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High-resolution one and two photon excitation spectra of *trans, trans*-1,3,5,7-octatetraene

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One and two photon excitation spectra for the lowest energy singlet transition ($2\,^1A_g \leftarrow 1\,^1A_g$) of *trans, trans* 1,3,5,7-octatetraene in *n*-octane at 4.2 K(0–0 at 28 561 cm^{-1}) have been measured and analyzed. The one photon spectrum is found to be vibronically induced while the two photon spectrum is electronically allowed. The contribution of the higher lying $1\,^1B_u \leftarrow 1\,^1A_g$ transition (0–0 at approximately 32 100 cm^{-1}) to the observed two photon excitation spectrum is found to be negligible allowing vibrational overtones of the $2\,^1A_g \leftarrow 1\,^1A_g$ system to be observed. On the bases of frequency, intensity, and one or two photon allowedness, 128 measured lines are assigned as combinations of 4 antisymmetric and 11 symmetric normal modes.

I. INTRODUCTION

Well resolved absorption and emission spectra for the polyene diphenyloctatetraene that showed the presence of an excited singlet state, nearly forbidden in absorption, below the strongly absorbing $1\,^1B_u$ state were presented by Hudson and Kohler in 1972.[1,2] The assignment of this level to a "doubly excited" $2\,^1A_g$ state followed from the calculations of Schulten and Karplus.[3] Using already published low resolution absorption and fluorescence spectra, fluorescence lifetimes and yields, and the observed solvent shift behavior of fluorescence and absorption for other polyenes, Hudson and Kohler further argued that this state ordering ($2\,^1A_g$ below $1\,^1B_u$) would hold for all polyenes except, perhaps, the shortest ones butadiene and hexatriene.[2,4] This has been confirmed for a number of polyenes containing three, four, five, and six double bonds in conjugation.[5-13]

The mutually exclusive selection rules for one and two photon absorption of systems having inversion symmetry are of great utility both for making electronic assignments and studying the vibronic development of polyene states. The complementary information on excited state properties that can result from the combination one and two photon studies are nicely demonstrated in recent studies on benzene,[14] triphenylene,[15] and biphenyl.[16]

Past studies on the diphenyl polyenes have relied on the observed intensity of the two photon absorption to distinguish between states of *g* and *u* symmetry.[7,8] However, in these studies the origin region of the $2\,^1A_g \leftarrow 1\,^1A_g$ transition showed significant intensity for both one and two photon absorption. Recently we reported high resolution spectra for *trans,trans*-1,3,5,7-octatetraene in which the one photon forbidden, two photon allowed nature of the origin could be clearly seen.[13]

The possibility of obtaining extremely well resolved spectra for octatetraene in a situation where the symmetry labels *g* and *u* are strictly valid, and hence where the higher lying vibronic levels of the $2\,^1A_g$ state can be determined without interference from the overlapping $1\,^1B_u$ manifold, provided the stimulus for this work. This paper contains the vibrationally resolved one and two photon excitation spectra of *trans,trans*-1,3,5,7-octatetraene in *n*-octane at 4.2 °K together with analysis and assignments.

II. EXPERIMENTAL PROCEDURES AND SPECTRA

The synthesis of octatetraene was performed using the method described by Lippincott *et al.*[17] and discussed in detail by Manos.[18] 2,4,7-octatriene-6-ol was dehydrated in the vapor phase over Al_2O_3 at 250 °C. The resulting white crystalline flakes were collected in a cold trap at − 30 °C and recrystallized several times from hexane, yielding faintly yellow crystals of pure all-*trans*-octatetraene. The isomeric purity of the crystals was verified by high pressure liquid chromatography as previously described.[19]

n-Octane, 99.9% pure from Chemical Samples Co., was made into spectroscopic grade solvent by chromatography over silver impregnated alumina followed by activated alumina. Solutions were prepared with the freshly recrystalized octatetraene and immediately stored at 77 °K until used. Samples were lowered directly into liquid helium resulting in a polycrystalline matrix. The spectra were independent of the rate at which the samples were frozen.

