B through the bonds, and N is normal to the plane.

and suggests that it is in fact an e_{2g} vibration.

To our knowledge, the phosphorescence spectrum of deuterated coronene has not been previously reported. The spectrum itself appears to have a site structure very similar to that of coronene. The observed 0,0 transitions are listed in Table 1. Vibrational frequencies are listed in Table 2. There was a shift of +41 cm^{-1} in the positions of the 0,0 bands for the deuterated compound as compared to the undeuterated which is attributed to differences in the shifts of the zero point energies of S_0 and T_1.

Many of the vibrations observed in the two phosphorescence spectra had similar frequencies. In general, those of the deuterated coronene were slightly lower in frequency. This fact implies that these vibrations involve primarily ring carbons. There is one major difference between the spectra. The two vibrations at 0,1159 cm^{-1} and 0,1225 cm^{-1} in the coronene phosphorescence disappeared upon deuteration and were replaced by a 0,833 cm^{-1} vibration. Clearly this vibration involves a large amount of hydrogen atom motion since the replacement with deuterium leads to such a large change in vibrational frequency. We propose that one of the two bands in the coronene spectrum arises due to Fermi resonance with the other since only one of them is still present for the deuterated case. In previous work(16,17) the 0,1225 cm^{-1} has been assigned as an e_{2g} and it is most likely that it corresponds to the one observed at 0,833 cm^{-1} in the deuterated coronene. Such an assignment is supported by the observation of a site splitting in the 0,1225 cm^{-1} phosphorescence band of coronene (see Table 2).

3.3 The first excited singlet excitation spectrum

The positions of the 0,0 bands for each site observed in the laser induced phosphorescence excitation spectra are listed in Table 1. Values of vibrational frequencies measured in this excited state are compiled in Table 4. In general, the vibrational frequencies measured in the ground state and first excited singlet state are very similar. This similarity has been used as the basis for the assignment of vibrations given in Table 4. The lower energy bands observed in the excitation spectrum were sharp and the use of the laser allowed increased spectral resolution. The sharpness of the bands revealed that the 0,0 band of $S_1 \leftarrow S_0$ for the γ site actually consists of two sharp bands spaced 2.8 cm^{-1} apart (see Fig. 2). By selective excitation, it was possible to demonstrate the presence of these two sites in the phosphorescence emission as well, but it is clear that the energy separation of the two sites in the triplet is greatly reduced. It is felt that this discovery does not challenge the validity of conclusions reached in this work.

The 0,0 and lower vibronic bands of the excitation spectra were very sharp (2-4 cm^{-1}). However, when exciting into vibronic bands at higher energies than 976 cm^{-1} above the 0,0 there was a sudden broadening (8-10 cm^{-1}). In general, such a broadening indicates a shortening of the lifetime for the state being excited. In the case of coronene this broadening may be due to an increased rate of vibrational relaxation, internal conversion, intersystem crossing, or isomerization in the higher vibronic states.

4. Evidence for the Distortion of Coronene in n-Heptane

4.1 Distortion of coronene in its ground state

Site splittings have been observed for many of the degenerate e_{2g} vibrations which appear in the phosphorescence and fluorescence spectra of coronene. Such site splittings are clearly evident in the vibronic bands displayed in Fig. 1. Tables 2 and 3 contain summaries of the vibronic bands for which site splittings have been observed as well as the magnitude of the splittings in cm^{-1}.

Site splittings have not been observed for the α site in any spectra. Even though α only appears in the polycrystal, the observed bands are sharp enough that site splittings of comparable magnitude to those of the other sites would have been detected.

Site splittings are known to arise from a lowering in the symmetry of a molecule in the site of the lattice. In the case of coronene the e_{2g} vibrational modes are split when the molecule loses D_{6h} symmetry due to interactions within the n-heptane cage. The observation of site splittings in the emission spectra shows conclusively that the ground state of coronene is distorted.

