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Two-Photon Laser Excitation of Polycyclic Aromatic Molecules*

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The theory of two-photon absorption is extended to include vibronic mixing between electronic states. Theoretical expressions are derived which relate the possible transition pathways with measured quantities. The experimentally determined quantities are: the relative absorption cross sections of linearly versus circularly polarized exciting light, and the polarization of the fluorescence resulting from two-photon excitation by linearly polarized light. The theory is applied to measurements on two molecules of D_{2h} symmetry, anthracene and 9,10 dichloroanthracene. Utilizing the equations developed, the relative contributions of the three pathways, (1) both photons absorbed along the short axis, (2) both photons absorbed along the long axis, and (3) one photon absorbed along the long axis and the other photon absorbed along the short axis, are determined. From the deduced values of the transition pathways the relative contributions of different final vibronic states to the absorption of two laser photons ($\hbar\omega = 14\,400$ cm^{-1}) are determined.

I. INTRODUCTION

The simultaneous two-photon absorption experienced by molecules in a strong radiation field is now a well-documented and even commonplace phenomenon.[1–9] The quadratic interaction of the molecule with the radiation field leads to selection rules which are different from the case of the linear coupling or one-photon absorption process. In particular, a molecule possessing a center of symmetry can only undergo a *two-photon electric dipole* absorption if the initial and final states are of the same parity, whereas a *one-photon electric dipole* absorption requires the initial and final states to be of opposite parity. Thus, in a two-photon electric dipole absorption if the initial state is of even parity, then the final state must be of even parity, while the intermediate state must be of odd parity.

In this paper we consider two-photon absorption by polycyclic aromatic molecules having an inversion symmetry. The study is both theoretical and experimental in nature. In particular, we have:

(a) Introduced the mixing of electronic states through vibronic interactions so as to make parity-forbidden transitions allowed. The vibronic perturbations are especially important for the molecules which we have considered, anthracene and 9,10-dichloroanthracene, since the final electronic state at twice the ruby laser frequency is of opposite parity to the initial state and thus the absorption is parity forbidden.

(b) Utilized the observation of Hernandez and Gold[10] that the two-photon absorption cross section may be dependent on the polarization of the exciting radiation. This polarization dependence is determined by the symmetries of the states contributing to the absorption. Information about the pathways of the two-photon absorption can be obtained by such polarization measurements.

(c) Determined the relative two-photon absorption cross sections of circularly vs linearly polarized exciting light. This was done by measuring in solution the relative fluorescences effected by the two different exciting polarizations.

(d) Measured the polarization of the fluorescence relative to two-photon excitation with linearly polarized exciting light in a rigid medium. This type of measurement gives information about the direction in the molecule of the two-photon absorption with respect to the molecular direction of emission. Since the molecular fluorescence direction is known, we therefore gain information in this way about the direction or directions of two-photon absorption. The value obtained from the fluorescence polarization measurement combined with the measured ratio of cross-sections of circularly vs linearly polarized light permits a determination of the relative contributions of:

(1) both photons absorbed along a given axis of the molecule, e.g., the long axis.

(2) both photons absorbed along a different axis, e.g., the short axis.

(3) one photon absorbed along the short axis and the other photon absorbed along the long axis of the molecule.

Knowing these quantities we determined the relative contributions of the possible final vibronic states for two-photon absorption.

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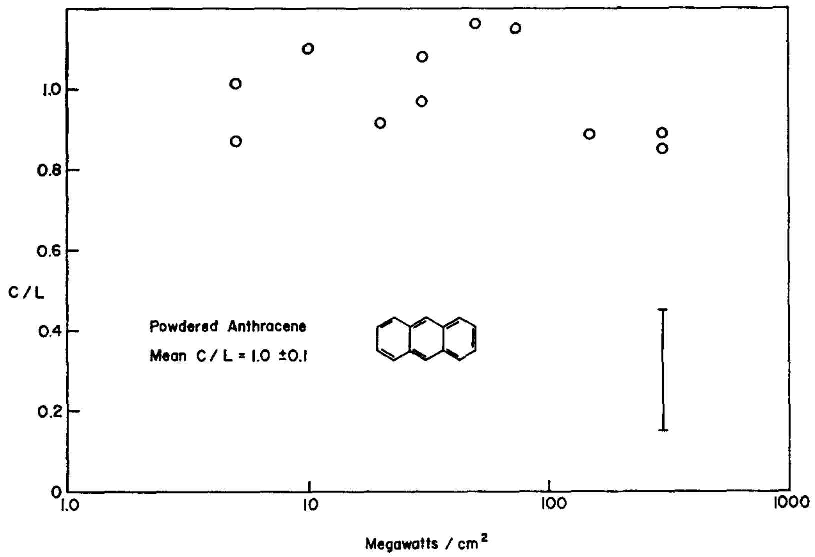

FIG. 1. Ratio (C/L) of fluorescence induced by circularly (C) and linearly (L) polarized laser light in powdered anthracene as a function of laser intensity.

II. CONTRIBUTION OF THE TERMS IN THE HAMILTONIAN TO TWO-PHOTON ABSORPTION

The interaction of electrons with monochromatic light in semiclassical form is

$$H'=\sum_j \{(-e/mc)\mathbf{A}_j\cdot\mathbf{p}_j+(e^2/2mc^2)\mathbf{A}_j\cdot\mathbf{A}_j\}, \tag{1}$$

where $\mathbf{A}_j$ is the vector potential evaluated at the position of electron j, $\mathbf{p}_j$ is the momentum of the jth electron and the sum is over all the electrons in the molecule. In this section we consider the relative importance of the terms in Eq. (1) to two-photon absorption.

A. The A·A Term

Although the interesting suggestion[11,12] that the **A·A** term in the interaction Hamiltonian is responsible for the two-photon absorption appears to be ruled out on theoretical grounds,[13,14] as well as by some earlier polarization experiments,[4] one discrepancy has not yet been cleared up completely. Measurement of the intensity of the fluorescence of circularly and linearly polarized light incident on a powdered anthracene sample indicated that the **A·A** term was important.[12] The matrix element of the **A·A** term vanishes for circularly polarized light so that if this term is important, the relative intensity of the fluorescence induced by the linearly polarized light should be much greater than that from circularly polarized light. This is essentially what the initial measurements demonstrated.[12] However, since anthracene is a biaxial crystal, the polarization of an incident beam will be altered as it propagates through the crystal along any axes except the optic axes. In addition, the powdered sample which was utilized must lead to extensive depolarization due to scattering. It is, therefore, surprising that one would obtain such a marked difference in the fluorescence for the two cases even if the **A·A** term was of importance. It seemed, therefore, worthwhile to carefully repeat these latter measurements.

The experiments of Ianuzzi and Polacco on powdered anthracene were repeated and equal fluorescence intensity for both circularly and linearly polarized *incident* exciting light was observed as shown in Fig. 1. As mentioned before, this independence of polarization is expected with powdered crystals because of depolarization. To avoid the birefringent effects of the crystal, anthracene in an isotropic medium ($10^{-3}M$ in 95% ethanol) was studied. These results (see Fig. 2) show a significant absorption of the circularly polarized light and thus eliminates the **A·A** term as the major contributing term in the Hamiltonian. It is apparent in view of the present experimental work that the contribution of the **A·A** term must be very small at best. Furthermore, theoretical work in two laboratories[13,14] has indicated that the contribution of the **A·A** term is negligible.