One photon excitation spectra were recorded with a conventional apparatus arranged as shown in Fig. 1. In order to prevent production of photoproducts, the incident light intensity was kept as low as possible. The spectrum could be repeated without additional features from photoproducts only at very low light dosages. A quantum counter and analog divider corrected for changes in excitation flux as the wavelength was scanned. A calibration of the monochromator with a low pressure Hg lamp indicated an accuracy and precision of 0.1 Å at numerous points within the excitation scan. Instrumental resolution was 0.8 Å. Sharp features have an apparent width of about 10 cm^{-1} measured at half-maximum.

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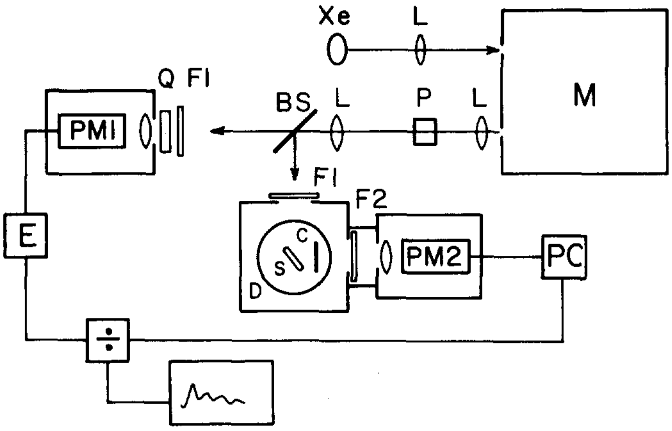

FIG. 1. One photon excitation apparatus. Xe is a 75 W xenon arc lamp. M is a 1.5 m monochromator. L are fused silica lenses. P is a glan prism to select vertically polarized light. BS reflects a small portion of the monochromatic light onto the sample S, placed in a liquid helium cryostat D. Filters F1 are Corning 9863, which prevent low level ambient light from entering the detectors. C is an acrylic Fresnel lens located within the helium Dewar. F2 is a Corning 3389 filter to block scattered excitation light. The excitation light flux is focused onto a quantum counter Q, a cuvette of 3 g/l Rhodamine G in ethylene glycol. PM1 is an EMI 6256B photomultiplier whose current is measured by an electrometer E. Sample fluorescenc is detected by a RCA 31034A photomultiplier with photon counting electronics PC. Both tubes are cooled to eliminate dark current. The excitation signal is the ratio of the fluorescence intensity to excitation light flux.

TABLE I. Laser dyes used in the two photon excitation spectrum. All dyes were purchased from Exciton Chemical Co.

Region (nm)	Dye	Concentration (g/l)	Solvent
663–701	RL-610 LD-690	1.5 0.7	DMSO/EtOH 2:1
656–666	RL-640	2.9	DMSO
623–660	RL-640	3.4	EtOH
600–635	RL-610	1.5	EtOH

Three different concentrations of octatetraene were necessary to maintain an optically thin sample as the excitation wavelength passed from the very weak $2\,^1A_g$ to the strongly allowed $1\,^1B_u$ origin. The raw spectrum generated by scaling the three concentrations to match where their spectra overlapped was converted digitally from the absorbed intensity to relative molar absorptivity. This is plotted in Fig. 2.