There are several trends which can be observed in the behavior of the site splittings described in Tables 2 and 3. As already noted, site α does not show site splittings. Site γ seems to have smaller splittings which appear for fewer vibrations than site δ. This observation is dramatically displayed for the 0,1635 cm^{-1} vibration in the phosphorescence spectrum. A quite well resolved site splitting is observed for the δ site and no splitting is evident for the γ site. In general, the site splittings of β are the largest and most numerous in the bands for which it is intense enough to be observed.

Further evidence for a distorted ground state of coronene is given by the observation of emission intensity in the 0,0 band of the fluorescence and phosphorescence. For undistorted D_{6h} coronene such transitions are electric dipole forbidden. These transitions only become partially allowed when the symmetry of the molecule is lowered.

As noted earlier, there is a constant distribution of optical intensity among the various sites for all vibronic bands. This is no longer true when 0,0 band emission is considered. Fig. 2 shows the 0,0 band emission for both fluorescence and phosphorescence. Note that site α (observed in the polycrystal) was recorded separately and its actual size in relation to the vibronic bands is considerably smaller than indicated in Fig. 2. By comparing Fig. 1 and Fig. 2, it is clear that the probability of 0,0 emission (both fluorescence and phosphorescence) increases as the optical energy of the transition decreases. In the case of the triplet state, this observation is consistent with the conclusion that the amount of distortion of the molecule follows the same trend.(10) The conclusion which can be reached, at least in the case of the lowest triplet state and most likely for the lowest singlet state as well, is: the radiative character of 0,0 emission bands in coronene is enhanced by distortion of the molecule and such distortion is correlated with the optical energies of the transitions observed in different sites.

Observation of site splittings of degenerate vibrational bands and 0,0 intensity in the emission spectra proves conclusively that the ground state of coronene is distorted.

4.2 Distortion of coronene in its first excited singlet state

Just as the observation of site splittings in the coronene emission spectra provides proof that the ground state is distorted, the same observation for degenerate vibrations in the lowest excited singlet state (observed from the phosphorescence excitation spectrum) indicates that the first excited singlet state is distorted as well (see Table 4). In fact, the similarities between the first excited singlet state and the ground state are striking. Tables 3 and 4 demonstrate that the vibrational frequencies observed in both states are very close in value. The strengths of absorption for the various vibrations within a particular site were found to be very similar to the intensity distribution observed in the fluorescence spectrum (i.e., the 0,976 cm^{-1} band was the strongest vibronic band in the excitation spectrum while the 0,995 cm^{-1} band was the most intense band in fluorescence). Furthermore, the absorption probability distribution for the various sites was the same as for the emission spectra (in the single crystal $\gamma > \delta > \beta$). Table 4 shows that the site splittings behavior within the first excited singlet state is analogous to that within the ground state. The 0,0 intensity distribution of the excitation spectrum is also similar to those of the emission spectra (i.e., the δ site has by far the strongest absorption in the 0,0).

The great similarities between the absorption spectrum into the lowest singlet state and the fluorescence spectrum not only prove that the two states are distorted, but indicate that within a given site the distortions of the ground state and first excited singlet state are very much alike. The absence of large changes in site energy separations or orderings coupled with the observed small modifications in vibronic transition probabilities and vibrational frequencies for the two states argues strongly that any strong pseudo Jahn-Teller effects present within these two states of coronene must be nearly the same for each state. Since the ground state is not expected to exhibit a strong pseudo Jahn-Teller coupling, it is concluded that such a coupling is absent in the first excited singlet state as well. The distortions observed in these two states must be induced purely by the crystal field and the distortions must not depend strongly on whether the molecule is in its first excited singlet or ground state.

4.3 Distortion of coronene in its lowest excited triplet state

Previous experiments(10) have demonstrated unambiguously that the triplet state of coronene in n-heptane is distorted in its lowest excited triplet state. The observation of a nonzero E values for each of the sites observed in phosphorescence proves that the symmetry of the coronene molecule is lower than D_{3h} within the n-heptane lattice. In the same work it was demonstrated that there is a very good correlation between the optical transition energies of the site in phosphorescence and the values of D and

E observed for the triplet state within that site. As the phosphorescence frequency decreased, the molecule changed from a small quinoic distortion to increasingly antiquinoic ones.

