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Rotationally resolved $S_1 \leftarrow S_0$ electronic spectra of fluorene, carbazole, and dibenzofuran: Evidence for Herzberg-Teller coupling with the S_2 state.

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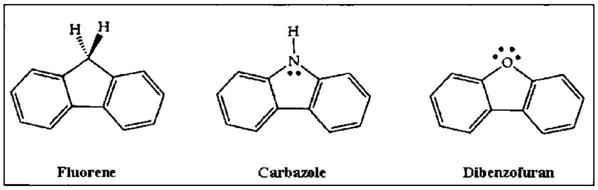
Rotationally resolved fluorescence excitation spectra of the $S_1 \leftarrow S_0$ origin bands and higher vibronic bands of fluorene (FLU), carbazole (CAR), and dibenzofuran (DBF) have been observed and assigned. Analyses of these data show that replacement of the CH_2 group in FLU with a NH group in CAR and an O atom in DBF produces only localized changes in structure, in the ground state. But the three molecules exhibit different changes in geometry when they are excited by light. The S_1 states of the three molecules also are electronically very different. The $S_1 \leftarrow S_0$ transition moments of CAR and DBF are parallel to the C_2 symmetry axis whereas the corresponding transition moment in FLU is perpendicular to this axis. Herzberg-Teller coupling involving the S_2 state also has been observed in the spectra of higher vibronic bands of CAR and DBF. Possible reasons for these behaviors are discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2206782]

I. INTRODUCTION

Fluorene (FLU), carbazole (CAR), and dibenzofuran (DBF) constitute an interesting family of molecules in which the CH_2 group in the 9–position of FLU is replaced by a NH group in CAR and an oxygen atom in DBF; see below. Even though these groups are isoelectronic, the resulting molecules exhibit different characteristics upon the absorption of light.Bree *et al.*[1–3] discovered in studies of low temperature crystals that their S_1-S_0 electronic transitions are differently polarized. The $S_1 \leftarrow S_0$ electronic origins in CAR and DBF are polarized along the short *b* axis, whereas the corresponding transition in FLU is polarized along the long *a* axis. All three molecules were studied by many authors in the gas phase[4] and later, in supersonic jets; FLU by Jortner and co-workers,[5,6] Meerts, *et al.*,[7] and Zhang *et al.*;[8] CAR by Auby *et al.*;[9] and CAR and DBF by Chakraborty and Lim,[10] and more recently by Baba, *et al.*[11] Photoexcited van der Waals dimers of these and many other molecules exhibit excimer formation on short time scales, a phenomenon that sensitively depends on the mutual orientation of their transition moments in both the gas phase and the condensed phase.



Here described are the rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectra of the origin bands and some higher energy vibronic bands of all three molecules in the gas phase. (Analogous experiments were attempted on the sulfur analog, dibenzothiophene, but these were unsuccessful.) We find that the origin bands of CAR and DBF are both perpendicular bands, while that of FLU is a parallel band, as in the condensed phase. We also find that some of the higher energy vibronic bands in CAR and DBF are parallel bands, evidencing vibronic coupling with a higher-lying S_2 electronic state. Possible reasons for these behaviors are discussed.

II. EXPERIMENT

FLU, CAR, and DFB were each purchased from Aldrich (>98% pure) and used without further purification. Low resolution experiments were performed by seeding the sample into 30 psi of Ar gas, expanding it into a vacuum through a 1 mm diameter orifice pulsed valve, and exciting it with the second harmonic of a Quanta Ray Nd^{3+}:YAG (Model DCR-1A) pumped dye laser (Model PDL-1). High resolution experiments were performed using the cw laser spectrometer, described elsewhere.[12] Briefly, the sample was seeded into Ar gas, expanded through a 240 μm quartz nozzle, and probed 15 cm downstream of the nozzle by an Ar^+ pumped cw tunable dye laser. The pulsed and cw lasers operated with Rhodamine 590 and DCM dyes; in the cw case, ~200 μW of UV radiation was obtained by intracavity frequency doubling using BBO 580 and LIO_3 640 crystals. The fluorescence excitation spectra, the iodine absorption spectrum, the relative frequency markers, and the laser output power were simultaneously collected and processed by an in-house data acquisition system; the high resolution data were analyzed using jb95.[13] Transition frequencies were calibrated by comparison with the I_2 absorption spectrum and frequency markers were obtained from a stabilized etalon with a free spectral range of 299.7520±0.0005 MHz.

