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Absorption and emission of 2,12-dimethyltridecahexaene

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We have obtained well resolved optical spectra of a simple, methyl substituted hexaene at 4.2 K. These spectra provide detailed information on the vibronic levels associated with the ground (1^1A_g) and first excited (2^1A_g) singlet electronic states. The strongest vibronic feature, due to a totally symmetric CC double bond stretch, shifts from 1576 cm^{-1} in the 1^1A_g state to 1779 cm^{-1} in the 2^1A_g state. This shift, not accounted for by current theoretical descriptions of polyene electronic states at the crude adiabatic level, may be rationalized as a manifestation of vibronic coupling between the ground and first excited singlet states.

I. INTRODUCTION

Increased understanding of linear polyene electronic states has been gained from both low and high resolution optical spectra. Low resolution experiments have helped in establishing the relative ordering of the lowest lying electronic levels¹⁻⁵ and have also provided information on how the energies of the electronic states vary with the length of the conjugated chain.^{3,6} High resolution experiments have been crucial in establishing state assignments by revealing patterns of vibronic intensities in both one and two photon absorption spectra.⁷⁻¹⁴

High resolution work on 2, 10-dimethylundecapentaene demonstrated the symmetry forbidden nature of the lowest energy singlet state.⁷ Both absorption and fluorescence spectra were found to be built on false origins as expected for an electronically forbidden transition. Similar effects were later observed for dimethyloctatetraene.⁸ An extremely clear demonstration of the dipole forbidden nature of the transition from the ground state to the first excited singlet state was recently presented for octatetraene.^{9,10} In these experiments octatetraene was put in a crystal site having inversion symmetry. The one photon spectra for the lowest energy singlet transition showed a rigorously forbidden electronic origin and the two photon absorption spectrum showed a strongly allowed origin. This observation plus the observed polarization behavior of the two photon absorption established that both the ground and first excited singlet states should be labeled 1^1A_g .

High resolution experiments have also revealed details of the ground state (1^1A_g) and lowest excited state (2^1A_g) vibrational modes.^{1,7-14} Absorption spectra of 2, 10-dimethylundecapentaene showed a prominent vibronic feature 1737 cm^{-1} above the electronic origin.⁷ The intensity of this band suggested that it was the counterpart of the 1598 cm^{-1} mode which dominates the fluorescence and which can be safely assigned to a CC double bond stretch. However, in these experiments, the 3300 cm^{-1} gap between the 2^1A_g and the higher lying 1^1B_u state

prevented a look at the full vibronic development and thus left open the possibility that the 1737 cm^{-1} frequency was not a symmetric double bond stretch but rather was some combination of lower frequency modes or a high frequency promoting mode (false origin). Subsequent high resolution spectra of octatetraene showed conclusively that the C=C mode was in fact higher in frequency (1605 cm^{-1} in 1^1A_g , 1754 cm^{-1} in 2^1A_g) in the first excited singlet state.¹⁰ Here we report vibrationally resolved absorption and emission spectra for the six double bond polyene 2, 12-dimethyltridecahexaene. For this polyene, the 4000 cm^{-1} gap between the 2^1A_g state and the dipole allowed 1^1B_u state allows overtones of the C=C stretch to be observed in one photon studies. These spectra reinforce the conclusion that in linear polyenes the double bond stretching frequency increases from $1575\text{--}1600\text{ cm}^{-1}$ in the ground state to $1730\text{--}1780\text{ cm}^{-1}$ in the first excited singlet state. Such frequency increases may be attributed to vibronic coupling between ground and excited states.^{13,15-17} The application of this model to the polyene case is also presented.

II. EXPERIMENTAL

A. Samples

2, 12-dimethyltridecahexaene (Fig. 1) was a gift from Professor Ted Sorensen, who has described its preparation and properties.¹⁸ Our sample was purified by column chromatography using Woelm alumina, activity grade I. The all-*trans*-hexaene was eluted with petroleum ether, benzene, and diethyl ether. An unidentified impurity preceded the desired hexaene but was cleanly separated from it. Absorption spectra of the hexaene from the leading and trailing fractions agreed with those given for the all-*trans* isomer¹⁸ and indicated a homogeneous sample. Small amounts of *cis* impurities may be present but these do not appear in the high resolution spectra presented here. After chromatography, the solvents were evaporated under vacuum and the hexaene was dissolved in small amounts of normal alkanes. The sample solutions were degassed by repeated freeze-pump-thaw cycles and were then sealed off under vacuum. Dilute solutions stored in the dark at temperatures below -15°C appear to be stable over a time span of several months. Spectral grade solvents were obtained from Aldrich and were used without further purification.