Such studies of triplet state distortion have been extended to deuterated coronene. As already noted, the site structure and intensity behavior of the phosphorescence of this compound was very similar to that of normal coronene. The zero-field splitting parameters measured for the various sites of the deuterated compound are listed in Table 5 along with those for normal coronene. The values for the two molecules are clearly very close in value and indicate that the distortions within each site for both types of molecules are comparable. Within the experimental error of the measurements these results demonstrate the normal effect of deuteration(19) on the triplet state fine structure parameters of aromatics -- a small increase in the value of D and minor variable magnitude changes in E. Such changes have been attributed to differences in the amount of electron donation from the protons or deuterons into the aromatic system of the ring.(20)

The absence of a significant change in triplet site energy orderings or intensity distribution as well as zero-field splitting parameters upon deuteration argues strongly against a strong pseudo Jahn-Teller effect within the lowest triplet state of coronene. Deuteration is expected to change the energy separation between the $^3B_{1u}$ and $^3E_{1u}$ electronic states. The pseudo Jahn-Teller effect is extremely sensitive to the size of this energy gap and its change should result in different distortions within the sites if such an effect is present. Further support for the conclusion of no activity of pseudo Jahn-Teller is found by noting the similarity in site ordering, site intensity distribution, and site splittings between the phosphorescence and fluorescence spectra. If there was indeed a large pseudo Jahn-Teller effect within the triplet the two emissions would be expected to show large differences since it has already been demonstrated that the first excited singlet state of coronene does not involve such coupling.

The similarities between the phosphorescence, fluorescence, and singlet excitation spectra with regard to site ordering, site intensity distribution, and behavior of $I^{0,0}/I^{\nu}$ as a function of site imply very strongly that the distortions within the ground state and the first excited singlet and triplet states are very much alike. The distortion behavior of the triplet has been ascertained. Presumedly, distortions of these types also apply to the two other states. On the basis of the results discussed, it is concluded that the spectral properties of coronene contained in a n-heptane lattice are determined primarily by the static distortions of the molecule due to the presence of different crystal fields. The amount of distortion within the molecule is related to potential energy considerations within each site and not to which of the three lowest energy states the molecule is in.

5. Comments on the Effect of the Lattice on Site Splitting of Degenerate Vibrations

Tables 2-4 list the site splittings of e_{2g} vibrations observed for the three types of spectra recorded. The same general behavior has been observed for all different types of spectra. Site α does not show any site splittings, site β has the largest and most numerous, and site δ shows slightly larger as well as more numerous site splittings than site γ. The magnitudes of vibrational site splittings differ for the type of spectra recorded and for the different vibrations of a given site observed within each of the spectra. The observation of two different energy orderings in the assignment of lowest energy vibrational components for the coronene phosphorescence spectrum indicates that the site splitting can be of opposite sign for different vibrations within the same site and electronic state.

Using these experimental observations, the following conclusions are reached concerning the site splitting of degenerate vibrations for coronene isolated in n-heptane:

1) There is a weak correlation between the amount of distortion and the magnitudes and generality of site splitting for sites α, β, and γ, but the primary important factor is the shape of the solvent cage surrounding the molecule within its site. This is most clearly seen in the case of the β site. As has been shown by polarized MIDP(10) experiments and suggested by alkane-aromatic interaction calculations,(21) this site is related to molecules which have an insertion position in the lattice which differs greatly from those of δ and γ. It is suggested that this particular position of the molecule in the n-heptane lattice favors the lifting of degeneracy as compared to the lattice positions of γ and δ sites, even though the molecules in site β are considerably less distorted than those in sites γ and δ.

2) Site splittings vary in both sign and magnitude in a manner which is correlated with the actual motions of the atoms within the molecule in a certain vibration mode. Certain degenerate vibrations in the recorded spectra have a tendency to be split in the spectra while others do not. This fact indicates that certain features of the vibrational motions determine their interaction with the surrounding potential created by the nearby n-heptane molecules.