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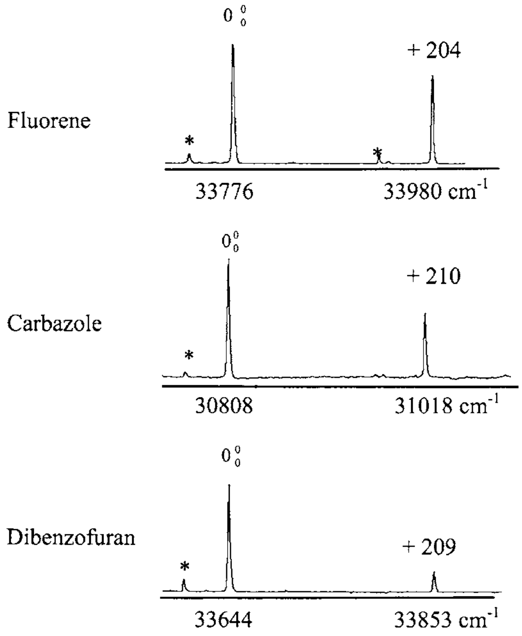


FIG. 1. Fluorescence excitation spectra of the $S_1 \leftarrow S_0$ electronic transitions of fluorene, carbazole, and dibenzofuran in a supersonic jet. The origins are indicated as 0_0^0 and the first vibronic bands of each molecule are also shown. Bands marked with asterisks are due to argon complexes.

III. RESULTS

Figure 1 shows the first ∼300 cm^{-1} in the vibrationally resolved fluorescence excitation spectra of FLU, CAR, and DBF in a supersonic jet. Surprisingly, the 0_0^0 bands of FLU and DBF appear at similar frequencies, but that of CAR is shifted ∼3000 cm^{-1} to the red. Not shown in full detail are the higher vibronic bands in each spectrum; FLU has bands at 0_0^0+204, +394, and +598 cm^{-1}; CAR has bands at 0_0^0 +210 and +511 cm^{-1}; and DBF has bands at 0_0^0+209 and +443 cm^{-1}. The latter band is much stronger than the 0_0^0 band in DBF. Also, all three molecules exhibit bands that have previously been assigned to weakly bound argon complexes.[5–7]

Figures 2–4 show the rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectra of the 0_0^0 bands of FLU, CAR, and DBF, respectively. Each spectrum spans approximately 2.5 cm^{-1}. As previously reported,[6] the 0_0^0 band of FLU is a pure *a*-type spectrum, indicating that its $S_1 \leftarrow S_0$ transition moment (TM) is parallel to the *a*-inertial axis. In contrast, the corresponding bands of CAR and DBF are pure *b*-type spectra, though this might not be readily apparent at first glance. All three bands were fit utilizing rigid-rotor Hamiltonians for both states, using previously described fitting strategies.[12] Examples of these fits are also shown in Figs. 2–4; the standard deviations of these fits (OMC observed minus calculated) are ∼2.0 MHz for all three molecules.

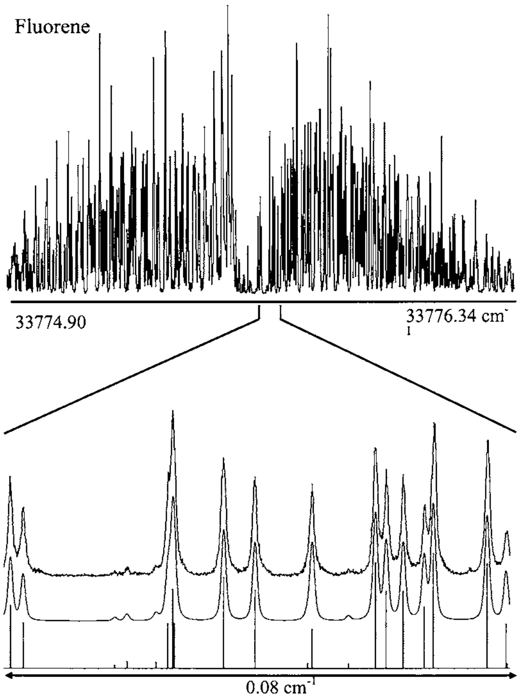


FIG. 2. Rotationally resolved fluorescence excitation spectrum of the electronic origin in the $S_1 \leftarrow S_0$ transition of fluorene (top). A portion of the experimental spectrum at full resolution and the corresponding simulated spectrum with and without a convoluted line-shape function are also shown (bottom).