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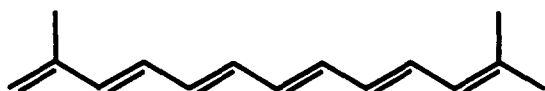


FIG. 1. 2,12-dimethyltridecahexaene.

B. Spectroscopy

High resolution optical spectra were obtained by freezing dilute ($10\ \mu\text{M}$) *n*-undecane solutions of the hexaene with liquid helium. As described previously¹², sharp spectra were obtained from both quickly frozen ($100\ \text{K/s}$) and slowly frozen ($1\ \text{K/s}$) solutions. The spectra presented here are from quickly frozen samples which typically show well resolved peaks on top of a broad continuous background. The background may be due to aggregates and/or molecules not in substitutional sites. The narrowest linewidths ($\text{FWHM} = 3\ \text{cm}^{-1}$) were not reduced by lowering the bath temperature from 4.2 to $1.5\ \text{K}$.

Fluorescence spectra were recorded with a Jarrell-Ash 1m Czerny-Turner monochromator utilizing an 1180 groove/mm grating operating in second order. Typical slit widths of 100 – $200\ \mu\text{m}$ provided an instrumental resolution of 2 – $3\ \text{cm}^{-1}$. The emission was excited by 1 – $2\ \text{mW}$ of the UV output (364 and $351\ \text{nm}$) from a Spectra Physics model 171-05 argon-ion laser, filtered by a Corning 9863 glass filter. Fluorescence perpendicular to the exciting light was collected and passed through a Corning 3389 filter before entering the monochromator. The light intensity was measured with an EMI 6256B photomultiplier and the spectra were collected digitally as described below. The emission spectrum presented here is not corrected for the relative sensitivities of the monochromator and photomultiplier.

The absorption spectra were obtained using fluorescence excitation techniques. This was required by the

rather low oscillator strengths of the vibronically induced 1^1A_g – 2^1A_g transition. By monitoring certain sharp features in emission, we were able to greatly reduce the contributions from the broad background. The fluorescence excitation spectra establish a strong connection between the weak absorption and the sharp emission and provide proof that these two transitions arise from the same molecule in a single site.

Excitation spectra were obtained by exciting the sample with a tunable dye laser and monitoring the fluorescence with the 1m monochromator. A schematic of the experimental arrangement is given in Fig. 2. The output of a home built nitrogen laser ($10\ \text{n}$ pulse width, $500\ \text{kW}$ peak power) was used to pump a Moletron DL-400 dye laser. The output of the dye laser was monitored by a fluorescence quantum counter (rhodamine B in ethylene glycol), the output from which served as the *B* input of a PAR model 122 divider. For most excitation scans, the origin of emission ($459.0\ \text{nm}$) was monitored. For excitation scans near the origin, the fluorescence was detected on the prominent line at $494.8\ \text{nm}$. The emission intensity was measured with an EMI 6256B photomultiplier and a Keithly 610C electrometer. This signal then entered the *A* channel of the PAR divider. The *A/B* output of the divider thus represented the true excitation spectrum corrected for the intensity variations in the tunable dye laser.

Because of the narrow band detection and rather low fluorescence quantum yield, signal averaging was employed. As shown in Fig. 2, the detection system was triggered by the dye laser pulse. After a $50\ \text{m}$ delay, the divider output (time constant = $1\ \text{s}$) was sampled for $120\ \text{m}$ and the value was stored on the Hewlett-Packard 9810 calculator. Ten to 20 laser shots were then averaged and this value, along with its standard deviation, was stored on a PDP-10 computer for later processing. The dye laser was stepped $0.2\ \text{\AA}$