6. Discussion

The conclusion that the lowest singlet state ($^1B_{2u}$) of coronene is not coupled to the degenerate $^1E_{1u}$ by pseudo Jahn-Teller coupling is in agreement with that reached for benzene. However, for benzene, it is believed that such coupling exists between the lowest triplet state ($^3B_{1u}$) and the $^3E_{1u}$ triplet state lying approximately 6900 cm^{-1}(22) above the origin of the $^3B_{1u}$ state. On the basis of the experimental results reported in this work, it has been concluded that the analogous pseudo Jahn-Teller coupling is not important for coronene. The question is obvious: What is the difference between the benzene and coronene molecules which determines whether or not pseudo Jahn-Teller coupling is effective within the triplet state of the molecule?

Van der Waals and coworkers(9) have performed a series of calculations with the aim of determining quantitatively the effect of pseudo Jahn-Teller coupling on the triplet levels of benzene and have obtained encouraging agreement with experiment. Such an analysis for coronene is beyond the scope of this work. In this case an answer to the question will be looked for in a simple but general theory of vibronic interaction between nearby electronic states which has been developed by Hochstrasser and Marzzacco.(23)

By starting with a set of crude Born-Oppenheimer wavefunctions and considering the effects of small nuclear displacements on the electronic wavefunctions these authors were able to show that the condition for the absence of a pseudo Jahn-Teller effect is

$$(f_{kb}\Delta\varepsilon_{12}) > 2^{1/2}V_{12}(k)$$

where f_{kb} is the Harmonic force constant of normal mode k, $\Delta\varepsilon_{12}$ is the energy separation of the two electronic states, and $V_{12}(k) = \frac{\partial H_0(Q)}{\partial Q_k}$ where $H_0(Q)$ is the nuclear position dependent but nuclear motion independent Hamiltonian and Q_k is the displacement along normal mode k.

$\Delta\varepsilon_{12}$ for the triplet states of coronene is estimated to be ~ 1/3 that for benzene(24) and should favor the psuedo Jahn-Teller effect in coronene as compared to benzene. f_{kb} is expected to be similar for both coronene and benzene since the C=C bond stretching vibration frequencies are similar for the two molecules. The only conclusion which can be reached is that $V_{12}(k)$ (the vibronic interaction term) must be much smaller for coronene than for benzene. This might be due to the larger number of carbon atoms in coronene (24) as compared to benzene (6). In a qualitative fashion this conclusion can be attributed to the smaller size of the one center terms in coronene. The vibronic interaction term, V_{12}, is the sum of the products of the transition dipole (ρ_j) and vibration atomic dipoles (μ_j) taken over the N different carbon atoms.(25)

$$V_{12} \propto \sum_{j}^{N} \rho_j \mu_j$$

The sums of the individual one center terms over the atoms are expected to be similar since the transition density and the sum of the atomic dipoles (as indicated by the small differences of the allowed triplet-triplet absorption and IR intensities between different molecules) are nearly the same. This implies that for any given carbon atom in coronene the AVERAGE value of the transition density or vibration atomic dipole is approximately one-fourth that of benzene. When these average values are used in the above summation, V_{12} for benzene is calculated to be four times larger than for coronene. In reality, this value is a lower limit since the cancellation of terms which occurs when the actual molecular orbital wavefunctions are used should be greater for coronene than for benzene due to the much greater number of nodes in the wavefunction of coronene.

If the above reasoning is indeed correct, it might be expected that benzene is a special case due to its small size and that for all larger molecules of high symmetry the pseudo Jahn-Teller effect will be unimportant.