Table I lists the rotational constants that were derived from these fits. The *A* rotational constant of the ground state (A'') value obtained for FLU (2175.6 MHz) is slightly different from that previously measured by Meerts *et al.* (2183.2 MHz).[7] All three rotational constants of ground-state CAR are in excellent agreement with those previously measured by microwave spectroscopy.[14] We estimate ∼15 MHz Lorentzian contributions to the Voigt line-shape profiles of single lines in all three spectra. The corresponding lifetime of 10 ns agrees reasonably well with the measured fluorescence lifetimes of 15.6 ns for FLU, 29.4 ns for CAR, and 14.8 ns for DBF.[15]

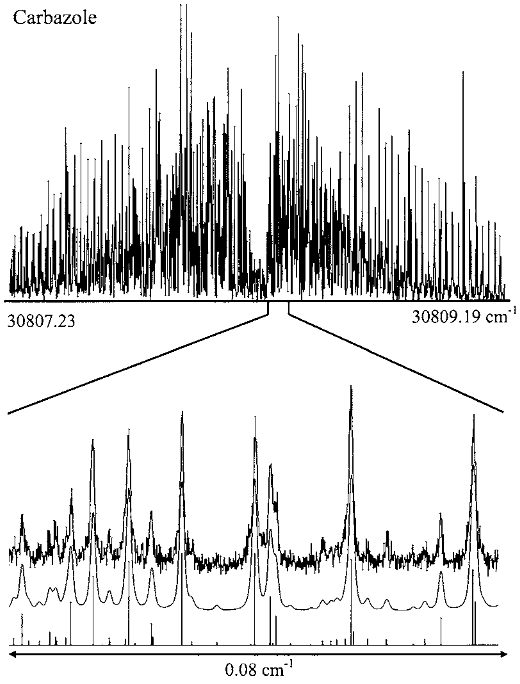


FIG. 3. Rotationally resolved fluorescence excitation spectrum of the electronic origin in the $S_1 \leftarrow S_0$ transition of carbazole (top). A portion of the experimental spectrum at full resolution and the corresponding simulated spectrum with and without a convoluted line-shape function are also shown (bottom).

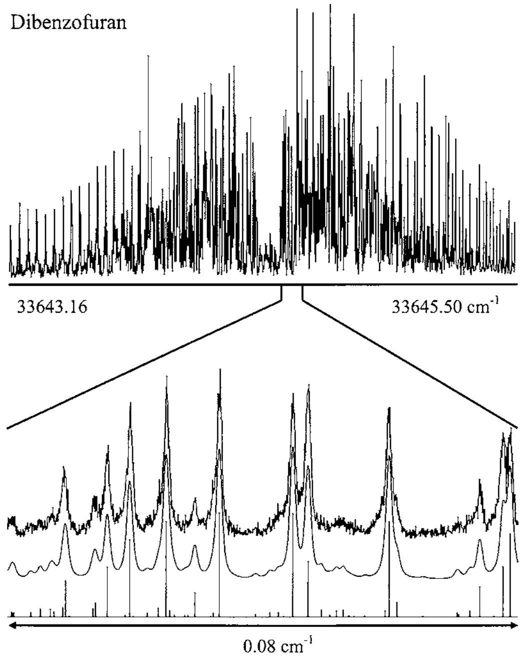


FIG. 4. Rotationally resolved fluorescence excitation spectrum of the electronic origin in the $S_1 \leftarrow S_0$ transition of dibenzofuran (top). A portion of the experimental spectrum at full resolution and the corresponding simulated spectrum with and without a convoluted line-shape function also are shown (bottom).

Figure 5 shows the rotationally resolved fluorescence excitation spectra of four higher vibronic bands of the three molecules; FLU+204, FLU+394, CAR+210, and DBF +209. The spectra of FLU are both *a*-type spectra whereas those of CAR and DBF are *b*-type, just as their respective origin bands. Analyses of these spectra proceeded as before with one exception; the FLU+204 spectrum could not be properly fit using rigid-rotor Hamiltonians for both electronic states. High J' value lines are shifted by as much as 100 MHz with respect to their predicted positions, leading to large standard deviations. Attempts to fit this band with the distortable rotor Hamiltonian of Watson[16] have so far been unsuccessful. No such perturbations were observed in the higher energy FLU+394 band.

TABLE I. Inertial parameters of the zero-point vibrational levels of the S_0 and S_1 electronic states of fluorene, carbazole, and dibenzofuran. Standard deviations (in MHz) are given in parentheses.

	Fluorene[a]	Carbazole[b]	Dibenzofuran[c]
S_0			
A''(MHz)	2175.6 (1.1)	2253.2 (0.1)	2278.2 (0.1)
B''(MHz)	586.6 (0.1)	594.2 (0.1)	601.1 (0.1)
C''(MHz)	463.6 (0.1)	470.4 (0.1)	475.8 (0.1)
S_1-S_0			
ΔA(MHz)	−73.4 (1.1)	−2.6 (0.1)	−21.3 (0.1)
ΔB(MHz)	6.7 (0.1)	−7.9 (0.1)	−6.7 (0.1)
ΔC(MHz)	0.7 (0.1)	−5.1 (0.1)	−5.1 (0.1)
Band type	*a*	*b*	*b*
Band origin (cm^{-1})	33775.55	30808.13	33644.36
OMC (MHz)	2.07	2.24	2.14
Temp. (K)	2.8	2.5	2.3

[a] MP2/6-31G^{**} values: $A''=2177.67$, $B''=586.56$, and $C''=463.41$ MHz.
[b] MP2/6-31G^{**} values: $A''=2253.98$, $B''=593.99$, and $C''=470.10$ MHz.
[c] MP2/6-31G^{**} values: $A''=2273.18$, $B''=600.63$, and $C''=475.10$ MHz.

