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Vibronic coupling in polyenes: High resolution optical spectroscopy of a simple Schiff base

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High resolution fluorescence and fluorescence excitation spectra of a model polyene Schiff base have been obtained. 4.2 K spectra of N-(2, 4, 6, 8, 10-dodecapentaenylidine)butyl amine in *n*tetradecane exhibit well-resolved electronic spectra ($\pi\pi^*$) from a single mixed crystal site. The major vibronic features, in common with those of polyene hydrocarbons, are due to combinations of symmetric carbon-carbon stretching vibrations. These are dominated by a double bond mode which decreases from 1589 to 1544 cm⁻¹ upon electronic excitation. This decrease contrasts the 150-200 cm⁻¹ increases seen in analogous polyene hydrocarbons. This difference is discussed in terms of vibronic coupling in a model previously applied to the hydrocarbons.

I. INTRODUCTION

Linear polymers have experienced renewed experimental and theoretical interest in recent years.¹⁻³ This stems, in part, from their roles as chromophores in vision and photosynthesis. These processes depend on the unique changes in polyene structure brought about by the absorption of light. Any consideration of these changes and their photochemical consequences must take as a starting point the vibronic states observed in electronic spectroscopy.

High resolution optical spectroscopy of low temperature mixed crystals⁴⁻¹² and gases^{13,14} has provided information on polyene vibronic states and some insight on how these states are connected. For polyenes with a center of symmetry, these studies have led to a rigorous proof of the dipole forbidden nature of the lowest energy transition $(1^{1}A_{g} \rightarrow 2^{1}A_{g})^{10,11}$ One photon transitions between $1 A_{g}^{-}$ and $2 A_{g}^{-}$ are made allowed by Herzberg-Teller mixing of $2 \frac{1}{a} \frac{1}{g}$ and $1 \frac{1}{B} \frac{1}{u}$ via low frequency vibrations.^{5,6,11} High resolution experiments also have revealed some unexpected differences between ground and excited state vibrational modes. These peculiarities were first noted in the lowest excited state of 2, 10-dimethylundecapentaene which undergoes a large increase (1598 cm⁻¹ in $1 {}^{1}A_{s}^{-}$ to 1737 cm⁻¹ in 2 ${}^{1}A_{g}^{-}$) in the frequency of its symmetric (a_{g}) carbon-carbon double bond stretching mode.⁵ Similar increases in this mode, which dominates polyene vibronic intensities, subsequently were observed in 2,12-dimethyltridecahexane¹² (Fig. 1) and octatetraene.¹¹ These increases run counter to the expected decreases in carbon-carbon double bond orders in excited polyenes.¹⁵⁻¹⁸

The discrepancies between the expected and observed frequencies either could be due to errors in polyene bond order calculations, vibrational mixing within electronic states,^{5,15} or vibronic interactions between electronic states.^{7,12} For simple polyene hydrocarbons, vibronic coupling between the ground $(1 \ {}^{1}A_{g}^{-})$ and first excited $(2 \ {}^{1}A_{g}^{-})$ states is the most likely option.¹² This choice finds strong precedent in the work of Mikami and Ito^{19,20} who have used a similar vibronic coupling model to explain comparable,



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anomolous frequency increases in the lowest excited states of benzene $^{21-23}$ and naphthalene. 20,24,25

Previous high resolution experiments have centered on simple symmetric hydrocarbons. The connections between these molecules and the polyene Schiff bases used in photobiology^{1,2} are not yet clear. The lower symmetry of the Schiff bases results in a polar electron distribution which will vary with electronic state as well as on solvent environment. The introduction of low energy, solvent sensitive $n\pi^*$ states further complicates the photochemistries of these systems. Each of these effects (polarity, $n\pi^*$ states, solvent effects) will have spectroscopic consequences.²⁶ Some of these are explored in this paper. We have obtained well-resolved fluorescence and fluorescence excitation spectra of N-(2,4,6,8,10dodecapentaenylidine)butyl amine, "12SB" (Fig. 1). The $\pi\pi^*$ vibronic states of 12SB are remarkably different from those of comparable hydrocarbons. The dominant carboncarbon double bond stretch shows "normal" behavior, exhibiting a decreased frequency in the lowest excited state $(2^{1}A_{\circ}^{-})$. The differences between the spectra of 12SB and the hydrocarbons are considered within the vibronic coupling model mentioned above.