B. The A·p Term. Electric Quadrupole or Magnetic Dipole Transitions

If the initial and final states are of the same parity, then two-photon absorption resulting from electric dipole transitions is forbidden. However, the parity selection rule can be satisfied if one of the transitions is a dipole transition and the other is either an electric quadrupole or magnetic dipole transition. For either of

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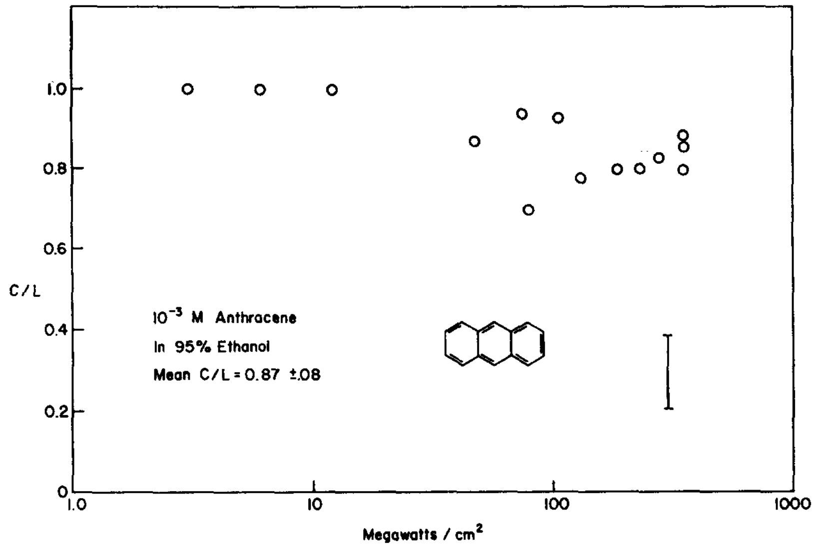

FIG. 2. Ratio of fluorescence induced by circularly and linearly polarized laser light in anthracene in solution as a function of laser intensity.

these, the probability for the over-all absorption is reduced by roughly 10^6 compared with two dipole allowed transitions. The contribution of dipole with electric quadrupole or magnetic dipole terms is therefore neglected.

C. The A·p Term. Electric Dipole Transition

In Secs. II.A. and II.B. the contributions of the **A**·**A** term and the higher order terms of **A**·**p** were asserted to be of negligible importance. The only remaining way to effect a two-photon transition between initial and final states of the same parity is via two dipole transitions one of which is made allowed by vibronic perturbations. Very roughly the absorption compared with two dipole allowed transitions should be reduced due to vibronic mixing by 10^2. Thus, the vibronic mixing pathway should be roughly 10^4 times more likely than mechanisms involving **A**·**A** or the higher order terms of **A**·**p**. In view of these considerations we consider only electric dipole transitions and vibronic mixing in this paper.

III. EXPERIMENTAL

Two distinct and separate measurements were made on each molecule. In one the molecules in solution at room temperature were irradiated in turn by linearly polarized and circularly polarized light and the resulting fluorescence monitored. These measurements yielded the ratio, C/L, of the fluorescence resulting from the different states of polarization of the exciting light. In the second set of experiments the molecules in a rigid matrix were irradiated with linearly polarized light and the polarization of the emission was obtained. In particular the intensity of emission polarized parallel to and perpendicular to the axis of polarization of the irradiating laser light was measured. These measurements yielded a second ratio $I_{\perp}I_{\parallel}$.

The experimental arrangement is shown in Fig. 3. The laser light first passes through a blue filter to remove flash-tube light, then through attenuating Corning filters and a Glan laser polarizer which insures that linearly polarized (vertical) light enters a $\frac{1}{4}\lambda$ plate which, depending on orientation, passes either circular

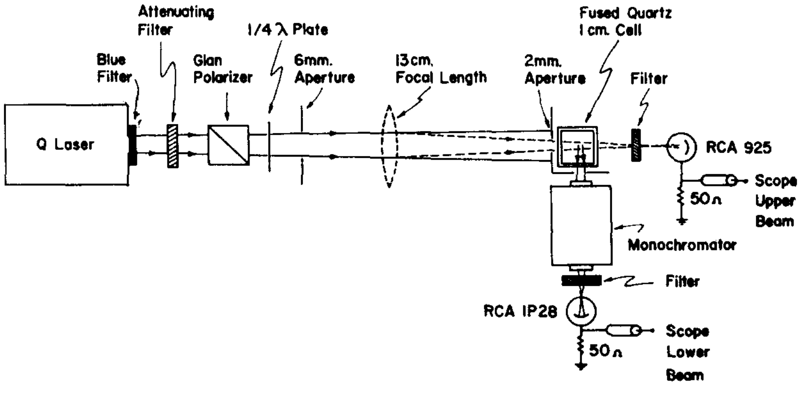

FIG. 3. Apparatus used to measure laser-induced fluorescence.

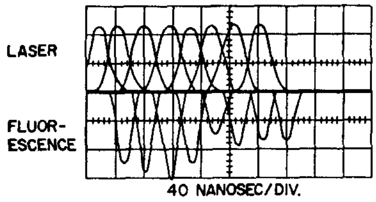

FIG. 4. Scope tracing of laser intensity (upper trace) and fluorescence (lower trace) from 9,10-dichloroanthracene. The first four upper traces are for linearly polarized laser light and the second set of upper traces are for circularly polarized laser light.

or linearly polarized light. A 6-mm-diam aperture in Al foil limits the beam which then may be gently converged by a 13-cm-focal-length lens when higher intensities are desired. The light passes through a second aperture of 2-mm diameter in Al foil and into the experimental cell. The intensity of the laser light is monitored after the cell with a 925 RCA photodiode run at 225V with 50-Ω load. Suitable filters ($NiSO_4$) attenuate the laser light. The fluorescence resulting from two-photon absorption is observed in a direction perpendicular to the laser light. It passes first through a monochromator or selected Corning filters and is monitored by a 1P28 which feeds a 50-Ω load. (The photomultiplier's linearity when suitably wired extends for pulses less than 100 nsec to anode currents of 8 mA.) The signals from the 925 and 1P28 are displayed and photographed on a dual beam Tektronix 555 using L plug-in units.

The laser we use is an Optics Technology Model 130. It is Q-switched by a Pockels cell. The pulse energy is quite constant when fired at 1-min intervals giving peak powers of up to 100 MW. The pulses have a 15-nsec half-width and the beam's divergence is 10 mrad. We find, however, that though the total pulse energy is fairly constant the energy distribution or intensity varies from pulse to pulse across the width of the pulse. Because of this there is considerable fluctuation in fluorescent output (which depends on I^2) for laser pulses that appear the same as monitored by the 925. To overcome this experimental difficulty we took many measurements for each of the two states of polarization at the different laser energies. The Glan laser polarizer together with a precision $\frac{1}{4}\lambda$ mica plate allows easy alternation between linearly (vertically) polarized light and circularly polarized light of either handedness. The purity of the circularly polarized light was checked by reflecting it from a metal mirror which changes the handedness, back through the $\frac{1}{4}\lambda$ plate and through the polarizer now acting as an analyzer. Pure circularly polarized light is indicated by no light returning through the analyzer. The $\frac{1}{4}\lambda$ plate was placed in a rotatable mount so that by merely rotating 45° the light was changed from linear to circular or vice versa without any change in beam intensity. The 6-mm aperture produces a beam of roughly uniform intensity throughout its cross section. The 2-mm aperture accepted a fraction of this beam which passed through the center of the experimental cell. Background fluorescence was reduced by preventing laser light from falling directly on the edges of the cell. However, the principal reduction in background signal was achieved by use of 95% ethanol as a solvent and a fused quartz cell.