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References

1. E. R. Bernstein, S. D. Colson, D. S. Tinti and G. W. Robinson, J. Chem. Phys. 48 (1968) 4632.
2. D. M. Burland, G. Castro and G. W. Robinson, J. Chem. Phys. 52 (1970) 4100.
3. M. S. de Groot and J. H. van der Waals, Mol. Phys. 6 (1963) 545.
4. A. M. Ponte Goncalves and C. A. Hutchison, J. Chem. Phys. 49 (1968) 4235.
5. G. C. Nieman and D. S. Tinti, J. Chem. Phys. 96 (1967) 1674.
6. G. C. Nieman, J. Chem. Phys. 50 (1969) 1674.
7. J. van Egmond and J. H. van der Waals, Mol. Phys. 26 (1973) 1147.
8. S. Leach and R. Lopez-Delago, J. Chim. Phys. 61 (1964) 1636.
9. J. H. van der Waals, A. M. D. Berghuis and M. S. de Groot, Mol. Phys. 13 (1967) 301; J. H. van der Waals, A. M. D. Berghuis and M. S. de Groot, Mol. Phys. 21 (1971) 497.
10. A. M. Merle, W. M. Pitts and M. A. El-Sayed, Chem. Phys. Letters 54 (1978) 211.
11. M. A. El-Sayed, W. R. Moomaw and J. B. Chodak, J. Chem. Phys. 57 (1972) 4061.
12. M. S. de Groot, I. A. M. Hesselmann and J. H. van der Waals, Mol. Phys. 16 (1969) 45.
13. M. Lamotte, A. M. Merle, J. Joussot-Dubien and F. Dupuy, Chem. Phys. Letters 35 (1975) 410.
14. K. Ohno, N. Nishi, M. Kinoshita and H. Inokuchi, Chem. Phys. Letters 33, (1975) 293.
15. K. Ohno, T. Kajiwara and H. Inokuchi, Bull. Chem. Soc. Japan 45 (1972) 996.
16. K. Ohno and H. Inokuchi, Chem. Phys. Letters 23 (1973) 561.
17. L. M. Babkov, V. I. Glyadkouskii, N. I. Davydova, V. A. Karpova, L. A. Klimova, M. A. Kovner, M. M. Suchinskii, A. A. Terekhov and E. V. Shpolskii, Opt. Spect. 34 (1973) 38.

18. W. Moffitt and A. D. Liehr, Phys. Rev. 106 (1957) 1195;
A. D. Liehr, Rev. Mod. Phys. 32 (1960) 436;
A. D. Liehr, Z. Naturf. A 16 (1961) 641.

19. A. S. Cullick, R. E. Gerkin, D. L. Thorsell and A. M. Winer, J. Chem. Phys. 61 (1974) 3450.

20. J. Schmidt, D. A. Antheunis and J. H. van der Waals, Mol. Phys. 22 (1971) 1.

21. A. M. Merle, M. F. Nicol and M. A. El-Sayed, Chem. Phys. Letters, accepted for publication.

22. S. D. Colson and E. R. Bernstein, J. Chem. Phys. 43 (1965) 2661.

23. R. M. Hochstrasser and C. A. Marzzacco, Molecular Luminescence, ed. by E. C. Lim, W. A. Benjamin, Inc. (1969) 631.

24. N. S. Ham and K. Ruedenberg, J. Chem. Phys. 25 (1956) 13.

25. J. A. Pople and J. W. Sidman, ibid 27 (1957) 1270.

Table 1

The values for the frequencies (± 3 cm^{-1}) of the 0,0 bands recorded for the four sites of coronene isolated in n-heptane.

Transition/Site	α	β	γ	δ
$S_1 \rightarrow S_0$	*	23491	23475	23451
$S_1 \leftarrow S_0$	23547	*	23477 23480	23451
$T_1 \rightarrow S_0$	19435	19401	19382	19349
(coronene-d_{12}) $T_1 \rightarrow S_0$	19493	19461	19440	19409

* Too weak to be recorded

TABLE 2

The values of the primary ground state vibrational frequencies (± 3 cm^{-1}), their assignments and their site splittings (in parentheses) observed in the phosphorescence of coronene and deuterated coronene.