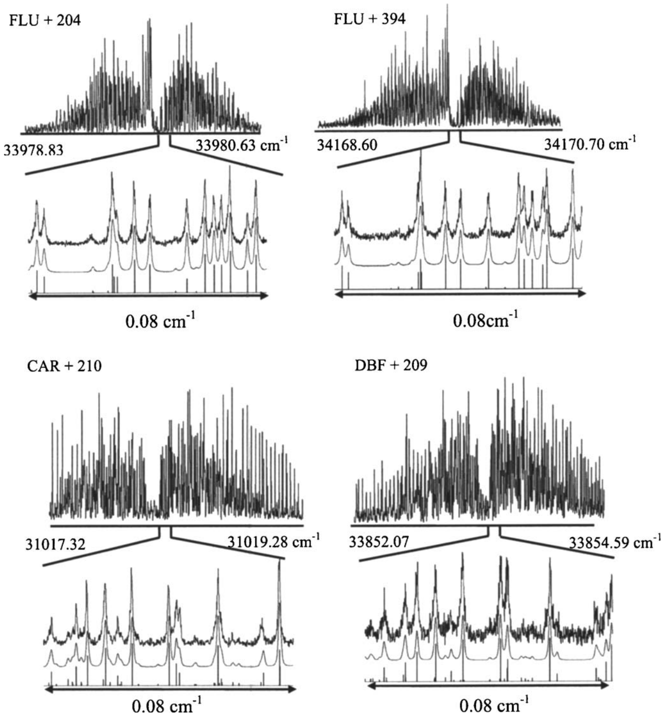


FIG. 5. Rotationally resolved fluorescence excitation $S_1 \leftarrow S_0$ spectra of the a_1-symmetry vibronic bands of FLU, CAR, and DBF in a molecular beam. A portion of each spectrum at full experimental resolution is also shown, together with the corresponding fits. Note that every spectrum is unique.

Figure 6 shows the rotationally resolved fluorescence excitation spectra of two additional higher vibronic bands, CAR+511 and DBF+443. Surprisingly, neither of these bands has the same band type as the respective origin bands; CAR+511 and DBF+443 are both pure *a*-type bands. No *b*- or *c*-type transitions were found in either spectrum. Both bands could be fit with rigid-rotor Hamiltonians, with standard deviations of 3.0 and 2.6 MHz, respectively. Table II lists the inertial parameters of the six examined vibronic bands of FLU, CAR, and DBF.

IV. DISCUSSION

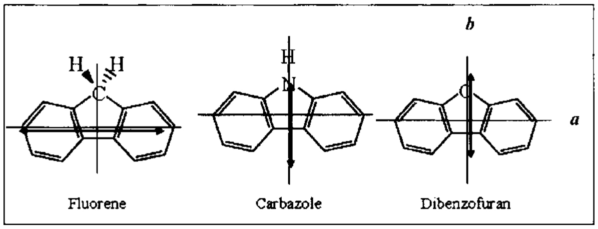
Electronic state mixing and/or reordering is at the heart of chemistry. The ability of one substance to be transformed into another depends on where its electrons are, and on how easily a given electronic distribution can be modified by its interactions with the electronic distributions of other substances. We find that FLU has a long-axis polarized $S_1 \leftarrow S_0$ electronic transition but that two closely related derivatives, CAR and DBF, have short-axis polarized $S_1 \leftarrow S_0$ transitions, in agreement with previous condensed phase results,[1–3] see below. The S_1 state of the isolated FLU molecule is an L_b state whereas the S_1 states of isolated CAR and DBF molecules are L_a states. This means that replacing the CH_2 group

TABLE II. Inertial parameters of some higher S_1 vibronic bands of fluorene, carbazole, and dibenzofuran. Standard deviations (in MHz) are given in parentheses.