The intensity of the laser light is monitored after transmission through the cell so we avoid reliance on the transmission characteristics of the intensity reducing filters. Furthermore, and more importantly, the polarization of the light can be checked after transmission through the sample. The polarization, linear or circular, is not altered by the sample in our experience.

Each of the solutions we report on was approximately of $10^{-3}M$ concentration in 95% ethanol and the starting materials were anthracene, zone refined, 20 passes and 9,10-dichloroanthracene, Eastman #1642. Care was taken to avoid as much as possible exposure to uv and oxygen. The fluorescence spectra of each of the samples was run using a Cary spectrophotometer Model #125 and the peak that most closely matched the photoresponse of the S5 photocathode of the 1P28 was observed with the monochromator Baush & Lomb 33-86-02. Usually a 200-Å band was observed. Scattered laser light is carefully filtered by a $CuSO_4$ solution in front of the 1P28. The monochromator also effectively reduces the scattered laser light. The monochromator is used also to roughly check the fluorescence spectrum of the sample under investigation, thus confirming that the observed fluorescence is from the experimental sample.

Data was recorded by photographing eight laser pulses at 1-min intervals with consequent fluorescence on a single photograph as is shown in Fig. 4. The first four are for linearly polarized light and the second four for circularly polarized light. The laser power remains fairly constant as can be seen from the figure. Several such pictures were taken at various laser intensities for each of the samples. The laser intensity was altered by introducing Corning filters in front of the Glan polarizer. A range of intensity of roughly 10:1 was covered in this way. Much higher intensities were achieved by introducing a 13-cm-focal-length lens between the 6-mm aperture and the cell and causing the beam to converge to approximately 2-mm diameter in the center of the 1-cm sample cell. The focal point was outside the cell to avoid cavitation in the liquid. A range of slightly over 100 in intensity was covered by these means.

The I^2 dependence of the emission was first established for each of the molecules. To determine the relative efficiencies of the two polarizations, the amplitude of each fluorescent signal (F) was measured and divided by the square of the amplitude of the corresponding laser pulse (I^2) giving F/I^2 for each laser shot. The mean value of several such efficiencies for approximately the same laser intensity was taken for both linearly and circularly polarized laser light giving $\langle(F/I^2)_L\rangle_{\mathrm{Av}}$

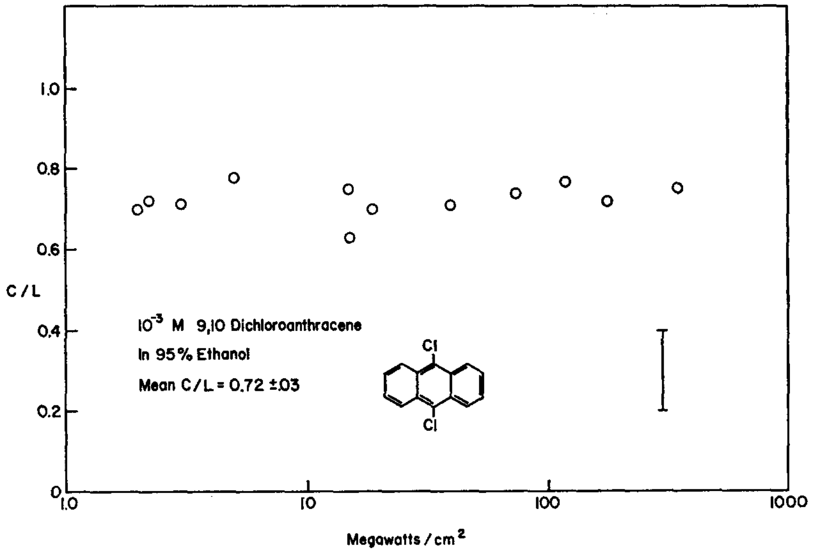

FIG. 5. Ratio of fluorescence induced by circularly and linearly polarized laser light in 9-10-dichloroanthracene in solution as a function of laser intensity.

and $\langle (F/I^2)_C \rangle_{\text{Av}}$. The ratio C/L of these two efficiencies was then taken and so values were obtained for this ratio at various laser intensities. These are plotted in Figs. 2 and 5. The flags in the figures indicate the approximate mean deviations of the ratios.

Mode jumping between various transverse spatial modes of the laser cavity is thought to be responsible for the fluctuations in the fluorescent output. In some of our most recent experiments on the polarization of the emission, to be described below, we sought to reduce the fluctuations in the measurements by measuring I^2, the square of the laser intensity, directly rather than measuring I, the laser intensity, and subsequently squaring. Our method was to allow the fraction of the laser beam, which would normally be monitored by the 925 to irradiate a solution of $0.1M$ phenanthrene in benzene. A strong fluorescence results, proportional to I^2, which is monitored by a 1P28 photomultiplier. In these latter experiments only linearly polarized light was used to irradiate the phenanthrene. Considerably better consistency was obtained by this technique. A second technique used in the measurements on the polarization of the emission was to simultaneously observe the two polarizations of interest using two matched photomultipliers symmetrically disposed on either side of the sample cell. One photomultiplier monitored the perpendicular polarization, the other parallel. In this method each laser shot yielded the information necessary to calculate the ratio of interest. Therefore, variations in laser intensity from shot to shot were less troublesome.

In order to make the measurements on the polarization of the emission by the first method described above the quarter-wave plate was removed and an analyzer placed between the sample cell and the monochromator. The polarization bias of the monochromator was reduced by tilting it at 45°. The slight remaining bias was measured and allowed for. It amounted to 3% in favor of horizontal polarization. In these measurements $10^{-3}M$ anthracene, and $10^{-3}M$ 9,10-dichloroanthracene were rigidly held in EPA glass at liquid-nitrogen temperature. As before, a cell of 1 cm^2 cross section was used. The cell was supported inside a clear walled Dewar vessel in which the liquid nitrogen level was held just below the height of the laser beam. In this way we experienced no trouble with bubbling or scattering in the liquid nitrogen. The results of these measurements are presented in Sec. V.

IV. THEORETICAL

In most molecules possessing a center of symmetry such as anthracene, the ground electornic state is of g symmetry. A two-photon dipole transition from the ground electronic state requires the intermediate state to be of odd parity (ungerade) and, hence, the final state must be of even parity (gerade). Since it is now well known that in the molecules of interest there exists a state at exactly twice the laser frequency which is two-photon accessible, this state must be of even parity. However, there are two possibilities: either it is an electronic state of odd parity vibronically mixed with states of even parity or it is an electronic state of even parity. Molecular orbital calculations tend to rule out the latter possibility because they place the electronic gerade states far too high.[15] Consequently, vibronic mixing between states of opposite parity must be considered.

In the following calculations we neglect the mixing of the ground state because of an unfavorable energy factor. We consider not only the vibronic mixing of the final state but also the vibronic mixing of the intermediate states.

