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TWO-PHOTON EXCITATION, HYPER-RAMAN SCATTERING, AND EXCITED STATE DECAY PROCESSES FOR POLYENES IN FREE JET EXPANSIONS

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Abstract - High resolution emission spectra, 1-photon and 2-photon excitation spectra, vibronic level decay times and saturation behavior have been measured for the polyenes diphenylbutadiene and diphenylhexatriene seeded in supersonic helium expansions. For isolated diphenylbutadiene hyper-Raman scattering enhanced by 2-photon resonances has also been observed. Taken together these data provide a detailed picture of the nature of the most probable intramolecular excited state decay processes as a function of vibronic energy for these flexible molecules.

I - INTRODUCTION

The electronic structure of conjugated linear polyenes is fundamental to understanding more complicated systems ranging from the visual pigment rhodopsin to conjugated polymers such as polyacetylene and the polydiacetylenes. It is reasonable to expect that the condensed phase photophysical and photochemical behavior of these molecules may be described in terms of intrinsic molecular potentials and, perhaps, the modification of these potentials by intermolecular interaction. However, while much is known about the relevant potential energy surfaces of many polyenes in the condensed phase [1], the role of intermolecular interactions in determining these potentials has been hard to evaluate because of the lack of detailed information on the isolated molecules. Accordingly, we have started to measure optical spectra for linear polyenes seeded in free jet expansions [2-8]. This paper summarizes some of the data that has been obtained for the symmetrically substituted polyenes diphenylbutadiene [3,6,8] and diphenylhexatriene [4,7] seeded in supersonic expansions of helium. Under our experimental conditions, highly structured spectra are observed. From the fluorescence spectra, 1-photon and 2-photon fluorescence excitation spectra, and the time dependence of the total emission it is clear that: 1) $^2\text{B}^\text{a}$ is the lowest energy excited singlet state for both molecules. 2) With increasing vibrational excitation in the excited electronic state there is increasingly rapid

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dephasing from the state initially prepared by the photon. 3) In diphenylbutadiene an extremely efficient radiationless decay channel appears at 1300 cm\(^{-1}\) above the 2\(^1\)A\(_g\) O-O. No such channel is seen in diphenylhexatriene up to 5200 cm\(^{-1}\) above the 2\(^1\)A\(_g\) O-O. 4) In the case of 2-photon excitation (so far only done for diphenylbutadiene), in addition to fluorescence, incoherent scattering at twice the laser frequency minus a vibrational Stokes shift is observed when the exciting laser is tuned to 1\(^1\)A\(_g\) - 2\(^1\)A\(_g\) 2-photon resonances. We ascribe this to 2-photon resonance enhanced hyper-Raman scattering.

II - EXPERIMENTAL

Diphenylbutadiene and diphenylhexatriene were obtained from Aldrich Chemical Company and further purified by vacuum sublimation. HPLC using an alumina column and absorbance detection showed that both compounds were free from impurities that absorbed in the region of our measured excitation spectra.

Gram quantities of the diphenylpolyenes were packed into a heated stainless steel tube that was part of the helium supply line for the nozzle. The source was heated to obtain diphenylpolyene pressures of less than 1 torr (140 C for diphenylbutadiene, 172 C for diphenylhexatriene), seeded into helium gas at 8-12 atm and then expanded through a 200 micron diameter nozzle (heated to 190 C to prevent clogging) into a chamber that maintained pressure at .35 torr. The jet was intersected at a right angle to the expansion direction approximately 3 mm from the nozzle by the laser beam (N\(_2\) or Nd-YAG pumped dye laser) and a f/1 mirror whose axis was perpendicular to both the laser beam and the jet flow direction focussed the interaction region into the detection system. The detection system consisted of filters to isolate the wavelength region of interest followed by a cooled photomultiplier tube. For recording the emission spectra, a monochromator was inserted between the filters and the photomultiplier. Photocurrent versus time from this photomultiplier was either captured directly by a Tektronix 7912AD transient digitizer for determining the decay profiles or integrated by an electrometer set to Coulomb mode for the excitation and emission spectra. Data were collected and processed by a HP 9835A microcomputer. Further experimental details are to be found in previous papers [2-8].

III - RESULTS AND DISCUSSION

1. Diphenylhexatriene

The absorption spectrum for diphenylhexatriene vapor at room temperature is shown in Figure 1.

Fig. 1 - Absorption spectrum of diphenylhexatriene vapor at 441 K in a 5 cm path length cell. Full scale corresponds to an optical density of approximately 1.5.
At this level of resolution, only the symmetry allowed $S_0 \rightarrow S_2 (1^1A_g \rightarrow 1^1B_u)$ transition is seen (0-0 at 29,157 cm$^{-1}$). When diphenylhexatriene is seeded into the supersonic expansion, there is a dramatic increase in the information content of the observed spectra as seen in Figure 2.