II. EXPERIMENTAL

A. Samples

N-(2,4,6,8,10-dodecapentaenylidine)butyl amine (hereafter referred to as 12SB) was prepared from *n*-butylamine and 2,4,6,8,10-dodecapentaenal. The butylamine (Baker) was distilled and stored over molecular sieves (Linde, 3A) to remove water. The dodecapentaenal was synthesized from crotonaldehyde (Aldrich) as described previously.^{26,27} Crude dodecapentaenal was recrystallized from hexane



FIG. 1. N-(2,4,6,8,10-dodecapentaenylidine)butyl amine (12SB) and 2,12dimethyltridecahexaene (TDH).

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TDH

(Burdick and Jackson) until HPLC procedures indicated an isomerically pure preparation. The fine, pale yellow crystals (in 166–167 °C) were redissolved in hexane and stored in the dark at -10 °C.

The Schiff base was prepared by dissolving 0.6 g of dodecapentaenal in 140 g of dry n-butylamine. This solution then was allowed to stand for 12 h at 5 °C in the presence of molecular sieves. The excess amine was removed by rotary evaporation and the solid residue redissolved in a minimum of hexane. The soluble fraction was maintained at 5 °C to yield orange crystals of 12SB. These were recrystallized from hexane and stored in cold (-10 °C), dry, dilute, $(<10^{-5} \text{ M})$ hexane solutions. Samples stored in this way gave low temperature absorption and emission spectra which did not change over periods of several weeks. The most important consideration in preserving 12SB was to insure that solvents and glassware were extremely dry. Small amounts of water lead to a broadening of the vibronic structure. This problem was particularly noticeable in 77 K fluorescence spectra and presumably is due to the effects of hydrogen bonding.²⁶ All solvents therefore were stored over freshly activated molecular sieves.

Samples for low temperature optical measurements were obtained by quickly freezing (100 K/s) undegassed solutions ($< 10^{-5}$ M) of 12SB in *n*-tetradecane. Spectra obtained under these conditions have for their sharpest lines bandwidths of < 6 cm⁻¹. Other *n*-alkanes (*n*-undecane through *n*-hexane) also gave well resolved spectra. However, these systems exhibited complicated superpositions of spectra due to the presence of multiple mixed-crystal sites.

B. Spectral measurements

The 12SB/*n*-tetradecane sample was placed in a 4×10 mm rectangular cuvette and quickly frozen by plunging into liquid nitrogen. The cuvette then was transferred to a Janis optical cryostat which maintained the sample in a bath of liquid helium. The sample was excited by a 100 W mercury lamp (Oriel) whose output was filtered by 10 cm of water, a Corning 7-51 filter, and a 365 nm interference filter (Ditric Optics, 10 nm bandpass). Fluorescence was collected at right angles to the exciting light off the front face of the snowy, multicrystalline sample. The emission was filtered (Schott KV-418) and then focused on the slits (200μ) of a 1 m monochromator (Instruments SA). The fluorescence was detected by an EMI 6256S photomultiplier cooled to -20 °C (Products for Research Housing) to minimize dark current. The signal was detected by a Keithly model 610C electrometer whose output was then stored on a Digital Equipment Corporation MINC-11 computer.

Absorption spectra were acquired by fluorescence excitation techniques. Light from a 75 W xenon lamp (Oriel) was filtered by 10 cm of a CuSO₄ solution before entering the 1 m monochromator (slits $\sim 200 \ \mu$). The exiting light was focused on the same 4.2 K sample used in the fluorescence measurements. Emission from the sample's front surface was filtered by a Schott KV-418 and a 480 nm interference filter (Ditric, 10 nm bandpass) before passing into the cooled photomultiplier. The emission filters selected the strong, sharp fluorescence peak at 479.8 nm (see Fig. 2) and discri-



FIG. 2. 4.2 K fluorescence spectrum of 12SB in *n*-tetradecane ($\lambda_{ex} = 365$ nm). Spectrum is corrected for wavelength dependences of the detection system.

minated against light from minor sites. The excitation spectrum was stored on the MINC-11 computer as described above.