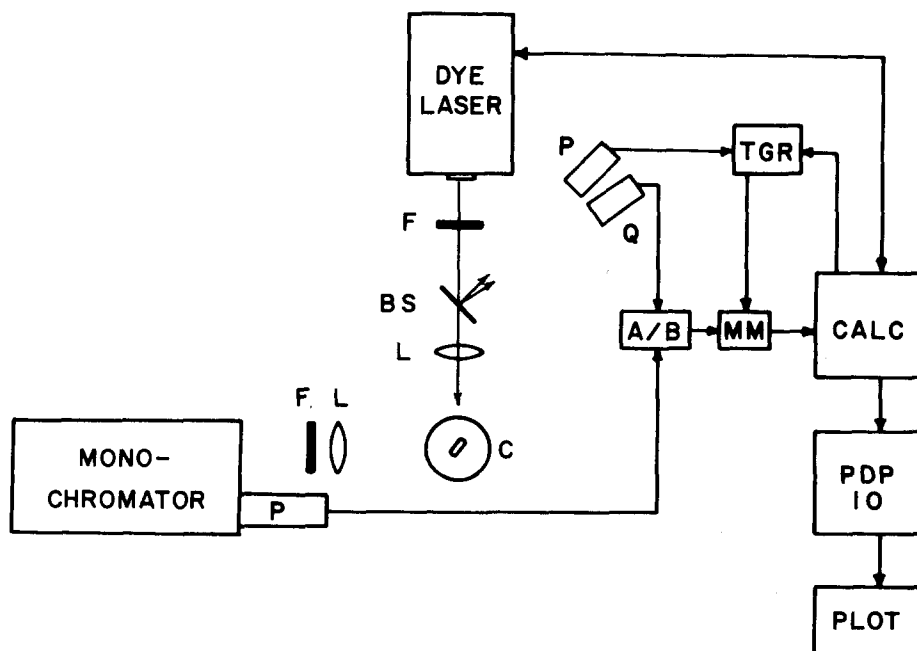


FIG. 2. Apparatus used to obtain the fluorescence excitation spectrum. F are glass filters; L are quartz lenses; BS is a beam splitter; P are photomultipliers; Q is a rhodamine quantum counter; C is the liquid helium cryostat and sample; A/B is an analog divider; MM is an externally triggered digital voltmeter; CALC is a Hewlett-Packard 9810A calculator; and TGR is a synchronization circuit for the voltmeter which is armed by the calculator and triggered by the dye laser pulse.

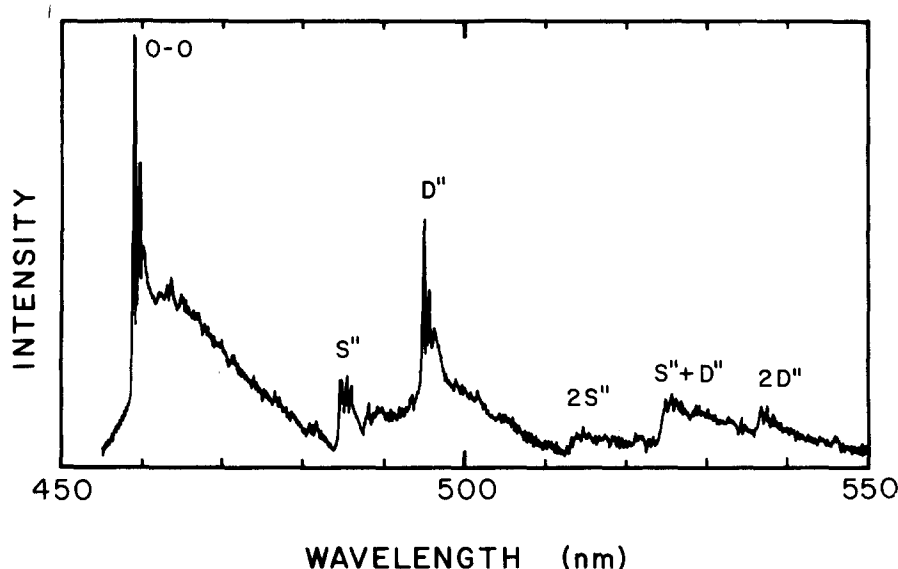


FIG. 3. The 4.2 K fluorescence spectrum of 2,12-dimethyltridecahexaene in a quickly grown *n*-undecane polycrystal. The emission was excited with the UV lines of an argon-ion laser. The intensity has not been corrected for instrumental response.

and the process repeated to record the complete excitation spectrum.