Coronene-h_{12}

Vibrational frequency (cm^{-1})	Assignment[†]
368 (4.9, 3.3, 4.4)[*]	e_{2g}
485 (- , 4.6, 5.6)	e_{2g}
1159 (4.8, - , 5.0)	a_{1g}
1225	e_{2g}
1439	e_{2g}
1624 (- , - , 2.5)	e_{2g}
1639	e_{2g}

Coronene-d_{12}

363 (5.1, 4.4, 4.4)	e_{2g}
446 (- , 3.2, 5.4)	e_{2g}
833	e_{2g}
1415	e_{2g}
1618	e_{2g}
1625	e_{2g}

[*] The three numbers represent the site splittings (β, γ, δ) in cm^{-1} (± .3 cm^{-1}).

[†] Listed assignments are based on Refs. 13-17 and the results of this work.

Table 3

The values of the ground state frequencies (± 3 cm^{-1}), their site splittings (in parentheses) and possible assignment of the vibrations observed in the fluorescence of coronene. The three numbers represent the site splittings (β, γ, δ) in cm^{-1} (± .3 cm^{-1}).

Vibrational Energy	Assignment [†]
366 (4.3, -, 3.7)	e_{2g}
995 (3.5, -, -)	e_{2g}
1355	e_{2g}
1402	e_{2g}
1436	e_{2g}
1452	*
1474	*

*unassigned

[†] Listed assignments are based on Refs. 13-17.

Table 4

The values of excited singlet state frequencies (± 3 cm^{-1}), their assignment and site splittings (in parentheses) of vibrations observed in the phosphorescence excitation spectrum of coronene.

Vibrational Energy	Assignment
365 (4.0, 3.6, 5.1)[†]	e_{2g}
976 (5.4, - , -)	e_{2g}
1390	e_{2g}
1421	e_{2g}
1451	*
1624	*
1730	*

*unassigned

[†] The three numbers represent the site splittings (β, γ, δ) in cm^{-1} (± .3 cm^{-1}). Listed assignments are by comparison with Table 3.

Table 5

The zero field splittings parameters (± 0.002 GHz) for the lowest triplet state of coronene-h_{12} and coronene-d_{12} for each of the sites observed in phosphorescence.

coronene-h_{12}	α	β	γ	δ
D	2.941	2.905	2.900	2.892
E	+.028	-.083	-.105	-.132
coronene-d_{12}				
D	2.951	2.907	2.901	2.892
E	+.029	-.087	-.114	-.135

FIGURE CAPTIONS

Fig. 1 Phosphorescence (a), fluorescence (b), and lowest singlet phosphorescence excitation spectra (c) of coronene-h_8 isolated in n-heptane spectra for the region of the lowest e_{2g} vibrations (368 cm^{-1} in phosphorescence, 366 cm^{-1} in fluorescence, and 365 cm^{-1} in excitation). In all three, site α was recorded in a polycrystal while sites β, γ, and δ were recorded in a single crystal of the alkane. For (a) and (b), sites β, γ, and δ were recorded in one sweep and are a true indication of relative site intensity. The excitation spectra were recorded separately for each site and the sizes of the bands give only an indication of the relative band strengths. All of the spectra show similar site structure and site splittings of the degenerate e_{2g} vibration. The peculiar appearance of site γ in (c) is due to the presence of two subsites (see text).

Fig. 2 Recordings of the various 0,0 bands of phosphorescence (a), fluorescence (b), and lowest singlet phosphorescence excitation spectra (c) of coronene-h_8 in n-heptane. In all cases site α was recorded in the polycrystal while sites β, γ, and δ were observed in a single crystal. For (a) and (b), sites β, γ, and δ were recorded in one sweep and the true relative intensities are indicated by the band heights. Each of the sites shown in (c) were taken separately and the intensities are only an indication of the relative strengths of the bands. Site α in fluorescence and site β in excitation were not observed. Note the substructure of site γ in the excitation spectrum (c).