The spectra were calibrated by a low pressure xenon lamp and an iron hollow cathode lamp. For the fluorescence spectra the calibrating light was shown on the sample and collected simultaneously with the true emission. Calibration lines bracketing desired fluorescence peaks were fit to a linear dispersion curve which with repeated scans gave the position of emission lines to an accuracy of 0.02–0.03 nm. The excitation spectra were calibrated by alternating excitation scans with scans of the iron lamp. The iron spectrum was detected by placing a second photomultiplier near the exit slit. This procedure gave an uncertainty of 0.03 nm in the location of excitation peaks.

The fluorescence spectrum was corrected for the wavelength dependent efficiencies of the monochromator, photomultiplier, and collection optics. A correction curve was obtained by recording the spectrum of a tungsten lamp which



FIG. 3. 4.2 K fluorescence excitation spectrum (1 ${}^{1}A_{g} \rightarrow 2 {}^{1}A_{g}$) of 12SB in *n*-tetradecane ($\lambda_{em} = 480$ nm). Spectrum is not corrected for instrumental response or scattering effects.

was calibrated (in quanta/nm bandpass) against NBS standards.²⁸ The fluorescence excitation spectrum was not corrected. The multicrystalline nature of our low temperature samples introduces unknown wavelength dependences due to scattering. The expected increase in scattering at shorter wavelengths should counteract the increased output of the xenon lamp at longer wavelengths. The relative spectral intensities (Fig. 3) are thus an approximate but reasonable representation of the transition strengths with the electronic origin being overestimated by no more than a factor of 2.

III. RESULTS

The 4.2 K fluorescence and fluorescence excitation spectra of 12SB are given in Figs. 2 and 3. These spectra can be assigned to $\pi\pi^*$ transitions between states correlating with the 1 ${}^{1}A_{g}^{-}$ (ground) and 2 ${}^{1}A_{g}^{-}$ (lowest excited singlet) states observed for polyene hydrocarbons.^{3,4–12} For 12SB the (0–0) of the lowest energy absorption band is about 50 times weaker than the (0–0) of the strongly allowed ($\epsilon \sim 10^5$ 1 mol cm) absorption at 380 nm ("1 ${}^{1}A_{g}^{-}$ ", \rightarrow "1 ${}^{1}B_{u}^{+}$ "). It thus is both useful and appropriate to retain the C_{2h} symmetry labels. Within the weak transitions ("1 A_{g}^{-} ", \leftarrow "2 A_{g}^{-} ") the electronic origins are neither forbidden nor even weak, relative to other vibronic bands. In this respect, the Schiff base spectra are almost identical to those of polyene hydrocarbons with small distortions (either from substituents or the environment)^{6,8,12} from C_{2h} symmetry.

Polyene hydrocarbons show a considerable decrease in fluorescence efficiency in going from tetraenes to pentaenes to hexaenes.²⁷ For example, high resolution spectra of 2,12dimethyl tridecahexaene (TDH—Fig. 1) only could be obtained by using a combination of laser excitation and considerable signal averaging. The Schiff base (with the same conjugated length as TDH) has a considerably higher (> 10 times) fluorescence yield than its hydrocarbon counterpart, and high signal to noise spectra are readily obtained with more conventional excitation and detection techniques.²⁶

The fluorescence spectrum (Fig. 2) shows many of the features previously noted in the high resolution emissions of polyene hydrocarbons.^{3,4-12} The positions and energies of

TABLE I. Analysis of prominent lines in 4.2 K fluorescence spectrum $(2^{1}A_{s}^{-} \rightarrow 1^{1}A_{s}^{-})$ of 12SB in *n*-tetradecane.

Peak position			
nm (air)	cm ⁻¹ (vacuum)	$\Delta \tilde{\nu}(\mathrm{cm}^{-1})$	Assignment
445.78 ± 0.02 ^a	22 427ª		(0-0)
470.21 ± 0.04	21 261	1166 ± 2.2	ν_1
479.77 ± 0.03	20 838	1589 ± 1.6	v_2
497.4 ₹ ± 0.02	20 096	2331 ± 1.3	$2\nu_1(-1)^{b}$
508.09 ± 0.04	19 676	2751 ± 1.8	$v_1 + v_2(-4)$
518.98 ± 0.03	19 263	3164 ± 1.5	$2\nu_2(-14)$
540.03 ± 0.04	18 512	3915 ± 1.7	$2v_1 + v_2(-6)$
552.30 ± 0.06	18 101	4326 ± 2.2	$v_1 + 2v_2(-18)$

^a Position of origin is average of positions obtained by calibration of emission and absorption (excitation) spectra.