The transition probability for two-photon absorption, $gi \rightarrow fl$, can be written (including the A^2 term in the

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[15] R. Pariser, J. Chem. Phys. **24**, 250 (1956).

dipole approximation so as to remove the frequency factor)[4,16]

$$P_{gi,fl}=C\left|\sum_{nj}\left\{\frac{(\mathbf{M}_{fl,nj}\cdot\hat{\epsilon}_\lambda)(\mathbf{M}_{nj,gi}\cdot\hat{\epsilon}_\mu)}{\omega_{nj,gi}-\omega_\lambda}+\frac{(\mathbf{M}_{fl,nj}\cdot\hat{\epsilon}_\mu)(\mathbf{M}_{nj,gi}\cdot\hat{\epsilon}_\lambda)}{\omega_{nj,gi}-\omega_\mu}\right\}\right|^2 \quad (2)$$

where n_j is the vibronic state corresponding to the jth vibrational level of the nth electronic state, $\hat{\epsilon}_\lambda$ and $\hat{\epsilon}_\mu$ are the polarization vectors of the photons λ and μ, respectively, and ω_λ and ω_μ are their frequencies. C is equal to $[(2\pi)^3/\hbar^4c^2]F_\lambda\hbar\omega_\lambda I(\omega_\mu)$, where F_λ is the number of photons per square centimeter·second at the frequency ω_λ, $I(\omega_\mu)$ is the energy flux per unit frequency in ergs per square centimeter of the secondary beam at the frequency ω_μ:

$$\mathbf{M}_{fl,nj}=\langle\phi_l^f(Q)\mid\mathbf{M}_{fn}(Q)\mid\phi_j^n(Q)\rangle, \quad (3)$$

where ϕ_l^f is the lth vibrational level of the electronic state f and

$$\mathbf{M}_{fn}(Q)=\langle\theta_f(q,Q)\mid\mathbf{M}(q)\mid\theta_n(q,Q)\rangle, \quad (4)$$

where $\theta_f(q,Q)$ is the electronic state f which is expressed as a function of the electronic coordinates q and the vibrational coordinates Q, and $\mathbf{M}(q)$ is the electronic dipole moment operator.

A. Vibronic Mixing of the Final State f with Other Electronic States

Following the Herzberg–Teller formulation,[17,18] $\mathbf{M}_{fn}(Q)$, for small displacements, can be expanded in a power series about the equilibrium value of the vibrational coordinates. $Q=0$. This expansion corresponds to a mixing of the electronic states due to an electronic-vibrational coupling. Retaining only those terms linear in the vibrational coordinates Q we finally obtain

$$\mathbf{M}_{fn}(Q)=\mathbf{M}_{fn}(0)+{\sum_s}'\lambda_{fs}(Q)\mathbf{M}_{sn}(0), \quad (5)$$

where the sum is over all electronic states s except f and

$$\lambda_{fs}(Q)=\sum_a\frac{\langle\theta_f(q,0)\mid(\partial H/\partial Q_a)_0\mid\theta_s(q,0)\rangle}{E_s-E_f}Q_a. \quad (6)$$

H is the Hamiltonian and the sum is over all normal modes a.

The dipole transition matrix element between the vibronic states fl and nj can thus be written

$$\mathbf{M}_{fl,nj}=\mathbf{M}_{fn}(0)\langle\phi_l^f\mid\phi_j^n\rangle+{\sum_s}'\mathbf{M}_{sn}(0)\times\sum_a\frac{\langle\theta_f^0\mid(\partial H/\partial Q_a)_0\mid\theta_s^0\rangle}{E_s-E_f}\langle\phi_l^f\mid Q_a\mid\phi_j^n\rangle, \quad (7)$$

where $\theta_f^0=\theta_f(q,0)$.

If the intermediate state n and the final state f are ungerade electronic states, then $\mathbf{M}_{fn}(0)$ is a symmetry forbidden transition. The transition between states fl and nj gains its intensity by borrowing from the transitions between the states n and s, where s must be a gerade electronic state. This requires that $\mathbf{M}_{sn}(0)$ be non-zero and simultaneously the states f and s must have an allowed vibronic coupling. Simple group theory shows that the vibrations Q_a necessary for the mixing of states f and s must be of symmetry such that it belongs to one of the irreducible representations of the product of the representations of θ_s^0 and θ_f^0. For example, in D_{2h} symmetry if f is of symmetry B_{2u} and s is of symmetry B_{1g}, then the Q_a must be of symmetry b_{3u}.

B. Vibronic Mixing of the Intermediate States

Following the procedure of the previous section, we obtain by mixing the intermediate state n with state r

$$\mathbf{M}_{fn}(Q)=\mathbf{M}_{fn}(0)+{\sum_r}'\lambda_{nr}(Q)\mathbf{M}_{fr}(0), \quad (8)$$

where the sum is over all electronic states r except the state n. The dipole transition matrix element between the vibronic states fl and nj is

$$\mathbf{M}_{fl,nj}=\mathbf{M}_{fn}(0)\langle\phi_l^f\mid\phi_j^n\rangle+{\sum_r}'\mathbf{M}_{fr}(0)\times\sum_a\frac{\langle\theta_n^0\mid(\partial H/\partial Q_a)_0\mid\theta_r^0\rangle}{E_r-E_n}\langle\phi_l^f\mid Q_a\mid\phi_j^n\rangle. \quad (9)$$

The vibrations Q_a necessary for the vibronic interaction between the states r and the intermediate state n must be of a symmetry such that they are contained in the product of the representations of the electronic states r and n. For the state, r, to contribute to the transition between fl and nj, there is also the requirement as seen in the equation (9), that $\mathbf{M}_{fr}(0)\neq 0$. It should be recognized that in addition to the necessary contributions made possible by vibronic interactions for the cases of symmetry forbidden transitions, the vibrational mixing of electronic states can also play a significant role for those cases where transitions are symmetry allowed but weak. This may be of special importance in two-photon spectroscopy. For those molecules where vibronic mixing is necessary for two-photon absorption, the 0–0 band will clearly not appear. The two-photon absorption spectra will start at an energy $E=E_{0\text{–}0}+E_{\text{vib}}$ where E_{vib} is the energy corresponding to the vibrational mode required for the vibrational mixing.

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[16] P. A. M. Dirac, *Principles of Quantum Mechanics* (Clarendon Press; Oxford, England, 1958), p. 247.

[17] G. Herzberg and E. Teller, Z. Physik Chem. **B21**, 410 (1933).

[18] A. D. Liehr, Z. Naturforsch. **13a**, 311 (1958).

The transition probability for the absorption of two photons of the same frequency ω and state of polarization $\hat{\epsilon}$ is

$$P_{gi,fl}=C'\left|\sum_{nj}\frac{\mathbf{M}_{fl,nj}\cdot\hat{\epsilon})(\mathbf{M}_{nj,gi}\cdot\hat{\epsilon})}{\omega_{nj,gi}-\omega}\right|^2, \qquad (10)$$

where $C'=4C$ and $\omega_\lambda=\omega_\mu=\omega$. See Eq. (2).

For plane polarized light, $\hat{\epsilon}=\hat{\epsilon}_Z$ where Z is a laboratory fixed direction. For circularly polarized light $\hat{\epsilon}=(2)^{-1/2}[\hat{\epsilon}_Z+i\hat{\epsilon}_Y]$, where Z and Y are laboratory fixed directions.