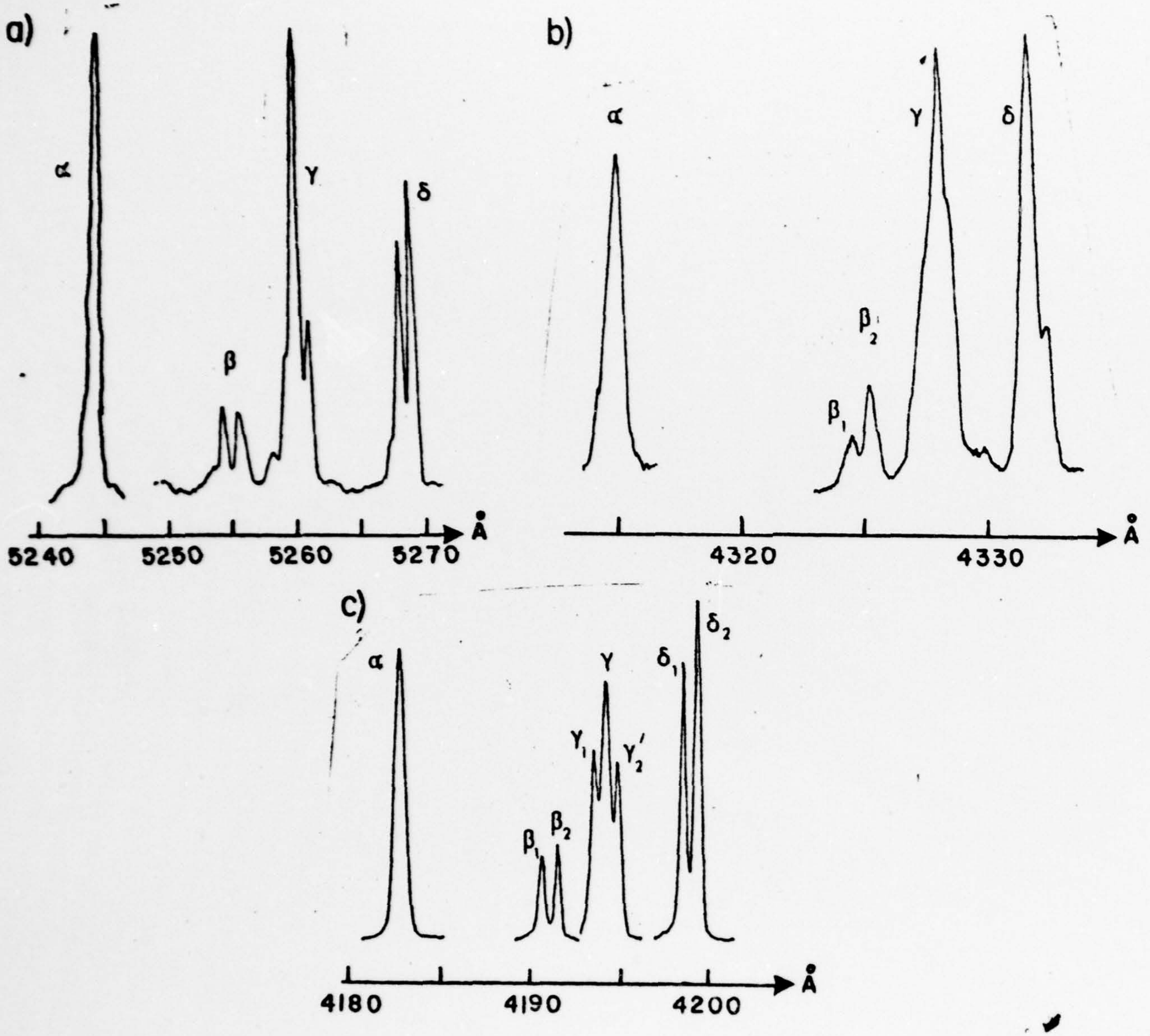
a)
α
β
γ
δ
5240
5250
5260
5270
Å
b)
α
β_1
β_2
γ
δ
4320
4330
Å
c)
α
β_1
β_2
γ_1
γ
γ'_2
δ_1
δ_2
4180
4190
4200
Å