The width of the excitation spectrum required the use of five dyes as follows: 385–405 nm, BDQ in DMF; 400–417 nm, diphenyl stilbene in DMF; 415–435 nm, bis-MSB in dioxane; 428–444 nm, coumarin 440 in ethanol; 443–462 nm, coumarin 460 in ethanol. The scans were spliced together by using regions of overlap to scale the spectra relative to each other. The region from 452–456 nm has not been included because of experimental difficulties in this spectral region. Given the errors propagated by linking five separate scans together, the relative intensities presented might be in error by as much as a factor of 2 between the ends of the spectrum. In addition, since we were working with highly absorbing samples, the relationship between our excitation intensities and relative extinction coefficients is not necessarily linear. The excitation spectra presented thus give only an approximate representation of the actual intensities. Nevertheless, the general rise in absorption intensity in going toward shorter wavelengths is a real effect, and we estimate that the 1^1A_g – 2^1A_g origin is at least 200 times weaker than the 1^1A_g – 1^1B_u origin.

The emission and excitation data were treated by mild smoothing techniques. Both fluorescence and fluorescence excitation spectra were calibrated by superimposing the line spectrum of a Fe–Ne hollow cathode lamp on the polyene spectra.

III. RESULTS

The 4.2 K fluorescence and fluorescence excitation spectra are given in Figs. 3 and 4, respectively. These spectra can be assigned to transitions between the ground state (1^1A_g) and lowest excited singlet state (2^1A_g) by the chain of experimental results discussed above. The spectra presented here were obtained from a quickly frozen *n*-undecane sample. Under these conditions, the polyene apparently distorts and loses its center of symmetry. As a result, the forbidden 1^1A_g – 2^1A_g transitions

have weakly allowed origins. Under more symmetric environmental constraints, such as those realized in slowly grown undecane crystals, the hexaene exhibits much weaker origins with the observed progressions being built on false origins.¹² For simplicity, we have chosen to present spectra of the allowed type. The vibronically induced spectra, however, give the same overall conclusions concerning changes in vibrational frequencies between the two states.

A strong dependence of the fluorescence quantum yield on the length of the conjugated polyene chain has been noted.⁶ Among the simple unsubstituted polyenes, octatetraene is roughly 100 times more efficient in fluorescence than dodecahexaene. 2, 12-dimethyltridecahexaene also has a very small fluorescence yield. The sharp line nature at 4.2 K reduced the seriousness of this problem somewhat, particularly for the emission spectra which can be pumped by the UV laser lines. The narrow band detection of the excitation spectrum, however, required considerable signal averaging.

The fluorescence spectrum (Fig. 3) shows many of the features noted before in the high resolution spectra of 2, 10-dimethylundecapentaene,⁷ 2, 8-dimethyloctatetraene,¹⁴ and octatetraene.¹⁰ The wave numbers for the most prominent features are listed in Table I. The bulk of the fluorescence intensity can be summarized by the following expression:

$$\nu = \nu(0-0) - m\nu_{S''} - n\nu_{D''} \quad (1)$$

where $\nu_{S''}$ represents ground state modes involving CC single bond stretches and $\nu_{D''}$ represents a dominant ground state mode which can be assigned to a CC double bond stretch. The general pattern expressed by Eq. (1) is one of the signatures of polyene spectroscopy.

The fluorescence excitation spectrum bears many similarities to the fluorescence spectrum. In Fig. 4 we have converted both spectra to a wave number scale (origin = 0 cm^{-1}) and plotted the mirror image of the emission next to the excitation to aid in the comparison of the vibronic levels associated with the 1^1A_g and 2^1A_g