^b Numbers in parentheses indicate anharmonicities in absence of errors in v_1 and v_2 . the strongest vibronic lines are given in Table I. These lines fit the following equation:

$$\tilde{\boldsymbol{v}} = \tilde{\boldsymbol{v}}(0-0) - \tilde{\boldsymbol{m}}\tilde{\boldsymbol{v}}_{S} - \tilde{\boldsymbol{n}}\tilde{\boldsymbol{v}}_{D}, \qquad (1)$$

where v_s and v_D are the frequencies (in cm⁻¹) of the strongest ground state vibrations and where *m* and *n* are integers. For 12SB we have located all bands for which m + n < 3. The pattern given by Eq. (1) also describes the high resolution spectra of other polyenes (2,12-dimethyltridecahexaene,^{6,12} 2,8-dimethyloctatetraene,⁸ and 2,4,6,8,10-dodecapentaenal²⁹), whose molecular structure or solvent environment does not contain a center of inversion. Fluorescence from polyenes which retain the ideal C_{2h} symmetry (2,10-dimethylundecapentaene⁵ and octatetraene^{10,11}) can be summarized by a similar equation. For these molecules, however, the true origins are forbidden or extremely weak, and the emissions are built on "false" origins of low frequency modes (b_u) which mix the 2 ${}^{1}A_{g}$ and 1 ${}^{1}B_{u}$ states (Herzberg-Teller coupling).^{5,10,30}

The fluorescence excitation spectrum $(1 {}^{1}A_{g} \rightarrow 2 {}^{1}A_{g})$ is given in Fig. 3. The vibronic pattern observed is in an approximate mirror image relationship to that of the fluorescence:

$$\tilde{v} = \tilde{v}(0-0) + m\tilde{v}'_{S} + n\tilde{v}'_{D},$$
 (2)

 $\tilde{\nu}'_{s}$ and $\tilde{\nu}'_{D}$ are the excited state counterparts of the ground state frequencies given in Eq. (1). The full development of the excited state combination bands is obscured by the strong absorption into the second excited singlet at 390 nm $(1 {}^{1}A_{g}^{-} \rightarrow 1 {}^{1}B_{u}^{+})$. Nevertheless, the $\sim 3200 \text{ cm}^{-1}$ gap between $1 {}^{1}B_{u}^{+}$ and $2 {}^{1}A_{g}^{-}$ allows an accurate determination of both $\tilde{\nu}'_{s}$ and $\tilde{\nu}'_{D}$.

The qualitative, mirror-image relationship between the emission and absorption spectra can be seen in Fig. 4. This plot of the two spectra on the same cm⁻¹ scale provides a clear comparison of the $1 {}^{1}A_{g}^{-}$ and $2 {}^{1}A_{g}^{-}$ fundamentals. A complete analysis of the spectra is given in Tables I and II. The main conclusions are that in 12SB the carbon-carbon single bond stretching frequency (v_{C}) increases and the dou-



FIG. 4. Comparison of fluorescence and fluorescence excitation spectra of 12SB in 4.2 K *n*-tetradecane. Spectra are plotted against the absolute value of energy (in cm⁻¹) from the origin.

TABLE II. Analysis of prominent lines in 4.2 K fluorescence excitation spectrum $(1 {}^{1}A_{s} \rightarrow 2 {}^{1}A_{s})$ of 12SB in *n*-tetradecane.

Peak position			
nm (air)	cm ⁻¹ (vacuum)	$\Delta \tilde{v} (\mathrm{cm}^{-1})$	Assignment
445.78 ± 0.02 ^a	22 427ª		(00)
422.91 ± 0.03	23 639	1212 ± 2.0	ν_1
417.06 ± 0.02	23 971	1544 ± 1.5	ν_2
399.34 ± 0.03	25 034	2607 ± 2.1	-
397.07 ± 0.03	25 177	2750 + 2.1	$v_1 + v_2$
395.84 ± 0.03	25 320	2893 ± 2.1	
393.25 ± 0.03	25 422	2995 + 2.1	

* Position of origin is average of positions obtained by calibration of absorption (excitation) and emission spectra.

ble bond stretching frequency (v_D) decreases upon electronic excitation. The Schiff base is the first polyene studied which does not show a large increase of v_D in $2 {}^{1}A_{g}^{-}$.