fig 1

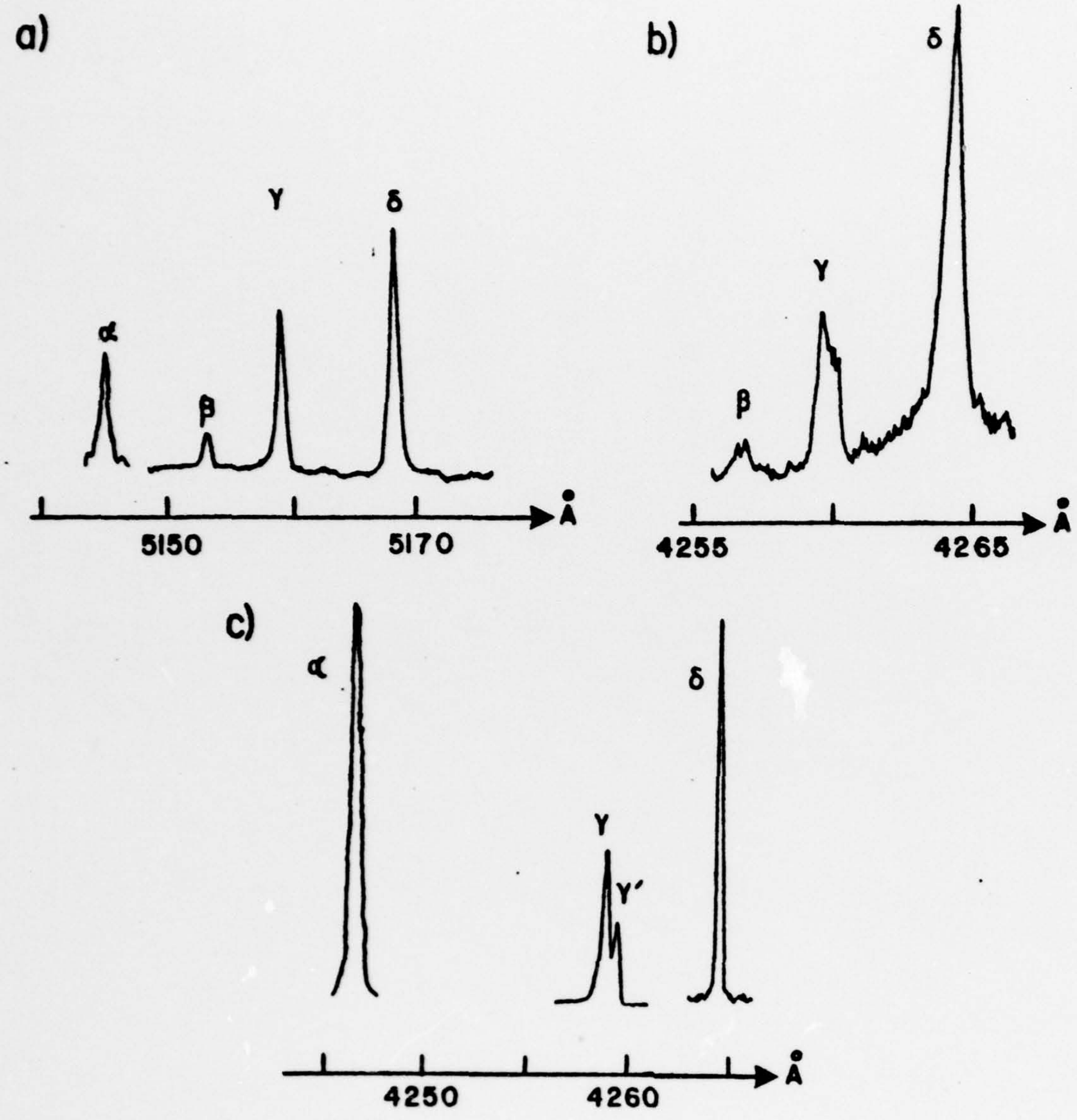

Fig 8

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