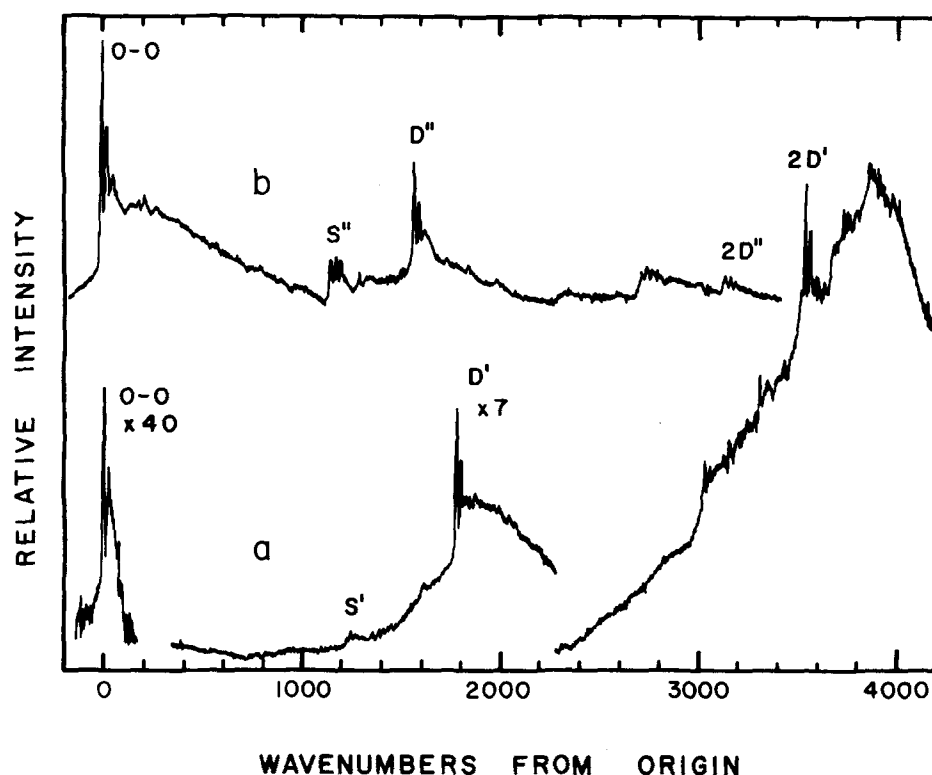


FIG. 4. The 4.2 K fluorescence excitation (a) and fluorescence (b) spectra of 2,12-dimethyltridecahexaene in a quickly grown *n*-undecane polycrystal. Both spectra have been plotted against the absolute value of energy from the origin. The spectra have not been corrected for instrumental response or concentration effects.

states. Equation (1) then serves as a guide for summarizing the data presented in Table II. Again, the spectrum seems to follow a simple pattern:

$$\nu = \nu(0-0) + m\nu_{S'} + n\nu_{D'} \quad (2)$$

where $\nu_{S'}$ and $\nu_{D'}$ are the frequencies of excited state vibrational modes.

IV. DISCUSSION

The emission and excitation spectra exhibit the qualitative similarities expressed by Eqs. (1) and (2). Their approximate mirror image is useful in comparing the

excited state vibrational modes with those of the ground state. The ground state modes are rather well understood since, in addition to optical experiments, a considerable amount of Raman and resonance Raman work is now available on the polyene family. We wish to emphasize the following:

(1). $\nu_{D'}$ plays the same role in absorption as $\nu_{D''}$ plays in emission.

(2) $\nu_{D'}$ has a frequency 200 cm^{-1} larger than $\nu_{D''}$.

From previous vibrational studies we can assign $\nu_{D''}$ to a totally symmetric CC double bond stretch.¹⁹ Because of the similarity between emission and absorption,

TABLE I. Prominent peaks in the 4.2 K fluorescence of 2,12-dimethyltridecahexaene in *n*-undecane.

Measured line position and relative intensity (cm^{-1})	Shift from origin (cm^{-1})	Assignment ^a
21 738 ± 2 (s)	0	0-0
21 763 ± 2 (s)	25	phonon
20 636 ± 1 (m)	1152	S_1''
20 608 ± 2 (m)	1180	S_2''
20 585 ± 2 (m)	1203	S_3''
20 212 ± 1 (s)	1576	D''
20 187 ± 1 (s)	1601	D'' + phonon
19 472 ± 10 (m)	2316	$2S_1''$
19 063 ± 5 (m)	2725	$S_1'' + D''$
18 642 ± 5 (m)	3146	$2D''$

^a S_1 , S_2 , and S_3 refer to a group of vibrational modes which contain large contributions of CC single bond stretching motions. D refers to a single predominant CC double bond stretching mode.

TABLE II. Prominent peaks in the 4.2 K fluorescence excitation spectrum of 2,12-dimethyltridecahexaene in *n*-undecane.