IV. DISCUSSION

The high resolution spectra of 12SB are dominated by a single vibrational mode which can be identified with motion along a symmetric $(a_g) C = C$ stretching coordinate Q_D .¹⁵ The decrease in v_D in 2 ${}^{1}A_g^{-}$ conforms with theoretical expectations that polyene excited states should show decreased C = C bond orders.¹⁵⁻¹⁸ The results for the Schiff base, however, contrast those obtained for several polyene hydrocarbons in which v_D undergoes a substantial *increase* in 2 ${}^{1}A_g^{-}$ (Table III). We thus must consider how a small structural change (as evidenced by similar ground state vibrational frequencies) leads to such a large difference in the 2 ${}^{1}A_g^{-}$ vibronic states.

A. Vibronic interactions in polyene hydrocarbons

The "anomalous" vibronic behavior of the polyene hydrocarbons might be due to the following: (i) Increases in C = C bond orders in $2 {}^{1}A_{g}^{-}$; (ii) mixing of normal modes within $2 {}^{1}A_{g}^{-}$ (Duschinsky effect)^{5,15,31}; (iii) vibronic coupling between $2 {}^{1}A_{g}^{-}$ and other ${}^{1}A_{g}^{-}$ states.

Theoretical studies have indicated that polyene hydrocarbons and Schiff bases should experience substantial decreases in C = C bond orders upon excitation into $2 {}^{1}A_{g}^{-}$.

TABLE II. Analysis of prominent lines in 4.2 K fluorescence excitation spectrum $(1 {}^{1}A_{g} \rightarrow 2 {}^{1}A_{g})$ of 12SB in *n*-tetradecane.

Peak position			
nm (air)	cm ⁻¹ (vacuum)	$\Delta \tilde{\nu} (\mathrm{cm}^{-1})$	Assignment
445.78 ± 0.02*	22 427*		(00)
422.91 ± 0.03	23 639	1212 ± 2.0	\boldsymbol{v}_1
417.06 ± 0.02	23 971	1544 ± 1.5	v_2
399.34 ± 0.03	25 034	2607 ± 2.1	-
397.07 ± 0.03	25 177	2750 ± 2.1	$v_1 + v_2$
395.84 ± 0.03	25 320	2893 ± 2.1	
393.25 ± 0.03	25 422	2995 ± 2.1	

^a Position of origin is average of positions obtained by calibration of absorption (excitation) and emission spectra. Duschinsky effects are implicitly included in the calculations of Lasaga *et al.*¹⁵ and there is no support for effects of the magnitude needed for a > 200 cm⁻¹ increase in an excited state vibrational frequency. We previously have shown, however, that vibronic mixing between $1 {}^{1}A_{g}^{-}$ and $2 {}^{1}A_{g}^{-}$ could well account for the hydrocarbon frequencies.¹²

Vibronic coupling between $1 {}^{1}A_{g}^{-}$ and $2 {}^{1}A_{g}^{-}$ via Q_{D} leads to a reduction in quadratic force constant in $1 {}^{1}A_{g}^{-}$ 12,32,33 .

$$k_{D} = k_{D}^{0} - \frac{2|\langle \Psi_{1A_{g}} - |\partial H / \partial Q_{D} | \Psi_{2A_{g}} \rangle|^{2}}{(E_{2A_{g}} - E_{1A_{g}})}, \qquad (3)$$

where k_D^{o} is the ground state force constant in the absence of vibronic mixing. $\Psi_{1A_g^{-}}$ and $\Psi_{2A_g^{-}}$ are the crude adiabatic functions defined previously.^{12,34} A similar expression gives the increase in force constant in $2 {}^{1}A_g^{-}$ and a small amount of mixing (<1%) can account for the observed frequencies.¹²