	FLU+204[a]	FLU+394	CAR+210	CAR+511	DBF+209	DBF+443
S_0						
A''(MHz)	2180.6 (2.7)	2176.1 (0.8)	2253.2 (0.1)	2255.8 (0.1)	2277.7 (0.1)	2275.8 (1.0)
B''(MHz)	586.8 (0.1)	586.7 (0.1)	594.2 (0.1)	594.3 (0.1)	601.1 (0.1)	601.1 (0.1)
C''(MHz)	463.5 (0.1)	463.6 (0.1)	470.4 (0.1)	470.2 (0.1)	475.7 (0.1)	475.8 (0.1)
S_1-S_0						
ΔA(MHz)	−58.9 (2.7)	−73.2 (0.8)	1.4 (0.1)	−1.6 (0.1)	−17.2 (0.1)	−26.9 (1.0)
ΔB(MHz)	6.7 (0.1)	6.6 (0.1)	−7.6 (0.1)	−7.6 (0.1)	−6.3 (0.1)	−5.8 (0.1)
ΔC(MHz)	0.8 (0.1)	0.6 (0.1)	−5.1 (0.1)	−5.0 (0.1)	−5.1 (0.1)	−4.7 (0.1)
Band type	*a*	*a*	*b*	*a*	*b*	*a*
Band origin (cm^{-1})	33979.80	34169.75	31018.12	31319.70	33853.38	34087.69
OMC (MHz)	5.25	1.87	3.63	2.20	3.32	2.21
Temp. (K)	2.8	3.0	3.0	3.0	3.3	2.6

[a] Several lines with J' values above 10 were not included in the fit.

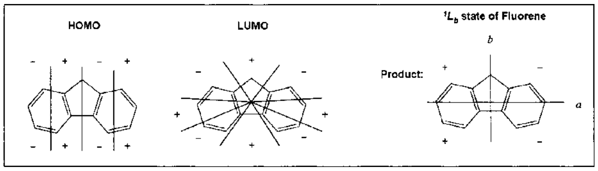
in the central five-membered ring with an NH group or an O atom modifies the distributions of electrons in the attached six-numbered rings, and leads to the expectation that the photochemical behavior of the S_1 states of CAR and DBF might be very different from that of FLU.



Ab initio calculations (MP2/6−31G** for the S_0 states, CIS/6-31G for the S_1 states)[17] have been performed to explore the reasons for these behaviors. The calculated rotational constants of all three molecules in their ground states are in excellent agreement with the experimental values (cf. Table I). The ground state values A'', B'', and C'' show the expected increases across the series FLU, CAR, and DBF owing to replacement of the CH_2 group by the NH group and the O atom closer to the center of mass. (Also, the C–X bond length decreases with X=C, N, and O.) Generally, the excited state A', B', and C' values are less than their ground state counterparts, owing to the small ring expansions that are typical of $\pi\pi^*$ states. But the values of ΔA, ΔB, and ΔC ($\Delta A = A' - A''$, etc.) in CAR and DBF are qualitatively different from those in FLU. FLU has a larger (in magnitude) ΔA value (−73.4 MHz), whereas the ΔA values of CAR and DBF are much smaller (−2.6 and −21.3 MHz, respectively).

Apparently, all three molecules are essentially planar in both electronic states. FLU has an inertial defect of −3.59 amu Å^2 in its ground state (Table III), a value that is consistent with two out-of-plane C–H bonds. The inertial defects of CAR and DBF are nearly the same, −0.36 and −0.34, respectively; the N–H hydrogen in CAR must lie in the plane of the concatenated rings. None of these values change substantially when the molecules absorb light.

Figure 7 shows a sketch of the relevant MO's of the energy-optimized structures that were derived from these calculations. According to CIS, the principal one-electron excitation that contributes to the S_1 state is the HOMO-LUMO transition (∼65%); three other excitations each contribute about 10%. The oscillating charge distribution that is associated with the HOMO-LUMO transition is oriented along the *a* axis, as shown below. Thus, CIS agrees with experiment in predicting a long-axis polarized $S_1 \leftarrow S_0$ transition. However, it is equally evident that CIS fails to predict the polarizations of the corresponding transitions in CAR and DBF. According to theory, the relevant orbitals (especially the HOMO and LUMO, see Fig. 7) and the principal excitation that contributes to the S_1 state in these two molecules are virtually the same as for FLU. Thus, theory predicts long-axis polarized 0_0^0 bands in CAR and DBF as well, in clear disagreement with experiment. The S_1 states of CAR and DBF are L_a states.