Measured line position and relative intensity (cm^{-1})	Shift from origin (cm^{-1})	Assignment
21 788 ± 2 (vw)	0	0-0
21 812 ± 4 (vw)	24	phonon
23 040 ± 4 (w)	1252	S_1''
23 065 ± 4 (m)	1277	S_2''
23 255 ± 4 (w)	1467	S_3''
23 404 ± 5 (w)	1616	
23 567 ± 1 (s)	1779	D''
23 593 ± 3 (s)	1805	D'' + phonon
24 601 ± 3 (m)	2813	
24 817 ± 3 (m)	3029	$D'' + S_1''$
24 841 ± 3 (m)	3053	$D'' + S_1''$ + phonon
25 096 ± 3 (m)	3308	
25 321 ± 1 (s)	3533	$2D''$
25 348 ± 1 (s)	3560	$2D''$ + phonon

we would like to assign ν_D to the same kind of normal coordinate. The strong feature at $2\nu_D$ eliminates the possibility that the 1779 cm^{-1} band is a high frequency promoting mode. In addition, this feature cannot be a combination of lower frequency modes whose fundamentals are not seen, such as the overtone of an antisymmetric vibration, because the observed intensity of the band would require a physically unreasonable frequency shift between the 1^1A_g and 2^1A_g states. ν_D is thus a symmetric fundamental and the Franck-Condon factors associated with this mode reflect changes in bond distances when the polyene changes electronic states.

The general similarities between the types of vibrational modes coupled to emission and absorption are in contrast to the observed frequencies. Simple theoretical considerations would indicate that the CC single bond orders should *increase* and the CC double bond orders should *decrease* in any polyene excited state.²⁰ Under the assumption that the electronic states do not depend strongly on displacement of the nuclei from the ground state equilibrium position, these changes would be accompanied by a parallel *increase* in the single bond stretching frequency and a *decrease* in the double bond stretching frequency. Our experiments show the expected behavior for ν_S but the wrong behavior for ν_D . Similar results were suggested by previous studies of diphenyloctatetraene,¹³ 2, 10-dimethylundecapentaene,⁷ 2, 8-dimethyllocatetraene,¹⁴ and octatetraene¹⁰ so the increase appears to be a general feature of polyene spectroscopy.

Possible explanations include the following:

- a real increase in local CC double bond order in 2^1A_g ;
- substantial mixing of normal modes in 2^1A_g ;
- vibronic coupling of the 2^1A_g and 1^1A_g electronic states.

The simplest explanation would be that there are C=C bonds in the 2^1A_g state with unusually high π bond orders (and also, therefore, some C=C bonds that are especially weak). In such a case, we would expect some anomalously low frequencies to be strongly coupled to the transition. There is no evidence for such modes in the spectra.

Substantial mixing of normal modes in the excited state (Duschinsky effect) could also account for the increase in ν_D . However, this type of explanation would require either the appearance of extra bands in the absorption spectrum or a single bond mode that decreased in frequency. Neither of these are observed. We feel that vibronic mixing of crude adiabatic 1^1A_g and 2^1A_g is the best explanation for the increase in the double bond frequency (for symmetric modes the mixing of A_g with B_u will not contribute).

At the crude adiabatic level,²¹ the electronic states of a polyene are given by

$$[T_e + U(x, 0) - \epsilon_i^0] \psi_i^0(x) = 0 \quad (3)$$

and the vibrational states are given by

$$[T_N + \epsilon_i^0 + \langle \psi_i^0 | U(x, Q) - U(x, 0) | \psi_i^0 \rangle - E_{it}^{CA}] \chi_{it}^{CA}(Q) = 0 \quad (4)$$

T_e and T_N are the kinetic energy operators for electrons and nuclei, respectively; $U(x, Q)$ is the total electronic-nuclear coulomb potential; x represents the electron coordinates; and Q represents mass weighted normal coordinates so that $Q=0$ is the ground state equilibrium geometry. ϵ_i^0 is the crude adiabatic electronic energy and E_{it}^{CA} is the total vibronic energy of the state $\psi_i^0(x) \chi_{it}^{CA}(Q)$. In what follows, we will restrict ourselves to two electronic states ($\psi_0^0 = 1^1A_g$; $\psi_1^0 = 2^1A_g$) and a single symmetric vibration which has the same normal coordinate Q_D in both states. For small displacements of the nuclei, we may use the approximation

$$U(x, Q) - U(x, 0) = [\partial U(x, 0) / \partial Q_D] Q_D + \frac{1}{2} [\partial^2 U(x, 0) / \partial Q_D^2] Q_D^2 \quad (5)$$

Equation (4) then describes a harmonic oscillator with the force constants of V_{00}^{DD} in the ground state and V_{11}^{DD} in the excited state, where

$$V_{ij}^{DD} = \langle \psi_i^0 | [\partial^2 U(x, 0) / \partial Q_D^2] | \psi_j^0 \rangle \quad (6)$$

Based on the bond order arguments given above, we expect $V_{00}^{DD} > V_{11}^{DD}$.