Fig. 2 - Fluorescence excitation spectrum of diphenylhexatriene seeded in a supersonic helium expansion. The lowest energy intense band at 29,157 cm$^{-1}$ is the $1^1A_g-1^1B_u$ 0-0. The weak sharp features going to lower energy come from vibronically induced $1^1A_g-2^1A_g$ absorption.

In this excitation spectrum the symmetry allowed $1^1A_g$ to $1^1B_u$ transition sharpens considerably allowing a number of vibronic features to be unambiguously assigned. Additionally, a set of weak sharp features can be seen going to lower energy from the $1^1A_g$ to $1^1B_u$ 0-0. These weak excitation bands belong to the symmetry forbidden $S_0 \rightarrow S_1 (1^1A_g \rightarrow 2^1A_g)$ transition and derive intensity through vibronic coupling.

From a detailed vibrational analysis [4] it is clear that the lowest energy 1-photon excitation feature at 29,742 cm$^{-1}$ is not the 0-0 band but comes from absorption from the zero point level of the ground state to a level in the excited state where 1 quantum of a 27 cm$^{-1}$ odd-symmetry vibration is excited. This confirms that this weak series of absorption bands belong to a symmetry forbidden transition and establishes that the equilibrium nuclear geometry is centrosymmetric in both the $1^1A_g$ and $2^1A_g$ states.

The time dependence of the fluorescence integrated over frequency is well fit by the convolution of a single exponential decay with the time profile measured for the laser pulse. The lifetimes for this exponential decay as a function of the amount of vibrational energy created in the excited state are shown in Figure 3.
Fig. 3 - Fluorescence decay lifetimes as a function of excitation energy relative to the $1^{1}A_g-2^{1}A_g$ 0-0 for diphenylhexatriene seeded in a supersonic helium expansion. The 4 points at highest energy (right hand side of the figure) correspond to excitation into the origin and higher lying vibronic features of the $1^{1}A_g-1^{1}B_u$ transition. The line that connects the points is merely a visual aid.

At low vibrational excitation the fluorescence spectra have the appearance of the excitation spectrum reflected through the laser wavelength. All of the decays measured for excitation into the $2^{1}A_g$ state are relatively long as expected for a symmetry forbidden transition. The gradual shortening of the observed lifetime with increasing vibrational energy is consistent with the increased absorption strength as the vibronically coupled $1^{1}B_u$ state is approached.

Long decays are also observed for excitation into the symmetry allowed $1^{1}B_u$ state (the last four points in Figure 3). In fact, the decay time measured for excitation into the $1^{1}B_u$ 0-0 of 48 nsec is more than an order of magnitude longer than the decay time derived from the integrated absorption intensity. The reason for this is clearly seen in the fluorescence spectrum for excitation into the $1^{1}B_u$ 0-0 shown in Figure 4.

Fig. 4 - Fluorescence from diphenylhexatriene seeded in a supersonic helium expansion for excitation at the $1^{1}A_g-1^{1}B_u$ 0-0. The sharp feature at 29,157 cm$^{-1}$ is due to stray light from the excitation laser. The monochromator bandpass was 12 Angstroms.
Even though the molecules are isolated and, hence, energy is conserved, the emission spectrum observed for $^{11}B_u$ excitation bears no relation to the mirror image of the $^{11}A_g$ to $^{11}B_u$ absorption spectrum. It does, however, have considerable overlap with the mirror image of the $^{11}A_g$ to $^{21}A_g$ absorption spectrum showing that, following excitation into a vibronic level of the $^{11}B_u$ state, there is rapid relaxation into the dense bath of isoenergetic $^{21}A_g$ vibronic levels which, by the Franck-Condon principle, emit to highly excited vibronic levels of the $^{11}A_g$ state.

2. Diphenylbutadiene

As in the case of diphenylhexatriene, the fluorescence excitation spectrum of diphenylbutadiene sharpens considerably when these molecules are seeded into a supersonic helium expansion (Figure 5).

![Fluorescence excitation spectra for diphenylbutadiene seeded in a supersonic helium expansion](image)

Fig. 5 - Fluorescence excitation spectra for diphenylbutadiene seeded in a supersonic helium expansion. In the case of 2-photon excitation (upper spectrum) the spectrum has been plotted against 2 times the laser energy.

However, in sharp contrast to the situation for diphenylhexatriene it is not possible to measure fluorescence excitation spectra beyond the $^{11}A_g$ to $^{11}B_u$ 0-0 at approximately 30,800 cm$^{-1}$ due to the onset of a fast radiationless channel. In the case of 1-photon excitation, the fluorescence decays are again well fit by the convolution of a single exponential decay with the measured laser pulse profile. The appearance of the radiationless decay channel at approximately 1300 cm$^{-1}$ above the $^{11}A_g \rightarrow 2^{1}A_g$ O-O is evident in the rapid decrease of fluorescence lifetime with vibrational excitation as is shown in Figure 6.