This model is similar to Mikami and Ito's treatment^{19,20} of vibronic mixing between the ground and first excited states in benzene²¹⁻²³ and naphthalene.^{20,24,25} Two photon excitation spectra have shown that in benzene v_{14} (b_{2u}) increases from 1309 cm⁻¹ in the electronic ground state (${}^{1}A_{1g}$) to 1566 cm⁻¹ in the lowest excited singlet (${}^{1}B_{2u}$). Naphthalene's v_{21} (b_{2u}) shows a similar increase from 1361 cm⁻¹ in ${}^{1}A_{g}$ to 1535 cm⁻¹ in ${}^{1}B_{2u}$. These modes, like v_{D} in the polyenes, primarily involve bond alternating carbon-carbon stretches and completely dominate the two-photon vibronic intensities.

Mikami and Ito have suggested that vibronic interactions with the ground state are responsible for the anomalous excited state frequency increases in the aromatics. There is supporting evidence that the ground states frequencies of v_{14} (benzene) and v_{21} (naphthalene) are unusually low.^{35,36} These frequencies are uniquely overestimated by conventional (Urey–Bradley) force field calculations and can only be accounted for by the addition of bond alternating, Kekule' structures.^{35,36}

The apparent dominance of v_{21} in mixing ${}^{1}A_{g}^{-}$ and ${}^{1}B_{2u}^{-}$ in naphthalene can be attributed to the large overlap between the normal mode and the ${}^{1}A_{g}^{-} \leftrightarrow {}^{1}B_{2u}^{-}$ transition density.²⁰ This idea can be extended to the polyenes by rewriting the matrix element in Eq. (3):

$$\langle \Psi_{1A_{g}^{-}} | \partial H / \partial Q_{D} | \Psi_{2A_{g}^{-}} \rangle = \int \rho(1A_{g}^{-} \leftrightarrow 2A_{g}^{-}) \partial H / \partial Q_{D} d\tau. (4)$$

We thus expect strong vibronic interactions for modes in which ρ and $\partial H / \partial Q_D$ ($\propto \Sigma_{\text{bonds}} \partial R_{cc} / \partial Q_D$ where R_{cc} is a bond length²⁰) share the same topology.

The implications of Eq. (4) can be explored with octatetraene, a model polyene for which reliable electronic and vibrational wave functions now are available. The electronic functions used are based on the calculations of Schulten *et al.* which include all doubly excited configurations within the PPP-SCF framework.^{3,16,17}

$$\Psi(1^{1}A_{g}^{-}) = \Psi_{1}^{2}\Psi_{2}^{2}\Psi_{3}^{2}\Psi_{4}^{2}, \qquad (5a)$$

$$\Psi(2^{1}A_{g}^{-}) = 0.43 \ \Psi_{1}^{2}\Psi_{2}^{2}\Psi_{3}^{2}(\Psi_{4}^{1}\Psi_{6}^{1} - \Psi_{3}^{1}\Psi_{5}^{1}) + 0.59 \ \Psi_{1}^{2}\Psi_{2}^{2}\Psi_{3}^{2}\Psi_{5}^{2},$$
(5b)

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TABLE IV. Comparison of transition densities and normal mode components along the carbon-carbon bonds in octatetraene.

<u> </u>	Bond			
	C_1C_2	C_2C_3	<i>C</i> ₃ <i>C</i> ₄	C_4C_5
$\frac{1}{\rho(1^{-1}A_{g}^{-}\leftrightarrow 2^{-1}A_{g}^{-})^{a}}$	- 0.145	+ 0.235	- 0.282	+ 0.381
$Q_{CC}(1^{-1}A_{R}^{-})^{b}$	-0.227	+ 0.130	- 0.120	- 0.059
$Q_{cc}(2 A_{g}^{-})^{b}$	- 0.224	+ 0.151	- 0.026	- 0.051

^a Transition densities calculated from wave functions given by Schulten *et al.* (Ref. 3) (see the text).