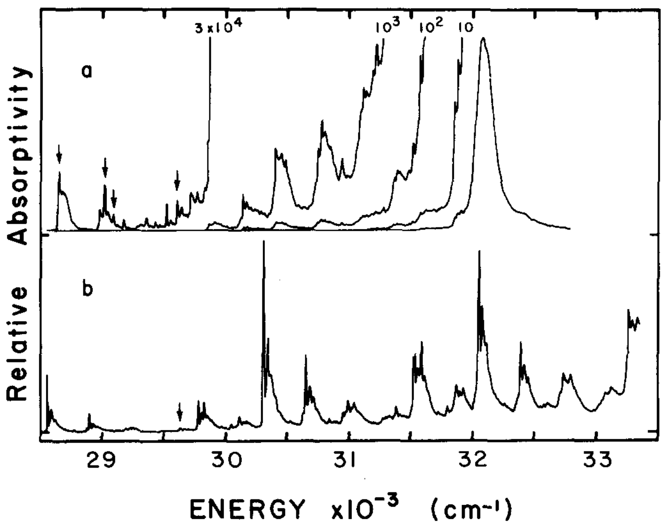

FIG. 2. Absorption spectra of *trans,trans*-1,3,5,7-octatetraene in *n*-octane at 4.2 °K. (a) One photon excitation. Arrows indicate the four false origins of the $2\,^1A_g$ state and the large peak at 32 100 cm^{-1} is the origin of the $1\,^1B_u$ state. (b) Two photon excitation. The sharp peak at 28 561 cm^{-1} is the origin of the $2\,^1A_g$ state and the arrow indicates the weak feature assigned as two quanta of a promoting mode (2P2). For both spectra, the relative molar absorptivity is plotted against vacuum wavenumbers.

The two photon excitation apparatus is shown in Fig. 3. To maintain undistorted linewidths and intensities, the dye laser power was held constant by blocking the nitrogen laser beam, as in the method described by Johnson.[20] Energy was flattened to about 65 nJ per laser shot at the sample. The dyes used are listed in Table I. A rotating polarizer and Fresnel rhomb allowed selection of linearly or circularly polarized light incident upon the sample in order to obtain information about vibronic symmetries.[21] Spectra

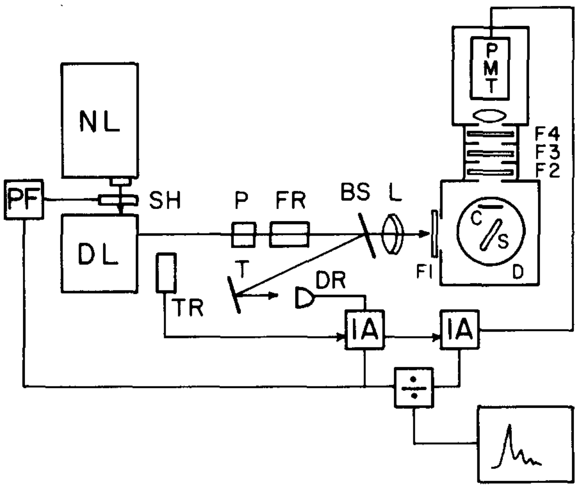

FIG. 3. Two photon excitation apparatus. A small portion of the ultraviolet beam from a molectron UV24 nitrogen laser NL is directed onto a trigger diode TR. The remainder passes through a rotating shutter SH and into a Molectron DL400 dye laser DL. The laser output is polarized by a glan prism P either vertically or at 45° from vertical in order to obtain linearly or circularly polarized light from the Fresnel rhomb FR. A beam splitter BS at nearly normal incidence directs a small amount of the beam to a target T which illuminates a reference diode DR. The reference signal is processed by an integrating sample and hold amplifier and passed to a divider and a power flattening circuit PF. Achromatic lens L focuses the dye laser onto the sample S in a liquid helium Dewar D. The fluorescence is collected by a plastic Fresnel lens C and is measured by an EMI 6256B photomultiplier PMT and a second integrating sample and hold amplifier. Filter F1 transmits light with λ > 600 nm and blocks light with λ < 500 nm, F2 is 1 cm of saturated aqueous $CuSO_4$, F3 is a BG-23-3 Schott filter, and F4 is a BG-25-3 Schott filter.

TABLE II. Normal mode frequencies determined from one (1PE) and two (2PE) photon excitation spectra. All frequencies are least-squares values in wavenumbers. $n = 0, 1$ included for all modes.