In developing more realistic electronic functions, we would like to solve the Born-Oppenheimer problem

$$[T_e + U(x, Q) - \epsilon_i(Q)] \Psi_i(x, Q) = 0 \quad (7)$$

$$[T_N + \epsilon_i(Q) - E_{it}^{BO}] \chi_{it}^{BO}(Q) = 0 \quad (8)$$

Using the crude adiabatic functions defined by Eq. (3) as a basis set, the Hamiltonian matrix for Eq. (7) is given by

$$h_{ij}(Q) = \langle \psi_i^0 | T_e + U(x, Q) | \psi_j^0 \rangle = \delta_{ij} \epsilon_i^0 + V_{ij}^{DD} Q_D + \frac{1}{2} V_{ij}^{DD} Q_D^2 \quad (9)$$

where $V_{ij}^{DD} = \langle \psi_i^0 | [\partial^2 U(x, 0) / \partial Q_D^2] | \psi_j^0 \rangle$. Note that $V_{00}^{DD} = 0$ by our definition of Q_D . Diagonalizing the 2×2 matrix (9), we get the electronic energies

$$\epsilon_{0,1}(Q) = \frac{1}{2} (h_{11} + h_{00}) \mp \left[\frac{1}{4} (h_{11} - h_{00})^2 + h_{01}^2 \right]^{1/2} \quad (10)$$

The series expansions for Eq. (10) truncated at the quadratic terms are

$$\epsilon_0(Q) = \epsilon_0^0 + \frac{1}{2} [V_{00}^{DD} - 2V_{01}^{DD}/(\epsilon_1^0 - \epsilon_0^0)] Q_D^2 \quad (11a)$$

and

$$\epsilon_1(Q) = \epsilon_1^0 + V_{11}^{DD} Q_D + \frac{1}{2} [V_{11}^{DD} + 2V_{01}^{DD}/(\epsilon_1^0 - \epsilon_0^0)] Q_D^2 \quad (11b)$$

Thus, Eq. (8) describes an oscillator whose force constant is *increased* in the excited state and *decreased* in the ground state relative to what would have been predicted at the crude adiabatic level. Similar effects have been noted to account for the two photon spectra of benzene and naphthalene.¹⁵⁻¹⁷ As is apparent in Eqs. (11), mixing with higher states would reduce the vibrational frequency in the excited A_g state.

Using the observed values of ν_D and assuming $V_{00}^{DD} = (3.24 \times 10^{14} \text{ s}^{-1})^2 \sim [(2\pi)(1720 \text{ cm}^{-1})]^2$, $V_{11}^{DD} = (3.09 \times 10^{14} \text{ s}^{-1})^2 \sim [(2\pi)(1640 \text{ cm}^{-1})]^2$, and $\epsilon_1^0 - \epsilon_0^0 = 4.66 \times 10^{-12} \text{ erg} \sim 23500 \text{ cm}^{-1}$, the value of the vibronic coupling constant can be determined from Eqs. (11). We find $V_{01}^{DD} = 1.98 \times 10^8 \text{ g}^{1/2} \text{ cm/s}^2$.

The degree to which the crude adiabatic states are

mixed by V_{01}^D in order to account for the observed frequencies is satisfyingly small. The ground state wave function corresponding to Eq. (10) is

$$\Psi_0(x, Q) = \psi_0^0(x) \cos \theta - \psi_1^0(x) \sin \theta, \quad (12)$$

where $\tan 2\theta = 2V_{01}^D Q_D / (\epsilon_1^0 - \epsilon_0^0)$ in the limits $\epsilon_1^0 - \epsilon_0^0 \gg V_{11}^D Q_D > \frac{1}{2} (V_{11}^D - V_{00}^D) Q_D^2$ and $V_{01}^D Q_D \gg \frac{1}{2} V_{01}^D Q_D^2$. At the classical turning point of the $n=0$ vibrational level, $Q_D = (\hbar/2\pi\nu_D)^{1/2} = 1.88 \times 10^{-21} \text{ g}^{1/2} \text{ cm}$ and the amount of $\psi_1^0(x)$ in $\Psi_0(x, Q)$ is only $100 \sin^2 \theta = 0.6\%$.

This kind of rationalization has the added virtue that it does not predict that additional modes will appear in the spectra. As has been noted above, one of the distinctive features of linear polyene electronic spectra is their simplicity in terms of the number of strongly coupled vibrational modes.

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