Since the NH group in CAR and the O atom in DBF both lie in plane, both molecules have out-of-plane lone pairs of electrons, unlike FLU. Thus, we speculate that these electrons play a significant note in the observed electronic state reordering in these molecules. Both Auty *et al.*[9] and Nitzsche *et al.*[18] have made similar arguments, noting that differences in the shifts of the absorption and fluorescence spectra of CAR and DBF relative to FLU could be explained by differences in their S_1-S_0 electronic distributions. A similar effect

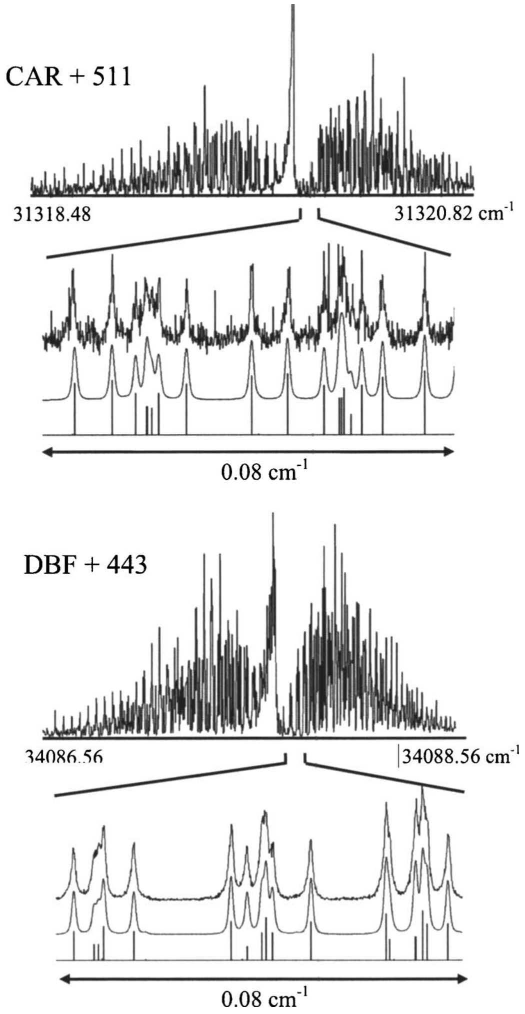


FIG. 6. Rotationally resolved fluorescence excitation $S_1 \leftarrow S_0$ spectra of the b_2-symmetry vibronic bands of CAR and DBF in a molecular beam. For each spectrum, a portion at full experimental resolution is also shown, together with their respective simulations.

has been observed in 1-aminonaphthalene (1AN).[19] 1AN exhibits a largely *b*-type origin band in its fully resolved electronic spectrum, whereas other 1-substituted naphthalenes exhibit largely *a*-type bands. Conjugation of the nitrogen lone pair electrons with the ring was offered as an explanation for this behavior. The conjugation leads to a twisting of the NH_2 group on S_1 excitation, perhaps suggesting the existence of a conical intersection along this coordinate. Similar effects have been revealed by CASSCF calculations on related systems.[20] Thus, significantly higher level calculations may be necessary to capture these behaviors in CAR and DBF. (CIS calculations based on DFT wave functions give the same result as *ab initio* ones.)

Assignment of the S_1 states of CAR and DBF as ^1L_a states and the S_1 state of FLU as a ^1L_b state helps explain the differences in the ΔA values of the three species. The electron density in L_a states is primarily localized on atoms whereas the electron density in L_b states is primarily localized at the centers of bonds.[21] Thus, FLU should have a relatively large negative value of ΔA, and relatively small values of ΔB and ΔC, owing to a ring expansion that preferentially lengthens the molecule in directions perpendicular to the *a* inertial axis. This is what is observed; $\Delta A=-73.4$, $\Delta B=6.7$, and $\Delta C=0.7$ MHz. On the other hand, CAR and DBF are qualitatively different. CAR has $\Delta A=-2.6$, $\Delta B=-7.9$, and $\Delta C=-5.1$ MHz. The three nearly equal values suggest that the resulting displacements now make nearly equal projections along both *a* and *b*. DBF has $\Delta A=-21.3$, $\Delta B=-6.7$, and $\Delta C=-5.1$ MHz, a slight difference in ΔA. The degree of conjugation between the double bonds and the lone pair electrons of the substituent atom must be different.

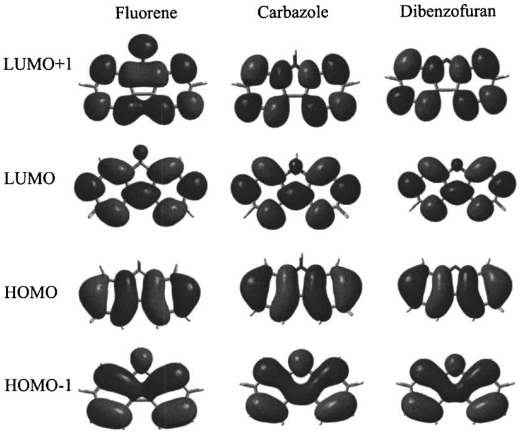
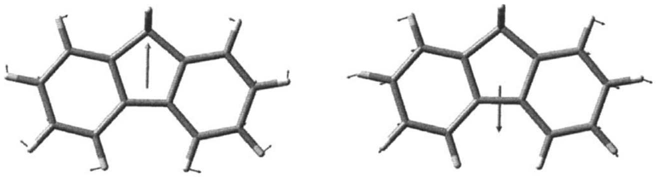


FIG. 7. MP2 6-31G^{**} molecular orbitals of fluorene, carbazole, and dibenzofuran.