Mode	2PE Harmonic[a] $\bar{\nu}$	1PE Harmonic[a] $\bar{\nu}$	1PE and 2PE harmonic $\bar{\nu}$	1PE and 2PE anharmonic[b] $\bar{\nu}$	$\chi\bar{\nu}$
0–0	28560.4 ± 0.7	28561.1 ± 1.3	28560.6 ± 1.0	Fixed at 28560.6	
L	29.8 ± 0.6	28.8 ± 0.9	29.5 ± 0.6	29.4 ± 0.5	
$T0$	219.3 ± 1.0		219.8 ± 1.2	219.8 ± 1.2	
$T1$	320.7 ± 0.9		321.2 ± 1.0	320.6 ± 1.0	
$T2$	340.7 ± 0.6	340.3 ± 0.8	340.8 ± 0.5	340.5 ± 0.5	1.4 ± 1.4
$T3$	400.6 ± 1.0		400.7 ± 1.2	399.8 ± 1.2	
$T4$	527.3 ± 1.2	530.1 ± 0.9	529.3 ± 0.7	529.3 ± 0.7	
$S1$	1217.7 ± 0.7	1220.9 ± 1.1	1219.0 ± 0.7	1219.1 ± 0.7	0.2 ± 1.8
$S2$	1270.6 ± 0.6	1271.0 ± 1.1	1271.4 ± 0.6	1270.5 ± 0.6	6.0 ± 1.6
D	1754.2 ± 0.5	1753.7 ± 1.0	1753.8 ± 0.5	1753.8 ± 0.5	15.8 ± 1.2
C	2964.2 ± 1.0		2965.0 ± 1.2	2964.5 ± 1.3	
$P0$		93.1 ± 1.2	94.5 ± 0.8	93.0 ± 0.6	
$P1$		462.7 ± 1.3	463.1 ± 0.8	462.5 ± 0.7	
$P2$	538.3 ± 0.5	537.7 ± 0.5	538.1 ± 1.0	538.1 ± 0.3	0.0 ± 1.2
$P3$		1054.4 ± 1.3	1054.5 ± 1.1	1054.4 ± 1.0	
No. lines in fit	48	52	86	128	

[a] $n = 2$ included for $P2$.

[b] $n = 2$ included for $T2$, $S1$, $S2$, D, $P2$.

run under identical conditions, except for polarization, were identical in relative intensities. Absolute intensities with circularly polarized light were about 60% greater than with linearly polarized light.

Signals were generally on the order of ten photons per laser shot at the peaks. Detection utilized a simple integrating amplifier and gated sample-and-hold circuit which has single photon sensitivity but is linear to at least 100 photons/pulse. This provided the additional advantages of rejecting noise between laser shots and a dc signal level which was updated after each laser shot. This signal was averaged over 50 laser shots by a ratio amplifier.

Some of the effects of shot-to-shot fluctuations in laser power were removed by taking the ratio of detected signal to laser power. At all major peaks in the spectrum, a determination of the power dependence of the signal was made to check that it varied as incident power squared. Sections of the spectrum obtained with different dyes overlapped with good agreement in relative peak heights. The final combined two photon excitation spectrum is shown in Fig. 2. Positions of important peaks were recorded with a Jobin–Yvon HR-1500 monochromator, calibrated with neon emission lines, and corrected to twice the vacuum fundamental wavenumbers. Irregularities in the grating drive of the dye laser resulted in two photon wavelengths that are less accurate than those measured in the one photon spectrum, but the experimental uncertainty of 2 cm^{-1} is within the observed linewidth.

III. ASSIGNMENT AND VIBRATIONAL ANALYSIS

The vibronic structure of the two photon excitation spectrum (Fig. 2) indicates an allowed $2\,^1A_g - 1\,^1A_g$ two photon absorption. All but four of the 73 measured peaks can be assigned as simple combinations of 11 fundamental frequencies as given by

$$E_j = E(0-0) + \sum_i n_{ij}\bar{\nu}_i, \tag{1}$$

where $E(0-0)$ is the origin position, $\bar{\nu}_i$ is the wavenumber of the ith normal mode, and n_{ij} is the number of quanta of mode i assigned to peak j. The strong fundamentals must be totally symmetric (a_g) due to their intensity and the increased cross sections observed with circularly polarized light. Some of the weaker features could have b_g symmetry.