Since we are not including vibronic mixing of the ground electronic state, we find that

$$\mathbf{M}_{nj,gi}=\mathbf{M}_{ng}(0)\langle\phi_j^n\mid\phi_i^g\rangle. \qquad (11)$$

By substitution of Eqs. (5), (8), and (11) into (10), we obtain

$$P_{gi,fl}=C'\mid\sum_{nj}[1/(\omega_{nj,gi}-\omega)](\hat{\epsilon}\cdot\mathbf{M}_{fn}(0)\langle\phi_1{}^f\mid\phi_j{}^n\rangle$$
$$+\sum_s{}'\hat{\epsilon}\cdot\mathbf{M}_{sn}(0)\langle\phi_1{}^f\mid\lambda_{fs}(Q)\mid\phi_j{}^n\rangle$$
$$+\sum_r{}'\hat{\epsilon}\cdot\mathbf{M}_{fr}(0)\langle\phi_1{}^f\mid\lambda_{nr}(Q)\mid\phi_j{}^n\rangle)$$
$$\times(\hat{\epsilon}\cdot\mathbf{M}_{ng}(0)\langle\phi_j{}^n\mid\phi_i{}^g\rangle)\mid^2. \qquad (12)$$

In this treatment only in-plane transitions are considered. In addition, it is assumed that the vibrational level i of the ground electronic state is the zero level. As a general example, molecules of D_{2h} symmetry, e.g., anthracene and 9,10-dichloroanthracene, are examined.

Since we have restricted this discussion to in-plane transitions, the possible intermediate states are of symmetries B_{2u} and B_{3u}. Thus, $\mathbf{M}_{ng}$ is short-axis (y) polarized for $n=B_{2u}$ and $\mathbf{M}_{ng}$ is long-axis (x) polarized for $n=B_{3u}$.

In this example $\mathbf{M}_{fn}(0)$ is a parity forbidden transition since f is assumed to be ungerade and n must be ungerade. The gerade states that enter via the vibronic mixing of electronic states are A_g and B_{1g}. These gerade states alone conform to the restriction of considering only in-plane transitions. For the case in which the final electronic state is of symmetry B_{2u}, e.g., anthracene, the only possible vibrational states consistent with these reservations are of symmetry b_{2u} or b_{3u}.

We now consider the two-photon absorption from the vibronic state gi to the vibronic state fl where the symmetries are

$g\rightarrow A_a$; $\quad i\rightarrow a_a$ (zero level),

$f\rightarrow B_{2u}$; $\quad 1\rightarrow b_{2u}$.

For linearly polarized exciting light $\hat{\epsilon}_Z$ we obtain

$$P_{gi,fl}=C'\mid 1_{xZ}{}^2\sum_{nj}(\omega_{nj,gi}-\omega)^{-1}$$
$$\times[\sum_s{}'M_{sn}{}^x(0)\langle\phi_1{}^f\mid\lambda_{fs}(Q)\mid\phi_j{}^n\rangle$$
$$+\sum_r{}'M_{fr}{}^x(0)\langle\phi_1{}^f\mid\lambda_{nr}(Q)\mid\phi_j{}^n\rangle][M_{ng}{}^x(0)\langle\phi_j{}^n\mid\phi_i{}^g\rangle]$$
$$+1_{yZ}{}^2\sum_{n'j'}(\omega_{n'j',gi}-\omega)^{-1}$$
$$\times[\sum_{s'}{}'M_{s'n'}{}^y(0)\langle\phi_1{}^f\mid\lambda_{fs'}(Q)\mid\phi_{j'}{}^{n'}\rangle$$
$$+\sum_{r'}^{a}{}'M_{fr'}{}^y(0)\langle\phi_1{}^f\mid\lambda_{n'r'}(Q)\mid\phi_{1j'}{}^{n'}\rangle]$$
$$\times[M_{n'g}{}^y(0)\langle\phi_{j'}{}^{n'}\mid\phi_i{}^g\rangle]\mid^2, \qquad (13)$$

where 1_{xZ} is the direction cosine for the intersection of the long axis (x) of some molecule of arbitrary orientation and the laboratory fixed axis Z. Similarly, 1_{yZ} is the direction cosine for the short molecular axis (y) and the fixed axis Z. The superscript on the transition moment indicates the polarization of the transition in terms of the molecular axes. Since $\phi_i{}^g$ is of a_g symmetry, $\phi_j{}^n$ and $\phi_{j'}{}^{n'}$ are of a_g symmetry. Since $\phi_1{}^f$ is of b_{2u} symmetry and $\phi_j{}^n$ and $\phi_{j'}{}^{n'}$ are of a_g symmetry, then λ_{fs}, λ_{nr}, $\lambda_{fs'}$ and $\lambda_{n'r'}$ are of b_{2u} symmetry. The states in the sum over n are of symmetry B_{3u}, those over n' are of symmetry B_{2u}. The states s are of symmetry A_g, r are of B_{1g}, s' are of A_g and r' are of A_g.

We set the first sum over nj equal to $D_{nj}{}^{xx}$ where the superscript xx indicates that both photons are absorbed along the long molecular axis x. We set the second sum over $n'j'$ equal to $D_{n'j'}{}^{yy}$. Hence,

$$P_{gi,fl}=C'\mid 1_{xZ}{}^2D_{nj}{}^{xx}+1_{yZ}{}^2D_{n'j'}{}^{yy}\mid^2. \qquad (14)$$

Since the molecules are randomly oriented in solution, we average over all angles and obtain for linearly polarized light (final vibrational state is b_{2u})

$$\langle P_{gi,fl}\rangle_{\text{Av}}=C'[\tfrac{1}{5}(D_{nj}{}^{xx})^2+\tfrac{1}{5}(D_{n'j'}{}^{yy2})+\tfrac{2}{15}D_{nj}{}^{xx}D_{n'j'}{}^{yy}]. \qquad (15)$$

For circularly polarized light, $\hat{\epsilon}=(2^{-1/2})(\hat{\epsilon}_Z+i\hat{\epsilon}_Y)$, and for the same initial and final states as for the linearly polarized case considered above, we obtain

$$P_{gi,fl}=\tfrac{1}{4}C'\mid(1_{xZ}+i1_{xY})^2D_{nj}{}^{xx}+(1_{yZ}+i1_{yY})^2D_{n'j'}{}^{yy}\mid^2. \qquad (16)$$

After performing the squaring and averaging over angles we obtain for circularly polarized light (final vibrational state is b_{2u})

$$\langle P_{gi,fj}\rangle_{\text{Av}}$$
$$=C'[\tfrac{2}{15}(D_{nj}{}^{xx})^2+\tfrac{2}{15}(D_{n'j'}{}^{yy})^2-\tfrac{2}{15}D_{nj}{}^{xx}D_{n'j'}{}^{yy}]. \qquad (17)$$