^b CC internal coordinate contributions to Q_D from Lasaga et al. (Ref. 15), Table XII. $Q_{CC} \propto \partial R_{CC} / \partial Q_D$ where R_{CC} is the length of the CC bond and Q_D is the normal coordinate (Ref. 19).

where Ψ_i^n denotes *n* electrons in the *i*th SCF MO. The functions given in Eq. (5) do not include small contributions from other configurations. These omissions should not change our conclusions. The vibrational wave functions are those of Lasaga *et al.*¹⁵ and are derived from potential surfaces constructed by the double CI methods mentioned above. The comparison of the $1 {}^{1}A_{g}^{-} \leftrightarrow 2 {}^{1}A_{g}^{-}$ transition density and the CC internal coordinate contributions to Lasaga's highest frequency $\nu_D(A_g)$ mode is given in Table IV.

For octatetraene the transition density is largest in the central CC bond whereas the largest contributions to Q_p (and thus to $\partial H / \partial Q_D$) come from the terminal CC bonds. Otherwise the bond alternating pattern in Q_D mimics that of ρ . We thus could expect effective vibronic coupling (and large Franck-Condon factors) for vibronic levels associated with Q_D . In octate trace $\rho(1 A_g^- \leftrightarrow 2 A_g^-)$ has modes on all carbon atoms with the first nonvanishing terms involving two-center, nearest-neighbor elements. This is also the case for the lowest energy transitions in benzene and naphthalene and can be shown to be common to electronic transitions involving states of the same pseudoparity ($-\leftrightarrow$ - or + \leftrightarrow +).³⁷⁻³⁹ These parallels as well as the similar, bond alternating character of the active modes lead to the conclusion that the aromatic and polyene hydrocarbons share a common mechanism for vibronic interactions.

B. Vibronic interactions in a polyene Schiff base

In extending the vibronic coupling model to 12SB we cannot use aza-aromatics (e.g., pyridine or pyrazine) as guides since their lowest excited singlets are invariably ${}^{1}n\pi^{*}$.^{40,41} Electronic transitions to these states do not involve modes correlating with ν_{14} (benzene) or ν_{21} (naphthalene). Vibronic coupling with ground states may well be important (ν_{14} in pyridine still requires Kekule' type terms to reproduce its low, benzene-like frequency⁴²) but the electronic spectra are dominated by other effects.^{40,43}

The lowest energy $(\pi\pi^*)$ transition density $[\rho(1 {}^{1}A_{g} \rightarrow 2 {}^{1}A_{g})]$ and Q_{D} for 12SB, however, should be quite similar to those of comparable polyene hydrocarbons. This is manifested by the almost identical vibronic intensities in high resolution fluorescence spectra^{6,12} and the small differences in ground state vibrational frequencies ($v_{D} = 1589$ cm⁻¹ in 12SB vs 1576 cm⁻¹ in TDH). $1 {}^{1}A_{g}$ and $2 {}^{1}A_{g}$ in 12SB thus should continue to interact via Q_{D} by the mecha-

nism discussed above [Eq. (4), Table IV]. For v_D to decrease its frequency in $2 {}^{1}A_{g}^{-}$ (1544 cm⁻¹ in 12SB vs 1779 cm⁻¹ in TDH) requires additional interactions between $2 {}^{1}A_{g}^{-}$ and higher lying electronic states. These couplings would lower k_D in $2 {}^{1}A_{g}^{-}$ [Eq. (3)] while having a considerably smaller effect on k_D in $1 {}^{1}A_{g}^{-}$, due to the larger energy denominator.

The transformation of a polyene hydrocarbon into a Schiff base both reduces the molecular symmetry and gives rise to $n\pi^*$ states. Reduction in symmetry will modify transition densities between $2 {}^{1}A_{g}^{-}$ and other ${}^{1}\pi\pi^*$ states and, along with shifts in ${}^{1}\pi\pi^*$ energy levels, could activate ${}^{1}\pi\pi^*/{}^{1}\pi\pi^*$ vibronic interactions not experienced by hydrocarbons. However, the limited data now available suggests that interactions between $2 {}^{1}A_{g}^{-}$ and closely lying ${}^{1}n\pi^*$ states are the major difference between the vibronic states of 12SB and those of its hydrocarbon counterparts.