The vibrational frequencies and origin position can be refined by fitting (in the least-squares sense) Eq. (1) to all the assigned lines having $n_{ij} \leq 1$. The results are shown in Table II. Normal modes marked T (220–530 cm^{-1}) are labeled as torsional modes, although their exact nature is unknown. $S1$ (1219 cm^{-1}) and $S2$ (1271 cm^{-1}) appear at characteristic carbon–carbon single bond frequencies and D (1754 cm^{-1}) is the symmetric olefin stretching vibration. C (2965 cm^{-1}) appears in the carbon–hydrogen stretch region and is not a simple combination of other frequencies. An apparent fundamental at 1076 cm^{-1} has been assigned as the second harmonic of an unsymmetrical promoting mode, $P2$, as discussed below.

The origin region shows two characteristic features which are repeated at each new fundamental and combination peak. A broader lattice or low frequency molecular mode L is displaced 30 cm^{-1} from the origin spike and a broad phonon wing extends to about 200 cm^{-1}. This complicated lineshape introduces some ambiguity into the interpretation of congested regions of the spectrum. However, we have found that by utilizing resolution enhancement techniques, well known to NMR spectroscopists, these characteristic features can be efficiently removed from the spectrum. For example, Fig. 4 shows the 0–0 and $2D$ regions of the spectrum before and after removal of the origin line shape.

The vibronic structure of the one photon excitation

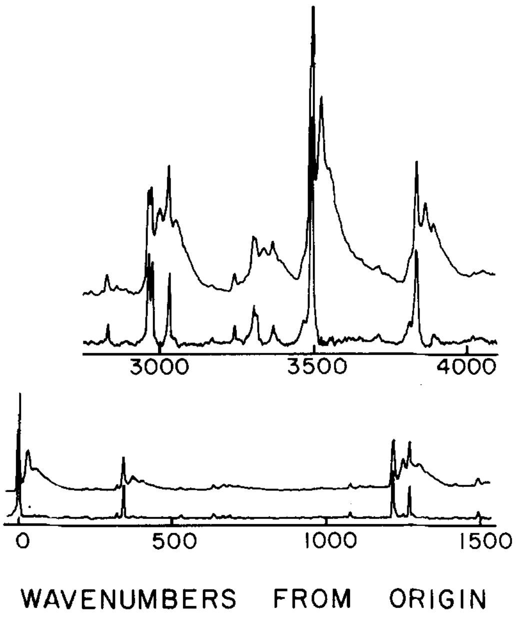

FIG. 4. Deconvolution to remove the origin line shape. The upper trace is the observed two photon excitation spectrum for the origin and 2*D* regions. The lower trace shows the result of applying resolution enhancement techniques. If $\hat{S}(\lambda)$ is the complex Fourier transform of the observed spectrum and $G(\lambda)$ is the transform of the line shape, then the complex Fourier transform of the enhanced spectrum $\hat{T}(\lambda)$ is given by $\hat{T}(\lambda) = \{(1+\gamma)\hat{G}^*(\lambda)/[|\hat{G}(0)|^2+\gamma|\hat{G}(\lambda)|^2]\}\hat{S}(\lambda)$. A value of $\gamma = 1000$ was found to be optimum for this spectrum.

spectrum is the direct result of the forbidden nature of the $2\,^1A_g \leftarrow 1\,^1A_g$ one photon absorption. As previously reported, the intensity at the origin is zero within the signal to noise limits of our apparatus.[13] Progressions are built on four false origins of 93, 463, 538, and 1054 cm^{-1}. These frequencies do not appear in the two photon excitation spectrum and are assigned as b_u symmetry promoting modes. Sixty-seven of the 72 measured peaks can be assigned as combinations of six fundamentals built on these false origins. Similar progressions are observed for each origin and all of the vibrational frequencies in these progressions appear as fundamentals in the two photon spectrum. As the transition energy approaches that of the one photon allowed $1\,^1B_u \leftarrow 1\,^1A_g$ transition, the excitation spectrum becomes quite congested making precise assignment difficult. However, all of the dominant features can be consistently assigned as a_g fundamentals built on one of the false origins.