In the preceding calculations, the final vibrational state l is of symmetry b_{2u}. We shall now consider the case where the final state l' is of symmetry b_{3u}. As before, f is B_{2u}, g is A_g, and i is a_g. For linearly polarized light $\hat{\epsilon}=\hat{\epsilon}_Z$:

$$P_{gi,fl'}=C'\mid 1_{yZ}1_{xZ}\sum_{nj}(\omega_{nj,gi}-\omega)^{-1}$$
$$\times[\sum_s{}' M_{sn}{}^y(0)\langle\phi_{l'}{}^f\mid\lambda_{fs}(Q)\mid\phi_j{}^n\rangle$$
$$+\sum_r{}' M_{fr}{}^y(0)\langle\phi_{l'}{}^f\mid\lambda_{nr}(Q)\mid\phi_j{}^n\rangle][M_{ng}{}^x(0)\langle\phi_j{}^n\mid\phi_i{}^g\rangle]$$
$$+1_{xZ}1_{yZ}\sum_{n'j'}(\omega_{n'j',gi}-\omega)^{-1}$$
$$\times[\sum_{s'}{}' M_{s'n'}{}^x(0)\langle\phi_{l'}{}^f\mid\lambda_{fs'}(Q)\mid\phi_{j'}{}^{n'}\rangle$$
$$+\sum_{r'}{}' M_{fr'}{}^x(0)\langle\phi_{l'}{}^f\mid\lambda_{n'r'}(Q)\mid\phi_{j'}{}^{n'}\rangle]$$
$$\times[M_{n'g}{}^y(0)\langle\phi_{j'}{}^{n'}\mid\phi_i{}^g\rangle]\mid^2. \quad (18)$$

Since $\phi_{l'}{}^f$ is now of b_{3u} symmetry and $\phi_j{}^n$ and $\phi_{j'}{}^{n'}$ are still of a_g symmetry, then λ_{fs}, λ_{nr}, $\lambda_{fs'}$, and $\lambda_{n'r'}$ are of b_{3u} symmetry. The states in the sum over n are now of symmetry B_{3u} and those over n' are of B_{2u} symmetry as before. However, the states s, r, s', and r' are not of the same symmetry as in the first example. The states s are symmetry B_{1g}, r are A_g, s' are B_{1g}, and r' are B_{1g}.

Set the sum over nj equal to $F_{nj}{}^{yx}$ where the superscript yx indicates that one photon is absorbed along the y axis and the other photon is absorbed along the x axis. Similarly we set the second sum equal to $F_{n'j'}{}^{xy}$. We then find

$$P_{gi,fl'}=C'\mid 1_{yZ}1_{xZ}F_{nj}{}^{yx}+1_{xZ}1_{yZ}F_{n'j'}{}^{xy}\mid^2. \quad (19)$$

Averaging this expression over angles yields for linearly polarized light (final vibrational state is b_{3u})

$$\langle P_{gi,fl'}\rangle_{\text{Av}}=\tfrac{1}{15}C'\mid F_{nj}{}^{yx}+F_{n'j'}{}^{xy}\mid^2. \quad (20)$$

For circularly polarized exciting light

$$P_{gi,fl'}=\tfrac{1}{4}C'\mid(1_{yZ}+i1_{yY})(1_{xZ}+i1_{xY})F_{nj}{}^{yx}$$
$$+(1_{xZ}+i1_{xY})(1_{yZ}+i1_{yY})F_{n'j'}{}^{xy}\mid^2. \quad (21)$$

Averaging this expression over angles gives for circularly polarized light (final vibrational state is b_{3u})

$$\langle P_{gi,fl'}\rangle_{\text{Av}}=\tfrac{1}{10}C'\mid F_{nj}{}^{yx}+F_{n'j'}{}^{xy}\mid^2. \quad (22)$$

In this section we have obtained expressions for the transition probabilities for linearly and circularly polarized exciting light. For the b_{2u} mixing vibration this transition probability includes two transition pathways. They are (1) both photons absorbed along the short axis and (2) both photons absorbed along the long axis. For the b_{3u} mixing vibration the two photons are absorbed along different axes, the orthogonal short and long axes. The total cross section for the absorption of two quanta of circularly polarized light is proportional to the sum of Eqs. (17) and (22). Similarly for linearly polarized exciting light the cross section is proportional to the sum of Eqs. (15) and (20). The ratio, Ω, of the cross sections for circularly vs linearly polarized light is

$$\Omega=\frac{C}{L}=\frac{3F^2+4D_{xx}{}^2+4D_{yy}{}^2-4D_{xx}D_{yy}}{2F^2+6D_{xx}{}^2+6D_{yy}{}^2+4D_{xx}D_{yy}}, \quad (23)$$

where

$$F^2=\mid F_{nj}{}^{yx}+F_{n'j'}{}^{xy}\mid^2 \qquad [\text{see Eq. (20)}].$$
$$D_{xx}{}^2=(D_{nj}{}^{xx})^2; \qquad D_{yy}{}^2=(D_{n'j'}{}^{yy})^2 \qquad [\text{see Eq. (15)}].$$

Since Eq. (23) contains three unknown terms an experimental determination of C/L in general will not reveal the relative importance of the three transition pathways. Only where the measured $C/L=0.25$ can we deduce the contributions of the different pathways. For this result $F^2=0$ and $D_{xx}=D_{yy}$, i.e., the b_{2u} vibration would be the only one. (See Table I.)

A theoretical expression for a second measurable ratio involving the three transition matrix elements is now deduced and it is later shown that using this and Eq. (23) the relative contributions of F^2, $D_{xx}{}^2D_{yy}{}^2$ for the molecules in question can be obtained. Knowing these the importance of the mixing vibrations b_{2u} or b_{3u} will result.

If the molecules in a rigid environment are irradiated with linearly polarized light and the polarization of the fluorescence is measured perpendicular to and parallel to the direction of polarization of the irradiating light, we obtain the ratio $I_\perp/I_\parallel$. It is important that the molecule does not rotate between absorption and emission, hence the rigid medium.

If the direction of the irradiating laser beam is X and its direction of polarization Z in the laboratory frame and if the fluorescence is observed along the Y laboratory axis, the appropriate expressions for the intensity of the emitted light polarized in the X direction (perpendicular) and in the Z direction (parallel) are as follows. For two-photon absorption due to a b_{2u} mixing vibration followed by emission polarized in Z direction using Eq. (14)

$$I_\parallel(b_{2u})\propto\langle P_{gi,fl}1_{yZ}{}^2\rangle_{\text{Av}}, \quad (24)$$

where 1_{yZ} is the direction cosine between the y, short molecular axis (the emission axis for anthracene and 9,10-dichloroanthracene) and the Z laboratory axis. For two-photon absorption due to b_{3u} mixing vibration followed by emission polarized in the Z direction using Eq. (19),

$$I_\parallel(b_{3u})\propto\langle P_{gi,fl'}1_{yZ}{}^2\rangle_{\text{Av}} \quad (25)$$

and the total intensity of Z polarized fluorescence is the sum of Eqs. (24) and (25),

$$I_\parallel(\text{total})\propto\langle P_{gi,fl}1_{yZ}{}^2\rangle_{\text{Av}}+\langle P_{gi,fl'}1_{yZ}{}^2\rangle_{\text{Av}}. \quad (26)$$

Similarly the total intensity of X polarized fluorescence

TABLE I. Two-photon absorption, $Ag \rightarrow\rightarrow B_{2u}$, in molecules of D_{2h} symmetry.