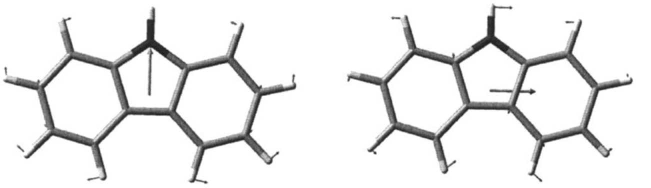
A relevant additional observation is that the 0_0^0 band of CAR is redshifted with respect to the corresponding band in FLU by ~3000 cm^{-1}. Similarly, the 0_0^0 band of 1AN is redshifted with respect to the corresponding band in naphthalene by ~2000 cm^{-1}.[19] This is the expected result if the affected electrons are significantly delocalized over the whole molecule. The 0_0^0 band of DBF is redshifted by only 132 cm^{-1} from the 0_0^0 band of FLU. But the $S_1 \leftarrow S_0$ origin band of dibenzothiophene, a related member of the family, is again shifted by ~2600 cm^{-1} to the red, and is also a *b*-type band (in the condensed phase).[22] Apparently, there is less delocalization of the more tightly oxygen lone pair electrons in DBF.

Higher vibronic bands that appear in the $S_1 \leftarrow S_0$ excitation spectra of FLU, CAR, and DBF show additional interesting properties. The TM orientations of the four bands shown in Fig. 5 (FLU+204, FLU+394, CAR+210, and DBF+209) are the same as their respective origins whereas the TM orientations of the two bands shown in Fig. 6 (CAR+511 and DBF+443) are different from their respective origins. Similar effects have been observed in the condensed phase.[1–3] A logical explanation, then, is that the two bands in question terminate in nontotally symmetric vibrational bands of the S_1 state, and that these molecules are active in Herzberg-Teller (HT) coupling[23] to the S_2 state.

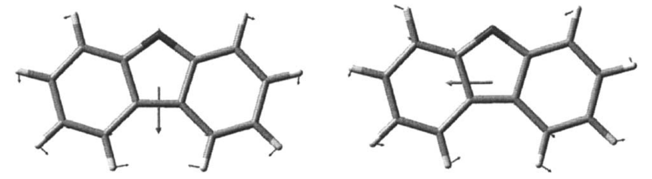
In HT coupling, if rovibronic wave functions are considered in the first approximation as a product of electronic, vibrational, and rotational wave functions, and higher order effects are neglected, then the transition dipole moment for an electronic transition between an upper and a lower vibronic state may be written as



a) FLU- symmetric in-plane bending mode (208 cm^{-1}) b) FLU-symmetric in-plane breathing mode (405 cm^{-1})



c) CAR- symmetric in-plane bending mode (208 cm^{-1}) d) CAR-asymmetric in-plane skeletal mode (506 cm^{-1})



e) DBF-symmetric in-plane bending mode (208 cm^{-1}) f) DBF- asymmetric in-plane distortion mode (500 cm^{-1})

FIG. 8. Vibrational modes of FLU, CAR, and DBF assigned to their corresponding vibronic bands in their S_1 state (CIS/6-31G). The polarization vectors are shown as arrows beginning at their corresponding centers of mass.

$$\begin{aligned}\langle\psi_e'\psi_v'\psi_r'|\mu_Z|\psi_e''\psi_v''\psi_r''\rangle \\ = \sum_g \Big\{ & \mu_g^0(e',e'')\langle\psi_e'|\psi_e''\rangle \\ & + \sum_s [\partial\mu_g(e',e'')/\partial Q_s]_0\langle\psi_v'|Q_s|\psi_v''\rangle \\ & + \sum_a [\partial\mu_g(e',e'')/\partial Q_a]_0\langle\psi_v'|Q_a|\psi_v''\rangle\Big\}\langle\psi_r'|\lambda_{Zg}|\psi_r''\rangle. \end{aligned} \tag{1}$$

Here, μ_Z is the component of the electric dipole moment operator along the space fixed axis Z, the μ_g are its projections along the inertial axes $g(=a,b,c)$, with direction cosines λ_{Zg}, and the $[\partial\mu_g(e',e'')/\partial Q]_0$ are the transition moment derivatives with respect to nuclear motions (s representing symmetric ones and a representing antisymmetric ones), evaluated at the equilibrium nuclear configuration. For symmetry allowed electronic transitions, the first two terms on the right-hand side of Eq. (1) are nonzero. But for symmetry forbidden transitions, only the last term in Eq. (1) is nonzero, and the transitions are said to be "vibrationally induced."[23] In that event, the polarization of the bands will depend upon the symmetry of the inducing coordinate Q_a, and that of the electronic state to which it is coupled.