Table II gives the least-squares refined vibrational frequencies obtained by fitting Eq. (1) to the measured peak positions. Antisymmetric promoting modes have been labeled *P*. The agreement between the one photon frequencies and two photon frequencies is excellent. Modes *T*0, *T*1, *T*3, and *C* do appear in the one photon excitation spectrum but the increased linewidth makes the measurement of these weak features much less certain than the features analyzed here. The deconvolution technique used on the two photon spectrum will not work for the one photon spectrum because there does not appear to be a consistent line shape throughout the spectrum.

The agreement between measured frequencies for combination and overtone bands and those calculated assuming that the modes are harmonic is satisfactory for all vibrations except the single bond stretch *S*2 and the double bond stretch *D*. Using the anharmonic expression

$$E_j = E(0-0) + \sum_i \left[n_{ij}\bar{\nu}_i - \tfrac{1}{2}n_{ij}(n_{ij}-1)\chi_i\bar{\nu}_i\right], \qquad (2)$$

it is possible to make a statistically meaningful test of anharmonicity for five of the observed vibrational modes. The last column of Table II shows the results of fitting Eq. (2) to both the one and two photon spectra.

IV. DISCUSSION AND CONCLUSIONS

The one photon excitation spectrum is clearly that of a symmetry forbidden transition. The vibronic coupling between the $2\,^1A_g$ and $1\,^1B_u$ states is evident in the rapidly rising intensity in the higher vibronic levels of the $2\,^1A_g$ manifold. The intensity increases nearly four orders of magnitude as the $1\,^1B_u$ origin is approached. Because of the single site nature of the observed spectra and the low temperature, contribution of the $1\,^1B_u - 1\,^1A_g$ transition to absorption in this wavelength region can be ruled out.

It is evident from the relative intensities found in the two photon spectrum that the geometries of the $1\,^1A_g$ and $2\,^1A_g$ states differ significantly. The fact that both the first and second harmonics of the mode *D* have greater intensity than the origin suggests that there are large bond distance changes in the carbon backbone, especially for the double bonds. The distortion is probably restricted to the plane of the octatetraene π-electron system since the orthogonality of the one and two photon spectra establishes that the center of inversion is retained in both the $2\,^1A_g$ and $1\,^1B_u$ states.

Detailed considerations of the geometry of the $2\,^1A_g$ state based on these excitation spectra depend on the successful analysis of the vibronic coupling problem. It is necessary to go beyond the usually applied Herzberg–Teller theory to generate the exponential increase in intensity found in the one photon spectrum. This will be treated in a subsequent paper.

Although the double bond bond orders are expected to decrease in the $2\,^1A_g$ state,[22] the double bond mode *D* increases in frequency from 1605 cm^{-1} in the ground state[16] to 1754 cm^{-1} in the excited state. This behavior has also been noted for 2,10-dimethylundecapentaene,[5] but the nature of the one photon spectra obtained made unambiguous assignment impossible.[6] The observation of the second quanta of this mode in the two photon excitation spectrum of 1,3,5,7-octatetraene removes this ambiguity in the sense that *D* can only be a fully symmetric vibrational fundamental. It cannot be a high frequency promoting mode or some strange combination band.

A detailed unravelling of the coupling between nuclear motion and electronic excitation in *trans,trans*-1,3,5,7-octatetraene will require further information, perhaps including spectra for isotopically substituted molecules. Given the quality of spectra that can be obtained, under conditions where the molecule is photochemically active,[19] the collection and interpretation of these spectra offer an unprecedented opportunity to develop insight into linear polyene *cis–trans* photoisomerization.

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