Mixing vibration	b_{2u}				b_{3u}			
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Initial electronic state	A_g	A_g	A_g	A_g	A_g	A_g	A_g	A_g
	$\downarrow$	$\swarrow$	$\downarrow$	$\swarrow$	$\downarrow$	$\swarrow$	$\downarrow$	$\swarrow$
Intermediate electronic state[a]	B_{2u}	$B_{2u}+\delta A_g$	B_{3u}	$B_{3u}+\delta B_{1g}$	B_{2u}	$B_{2u}+\delta B_{1g}$	B_{3u}	$B_{3u}+\delta A_g$
	$\searrow$	$\swarrow$	$\searrow$	$\swarrow$	$\searrow$	$\swarrow$	$\searrow$	$\swarrow$
Final electronic state	$B_{2u}+\delta A_g$	B_{2u}	$B_{2u}+\delta A_g$	B_{2u}	$B_{2u}+\delta B_{1g}$	B_{2u}	$B_{2u}+\delta B_{1g}$	B_{2u}
Absorption axes[b]	$\|\|$	$\|\|$	$=$	$=$	$-\|-$	$-\|-$	$-\|-$	$-\|-$
C/L	0.67	0.67	0.67	0.67	1.5	1.5	1.5	1.5
$I_\perp/I_\parallel$	0.20	0.20	3.0	3.0	0.67	0.67	0.67	0.67

[a] δ is the vibronic mixing coefficient.

[b] $\|$, $=$, and $-|-$ correspond respectively to two photons absorbed along the short axis, two photons absorbed along the long axis, and one photon absorbed along the short axis, and the other photon absorbed along the long axis. If Paths (1)–(4) contribute, then $0.25 \leq C/L \leq 1.5$ and $0.20 \leq I_\perp/I_{||} \leq 3.0$. If Paths (5)–(8) contribute, then $C/L = 1.5$ and $I_\perp/I_{||} = 0.67$.

is proportional to

$$I_\perp(\text{total}) \propto \langle P_{gi,fl} 1_y X^2 \rangle_{\text{Av}} + \langle P_{ai,fl} 1_y X^2 \rangle_{\text{Av}}. \quad (27)$$

Having performed the averaging we write the ratio

$$R = \frac{I_\perp}{I_{||}} = \frac{2F^2 + 9D_{xx}^2 + 3D_{yy}^2 + 4D_{xx}D_{yy}}{3F^2 + 3D_{xx}^2 + 15D_{yy}^2 + 6D_{xx}D_{yy}}, \quad (28)$$

where F^2, D_{xx}, and D_{yy} are defined as before.

Taking the equations for Ω and R we now show that the ratios $F^2:D_{yy}^2:D_{xx}^2$ can be obtained. In this derivation we let $D_{xx} = \gamma D_{yy}$ and solve the two simultaneous equations for γ in terms of the two measurable terms Ω and R. A quadratic equation in γ results with solutions

$$\gamma = -[b \pm (b^2 - 4ac)^{1/2}]/2a, \quad (29)$$

where $a = (4-6\Omega)(3R-2) - (9-3R)(2\Omega-3)$

$b = (4+4\Omega)(2-3R) - (2\Omega-3)(4-6R)$

$c = (4-6\Omega)(3R-2) - (3-15R)(2\Omega-3)$.

A positive and negative root for γ emerge.

We now obtain F^2/D_{yy}^2 by substituting the values of γ in either of the two simultaneous equations (23) and (28). Since F^2 and D_{yy}^2 are squared moduli, their ratio, F^2/D_{yy}^2, must be greater than or equal to zero. As we find at a later point, this requirement eliminates the negative root of γ for anthracene and 9,10-dichloroanthracene.

We therefore can find, from the measured values of Ω and R and the equations developed, the relative contributions of (1) both photons absorbed along the short axis, (2) both photons absorbed along the long axis, and (3) one photon absorbed along the short axis and the other photon absorbed along the long axis. Knowing the relative importance of the three transition pathways the importance of the b_{2u} versus the b_{3u} mixing vibration can be obtained.

For linearly polarized exciting light the ratio of the transition probabilities for b_{2u} mixing to b_{3u} mixing using Eqs. (15) and (20) is

$$\left(\frac{P_{b_{2u}}}{P_{b_{3u}}}\right)_L = \frac{\langle P_{gi,fl} \rangle_{\text{Av}}}{\langle P_{gi,fl'} \rangle_{\text{Av}}} = \frac{3D_{xx}^2 + 3D_{yy}^2 + 2D_{xx}D_{yy}}{F^2}. \quad (30)$$

For circularly polarized exciting light the analogous ratio, using Eqs. (17) and (22) is

$$\left(\frac{P_{b_{2u}}}{P_{b_{3u}}}\right)_C = \frac{\langle P_{gi,fl} \rangle_{\text{Av}}}{\langle P_{gi,fl'} \rangle_{\text{Av}}} = \frac{4D_{xx}^2 + 4D_{yy}^2 - 4D_{xx}D_{yy}}{3F^2}. \quad (31)$$

These ratios and those developed earlier are useful in understanding the experimental results obtained from anthracene and 9,10-dichloroanthracene. Before proceeding with a discussion of the experimental results, we illustrate some values of the ratios R and Ω which arise in specific cases. In Table I the transition pathways which may arise with a b_{2u} mixing vibration are shown in Columns (1), (2), (3), and (4). The absorption axis for each pathway is shown. The corresponding values of Ω and R if this pathway alone is important, are also shown. If Pathways (1) through (4) contribute, the limiting values of Ω and R are indicated. These limiting values were deduced from Eqs. (23) and (28). Similarly the pathways resulting from a b_{3u} mixing vibration are shown in Columns (5)–(8). For b_{3u} vibrational mixing the values of R and Ω are not dependent on whether one or more pathways contribute. If both b_{2u} and b_{3u} vibrations are important in the two-photon absorption process, then it is clear from Eqs. (23) and (28) that the values of Ω and R depend on the relative contributions of F^2, D_{xx}^2, and D_{yy}^2. Therefore, to determine the relative importance of the b_{2u} vibration to the b_{3u} vibration, we must first obtain the relative values of F^2 to D_{xx}^2 to D_{yy}^2.

V. RESULTS AND DISCUSSION

A. Anthracene

The experimentally determined values for anthracene are $\Omega = 0.87 \pm 0.08$ and $R = 1.08 \pm 0.10$. Using these values of Ω and R we solve Eq. (29) for γ. The negative root of γ is discarded because it yields a negative value for F^2/D_{yy}^2, a quantity which must be positive. The positive root of γ is equal to 3.1. Therefore $D_{xx}^2=9.6D_{yy}^2$. We obtain $F^2/D_{yy}^2=31$ from either Eq. (23) or (28). Thus

$$F^2:D_{xx}^2:D_{yy}^2::31:9.6:1.$$

We can now utilize these ratios to discuss the transition pathways outlined in Table I.

Since the lowest B_{2u} state, acting as an intermediate state, has a lower energy denominator, Eq. (10), than the transitions involving the B_{3u} states as intermediate states, the paths (1), (2) and (5), (6) in Table I might appear to be favored. However, this energy denominator advantage for the B_{2u} intermediate state is offset by the larger transition moment of the $A_g\rightarrow B_{3u}$ vs the $A_g\rightarrow B_{2u}$ transition. Perhaps more importantly, the proximity of the lowest B_{3u} state, at 4.8 eV, to the theoretically calculated[15] A_g and B_{1g} excited states at about 5 eV would strongly enhance the vibronic mixing of the B_{3u} with the B_{1g} and A_g vs the lowest B_{2u} at 3.3 eV mixing with either the B_{1g} or A_g. These considerations are consistent with the relative values found for F^2, D_{xx}^2 and D_{yy}^2 for anthracene.

The experimental value of D_{xx}^2 to D_{yy}^2 indicates that, for the case of the b_{2u} vibration, the B_{3u} states are 10 times more important than the B_{2u} as intermediate states. We cannot similarly separate the B_{2u} and B_{3u} intermediate states for the case of b_{3u} mixing. But more importantly we can deduce the ratio of the cross sections for b_{2u} to b_{3u} mixing vibrations.