That this interpretation is likely the correct one is supported by the results of our *ab initio* calculations. These calculations show that S_1 FLU has an a_1 symmetry in-plane bending mode at 208 cm^{-1}, and an a_1 symmetry breathing mode at 405 cm^{-1} [Figs. 8(a) and 8(b) sketch these two vibrational modes in the S_1 state]. Given their frequencies, and symmetries, the two observed bands at FLU+204 and FLU +394 may be assigned to these normal modes. The upper state rotational constants and inertial defects (Table III) are consistent with these assignments. Similarly, the two observed bands at CAR+210 and DBF+209 may also be assigned to the a_1 symmetry in-plane bending mode, since their calculated S_1 frequencies (208 cm^{-1}) are in good agreement with experiment [Figs. 8(c) and 8(e)]. But the CAR+511 and DBF+443 vibronic bands must involve nontotally symmetric modes, since their polarizations are different. The CAR +511 band has been assigned to the b_2 symmetry in-plane skeletal mode at 506 cm^{-1}, and the DBF+443 band has been assigned to the b_2 symmetry in-plane skeletal distortion mode at 500 cm^{-1}; according to the CIS calculations [Figs. 8(d) and 8(f)]. These latter two nontotally symmetric modes are likely candidates for the HT coupling mechanism; their symmetries make possible a mixing of the zero-order S_1 states of CAR and DBF with S_2 states having B_2 symmetry, which are expected to possess higher oscillator strengths. Thus explained are the observed a-axis polarizations of the corresponding vibronic bands.

TABLE III. Inertial defects (in amu Å^2) of fluorene, carbazole, and dibenzofuran in their S_0 and S_1 states. Standard deviations are given in parentheses.

Band		Experimental S_0	Experimental S_1	Theory[a] S_1
Fluorene	0_0^0	−3.59 (0.1)	−3.74 (0.1)	−3.11
	+204[b]	−2.87 (0.2)	−1.56 (0.2)	−3.03
	+394	−3.45 (0.0)	−3.49 (0.0)	−3.07
Carbazole	0_0^0	−0.36 (0.1)	−0.31 (0.1)	0.00
	+210	−0.40 (0.1)	0.45 (0.1)	0.08
	+511	0.26 (0.1)	0.76 (0.1)	0.03
Dibenzofuran	0_0^0	−0.34 (0.1)	−0.34 (0.1)	0.00
	+209	−0.38 (0.1)	0.52 (0.1)	0.08
	+443	−0.65 (0.1)	−0.98 (0.1)	0.04

[a] CIS/6-31G calculations; values for the higher vibrational levels have been corrected using Eq. (2).

[b] Several lines with J' values above 10 were not included in the fit.

The two nontotally symmetric modes in CAR and DBF also have unusual inertial defects, as shown in Table III. More positive values (than in the S_1 zero-point level) would be expected since in-plane vibrations make positive contributions to the inertial defect.[24] Estimates of these may be made by using Eq. (2),

$$\Delta I_{\mathrm{vib}} \approx \frac{4K}{\omega}, \tag{2}$$

where $K=h/8\pi^2=16.863$ amu Å^2 cm^{-1} and ω is the frequency of the vibration in cm^{-1}. The calculated values using this equation (*cf.* Table III) are smaller than the observed ones, but at least they display the correct trend. However, the experimental values of the two nontotally symmetric bands are very different from the calculated ones. Thus, it may be that the inertial defects also signal an important role for the nontotally symmetric modes in the intramolecular dynamics.

V. SUMMARY

Several unusual properties of the S_0 and S_1 electronic states of fluorene (FLU), carbazole (CAR), and dibenzofuran (DBF) are revealed by fluorescence excitation experiments on the isolated molecules in a molecular beam. These properties include differences in their rotational constants, in the orientations of their electronic transition moments, and in the polarizations of higher vibronic bands in their fully resolved spectra. Comparisons of the results for the three molecules with the predictions of theory suggest that the S_1 state of FLU is a L_b state, that the S_1 states of CAR and DBF are L_a states, and that couplings between these states of the Herzberg-Teller type are promoted by displacements along certain nontotally symmetric vibrational coordinates. A conical intersection along one or more of these modes may be responsible for these effects.

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