This conclusion is based on a comparison of v_D in 12SB, TDH, and 2,4,6,8,10-dodecapentaenal, the only other hetero-substituted polyene for which high resolution vibronic information is available.²⁹ The dodecapentaenal has a v_D $(1 {}^{1}A_{8})$ of 1575 cm⁻¹ (cf. 1589 cm⁻¹ for 12SB and 1576 cm⁻¹ for TDH) and v_D (2 ¹ A_g^{-}) of 1636 cm⁻¹ (cf. 1544 cm⁻¹ for 12SB and 1779 cm⁻¹ for TDH). If the primary reason for the lowering of v_D (2 ${}^{1}A_{g}^{-}$) in hetero-substituted polyenes were the reduction in symmetry, the oxygen would have a larger effect than the less electronegative nitrogen. We propose, therefore, that the Schiff base has a ${}^{1}n\pi^{*}$ state which lies close to (but above) $2 {}^{1}A_{g}^{-}$. Coupling between these two states reduces $v_D (2 {}^{1}A_{g}^{-})$ well below the frequencies seen in the aldehyde or the hydrocarbon. ${}^{1}n\pi^{*}/{}^{1}\pi\pi^{*}$ interactions are well known for aza-aromatics.³³ Indeed, the matrix elements linking $n\pi^*$ and $\pi\pi^*$ states are generally larger than those between $\pi\pi^*$ states.⁴⁴

Dodecapentaenal also has low energy ${}^{1}n\pi^{*}$ states. The fact that it does not fluoresce in carefully dried solvents indicates that free dodecapentaenal has ${}^{1}n\pi^{*} < 2 {}^{1}A_{g}^{-}$ with ${}^{1}n\pi^{*}$ undergoing substantial blue shifts in hydrogen-bonding environments.²⁹ The high resolution fluorescence spectra (and ν'_{D} s given above) are thus of hydrogen-bonded dodecapentaenal with ${}^{1}n\pi^{*} > 2 {}^{1}A_{g}^{-}$ and also with ${}^{1}n\pi^{*}$ at higher energies than the corresponding ${}^{1}n\pi^{*}$ states in free 12SB. The hydrogen-bonded aldehyde does not experience the strong ${}^{1}n\pi^{*}/{}^{1}\pi\pi^{*}$ couplings of the Schiff base and is still dominated by vibronic interactions with the ground state. This suggests that ν_{D} (2 ${}^{1}A_{g}^{-}$) in 12SB should increase in the presence of hydrogen bonders.

V. SUMMARY

The polyene Schiff base 12SB exhibits "normal" vibronic behavior, i.e., v_D decreases (by 45 cm⁻¹) upon excitation into 2 ${}^{1}A_{g}^{-}$. This contrasts the large increases observed in all other polyenes for which high resolution spectra are now available. For example, 2,12-tridecahexaene (TDH—Fig. 1) shows a 203 cm⁻¹ increase in v_D upon electronic excitation. The ~250 cm⁻¹ difference between 12SB and TDH in 2 ${}^{1}A_{g}^{-}$ can be explained by the vibronic coupling model previously applied to aromatic and polyene hydrocarbons. The two prototypes have much in common:

(i) Their electronic spectra (one photon for polyenes, two photon for aromatics) are dominated by carbon-carbon stretching vibrations $(Q'_{D}s)$ of bond alternating character.

(ii) The electronic states involved are connected by pseudoparity forbidden $(-\leftrightarrow -)$ transition densities (ρ 's) with modes through every carbon atom.

(iii) The topological maps of the transition densities are remarkably similar to the maps of the dominant vibrational modes.

These parallels support a common mechanism for vibronic coupling in the two molecular systems.

For all polyenes studied except 12SB, $2 {}^{1}A_{g}^{-}$ interacts most strongly with the electronic ground state $(1 {}^{1}A_{g}^{-})$. This scheme accounts for the high $v'_{D} \sin 2 {}^{1}A_{g}^{-}$ and suggests that (as for v_{14} in benzene and v_{21} in naphthalene) that the $v'_{D} \sin 1 {}^{1}A_{g}^{-}$ are anomalously low. The normal Schiff base $2 {}^{1}A_{g}^{-}v'_{D}$ s are then viewed as the consequence of additional vibronic interactions between $2 {}^{1}A_{g}^{-}$ and higher lying electronic states. A comparison of 12SB with the more polar, but hydrogen bonded dodecapentaenal indicates that $2 {}^{1}A_{g}^{-}/$ ${}^{1}n\pi^{*}$ couplings dominate. High resolution studies of hydrogen bonded 12SB would be useful in understanding these unusual vibrational effects.

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