Substituting the values obtained for $F^2:D_{xx}^2:D_{yy}^2$ in Eq. (30) we find for the case of linearly polarized exciting light

$$(P_{b_{2u}}/P_{b_{3u}})_L=1.2.$$

For circularly polarized exciting light we obtain from Eq. (31)

$$(P_{b_{2u}}/P_{b_{3u}})_C=0.32.$$

We note from these values the strong dependence of the ratio of the transition probabilities on the polarization of the exciting light. A two-photon absorption to the final vibronic state containing a b_{2u} vibration is favored over absorption to the final vibronic state containing a b_{3u} vibration for linearly polarized light. For circularly polarized light the b_{3u} mixing vibration is strongly favored. We draw attention to the fact that the same values for F^2, D_{xx}^2, and D_{yy}^2 are used in Eqs. (30) and (31). The difference in the ratios arises from the result of averaging the direction cosines for the two different polarizations of the exciting light in a two-photon absorption process. Even if $F^2=D_{xx}^2=D_{yy}^2$, the different exciting polarizations would lead to different cross sections.

It is particularly interesting that the nature of the final vibronic state (b_{2u} or b_{3u} vibration) is dependent upon the polarization of the exciting light.

B. 9,10-Dichloroanthracene

The changes in the electronic structure of 9,10-dichloroanthracene compared with anthracene are not major ones. As in anthracene this molecule is of D_{2h} symmetry and has a B_{2u} state as its lowest electronic excited state. Although the lowest B_{2u} state has red shifted relative to anthracene's lowest B_{2u} state there is no appreciable difference in the $A_g\rightarrow B_{2u}$ transition strengths in these molecules. Similarly the $A_g\rightarrow B_{3u}$ transitions in these two molecules are of comparable intensities. We might anticipate therefore that the two-photon absorption would have similar characteristics for these molecules.

The experimentally determined values for 9,10-dichloroanthracene are $\Omega(C/L)=0.72\pm0.03$ and $R(I_\perp/I_{\parallel})=1.30\pm0.10$. Using the requirement $F^2/D_{yy}^2\geq 0$ we find, as we found for anthracene, that the negative root of γ must be discarded. The positive root of γ is 3.6. Hence, $D_{xx}=3.6D_{yy}$ and solving for F^2/D_{yy}^2 we obtain $F^2/D_{yy}^2=19$. Therefore,

$$F^2:D_{xx}^2:D_{yy}^2::19:13:1.$$

Using Eq. (30) we find that the ratio of the transition probabilities for linearly polarized light is,

$$(P_{b_{2u}}/P_{b_{3u}})_L=2.6, \qquad \text{linearly polarized light.}$$

For circularly polarized exciting light using Eq. (31) we find

$$(P_{b_{2u}}/P_{b_{3u}})_C=0.73, \qquad \text{circularly polarized light.}$$

Compared with anthracene these ratios have increased by roughly a factor of two. This indicates that in 9,10-dichloroanthracene the absorption of both photons along a given axis is more likely than in anthracene. However, for both molecules the final vibronic state containing the b_{2u} vibration is favored for circularly polarized light.

It can be noted that the value of the b_{2u} to the b_{3u} final vibronic state transitions for linearly vs circularly polarized light is about the same for anthracene and 9,10-dichloroanthracene. In other words the ratio of Eq. (30) to Eq. (31) for both molecules is roughly equal to 4. This is not surprising since this ratio is only a function of γ which is nearly equal (3.1 vs 3.6) for the two molecules.

At this point it might be profitable to compare the findings for anthracene and 9,10-dichloroanthracene. The qualitative features for the two molecules, i.e., the ratios of the matrix elements and the relative importance of the b_{2u} to the b_{3u} mixing vibration, are similar. For the b_{2u} mixing vibration, which corresponds to a final vibronic state of A_g symmetry, the B_{3u} are more important than the B_{2u} as intermediate electronic states. We have offered an explanation for this result in terms of (1) the stronger $A_g\rightarrow B_{3u}$ transition and (2) the enhanced vibronic mixing of the lowest B_{3u} state due to its proximity to B_{1g} and A_g states. A unique feature of two-photon absorption, as demonstrated by these two molecules, is the polarization dependence of the absorption cross section. This is true even for a system of randomly oriented molecules.

VI. SUMMARY

In this paper we have developed a theoretical framework which can be applied to two-photon absorption in aromatic molecules. We have applied this treatment to the absorption of two ruby laser photons by anthracene and 9,10-dichloroanthracene. The theory is developed subject to the following assumptions:

(1) Only electric dipole transitions are considered.

(2) Only in-plane transitions are included. The out of plane transitions are much weaker and are at much higher energies than the lower $\pi\pi^*$ states.

(3) For the application to anthracene and 9,10-dichloroanthracene it is assumed that there is only one electronic state, the B_{2u} state, at twice the energy of a ruby photon.

With these limitations in mind we have:

(1) Extended the theory of two-photon absorption to include the vibronic mixing between different electronic states.

(2) Derived expressions which relate the possible transition pathways to the following experimental quantities. First, the relative absorption cross sections of linearly versus circularly polarized exciting light and second, the polarization on the fluorescence resulting from two-photon excitation by linearly polarized light.

(3) Determined for anthracene and 9,10-dichloroanthracene the relative contributions of the three possible pathways:

(a) both photons absorbed along the long axis,
(b) both photons absorbed along the short axis,
(c) one photon absorbed along the short axis and the other photon absorbed along the long axis.

(4) Determined for anthracene and 9,10-dichloroanthracene the relative contributions of the possible final vibronic states (one containing a b_{2u} vibration and the other a b_{3u} vibration) to the absorption of two ruby photons.

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Temperature Dependence of the Raman Spectrum of $SrTiO_3$ and $KTaO_3$*

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The temperature dependence of the second-order Raman spectrum of $SrTiO_3$ and $KTaO_3$ has been observed over the temperature range 4°–473°K using the mercury 4358-Å exciting line. From group-theoretical arguments for cubic perovskite lattices the spectra have been interpreted in terms of phonon pairs at critical points in the Brillouin zone using the experimental and theoretical dispersion curves determined by Cowley for $SrTiO_3$. Limited neutron data are available for $KTaO_3$, but the spectrum has been interpreted by analogy with the results for $SrTiO_3$. The energies of the phonon branches at the critical X point in the Brillouin zone have been deduced from the observed Raman spectra.

INTRODUCTION

The Raman spectrum of single crystals of $SrTiO_3$ and $KTaO_3$ has been observed from 30–1200-cm^{-1} frequency shift from the 22 938 cm^{-1} mercury "*e*" line over the temperature range 4°–473°K. The temperature dependence of the Raman spectrum of ferroelectric $BaTiO_3$ has been measured previously and for this material the bands were primarily interpreted as a first-order spectrum.[1] The room-temperature Raman spectrum of $SrTiO_3$ has been previously reported by Narayanan and Vedam[2] and their experimental results are in qualitative agreement with our measurements. Both $SrTiO_3$ and $KTaO_3$ are paraelectric cubic crystals at room temperature and apart from a slight structural change in $SrTiO_3$ at 110°K[3] and a possible phase transition in $KTaO_3$ at about 10°K,[4] no observation

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