When fluorescence is excited by 2-photon absorption, additional information on the $^{21}A_g$ excited state is obtained (Figure 5). First of all, the 1-photon and 2-photon excitation spectra are complementary in the sense that they have no lines in common. This confirms the symmetry forbidden nature of the transition and establishes that, in their equilibrium configurations, the $^{11}A_g$ and $^{21}A_g$ states are strictly centro-symmetric. Second, fluorescence decay times are approximately twice as long for 2-photon excitation within 150 cm$^{-1}$ of the O-O band as for 1-photon excitation in the same energy region (Figure 6). This is expected on the basis of vibronic coupling arguments as sketched in Figure 7.
Fig. 6 - Fluorescence decay lifetimes as a function of excitation energy relative to the $1^1A_g - 2^1A_g$ 0-0 for diphenylbutadiene seeded in a supersonic helium expansion. The points plotted as *'s are for 2-photon excitation and those plotted as I's are for 1-photon excitation. The lines connecting the points are visual aids only.

Fig. 7 - Selection rules for the symmetry forbidden $1^1A_g - 2^1A_g$ transition for molecules initially in the zero-point level of the ground state. 1-photon excitation prepares an odd-symmetry vibronic level in the excited state while 2-photon excitation is to an even symmetry vibronic level. Thus, for the fluorescence from isolated molecules, the odd symmetry intensity inducing vibronic level is in the excited state for 1-photon excitation and in the ground state for 2-photon excitation.
The coalescence of the fluorescence decay times for 1-photon and 2-photon excitation at higher vibrational energies reflects the onset of a dephasing process that scrambles g and u symmetry labels on the timescale of the fluorescence decay. It is reasonable to postulate that this is due to some sort of large amplitude motion such as internal rotation. The onset of this dephasing is also evident in the fluorescence spectra which change abruptly as the degree of vibrational excitation is increased beyond 150 cm$^{-1}$.

Third, and perhaps most striking, the fluorescence decay profiles for 2-photon excitation show two components (Figure 8).

![Fluorescence Decay Profiles](image)

Fig. 8 - Time profiles at different excitation energies for light at 2 times the excitation laser frequency minus a Stokes shift of 1000 cm$^{-1}$ to 9000 cm$^{-1}$ for diphenylbutadiene seeded in a supersonic helium expansion. The excitation frequencies for curves a, b and c are labeled in Figure 5.

One component (normal fluorescence as discussed above) decays exponentially with a measurable lifetime. The other component exactly tracks the time profile of the exciting laser within our experimental error of approximately 0.2 nsec. The spectrum for two photon excitation at 15,430 cm$^{-1}$ (0.8 prompt emission and 0.2 normal fluorescence) is shown in Figure 9.

The decay time and yield for the normal fluorescence decrease with increasing vibrational excitation reflecting the increasing rate of radiationless decay. The persistence of the prompt emission for 2-photon excitation energies well above the threshold for radiationless decay for either g or u vibrational levels together with the geometry of the experiment argue that the prompt emission must be explained in terms of an incoherent scattering process.

In hyper-Raman scattering, the scattered photons have twice the energy of the incident photons minus a vibrational Stokes shift.
Spectrum of Scattered Light

Fig. 9 - Spectrum of scattered light for 2-photon excitation of diphenylbutadiene seeded in a supersonic helium expansion. The excitation laser was set at 15,430 cm⁻¹.

Hyper-Raman scattering is enhanced by 2-photon resonances in an analogous way to the way in which normal Raman scattering is enhanced by 1-photon resonances. Further, for a strongly allowed 2-photon transition it can be shown that the intensity of hyper-Raman scattering should be comparable to the intensity of fluorescence excited by 2-photon absorption [6]. Thus, there is close agreement between all properties associated with the prompt emission (the spectral distribution of the scattered light, the temporal profile, the excitation profile and the intensity relative to 2-photon excited fluorescence) and the properties expected for hyper-Raman scattering. This correspondence together with the failure of kinetic schemes proceeding out of excited 2¹A₉ levels (with or without dephasing) to account consistently for all of the observations is the basis for attributing the prompt process to hyper-Raman scattering enhanced by 2-photon resonance.

IV - CONCLUSIONS

From these preliminary studies it is clear that: 1) Highly resolved electronic spectra can be obtained for isolated flexible molecules like the linear polyenes using free-jet expansion techniques. 2) These spectra show that the lowest energy excited singlet state in isolated diphenylbutadiene and hexatriene is 2¹A₉ and that the difference in energy between 2¹A₉ and 1¹B₈ increases with increasing chain length. 3) From the vibrational development of the 1¹A₉ to 2¹A₉ spectra (in particular, the 1-photon forbidden 2-photon allowed character of the O-O) it is clear that in the isolated molecules the relaxed equilibrium geometry is centrosymmetric in both 1¹A₉ and 2¹A₉. 4) As the degree of vibrational excitation in the excited state is increased, rapid vibrational energy redistribution is observed. This shows up in kinetic as well as spectroscopic measurements. 5) In the case of 2-photon excitation, prompt scattering at two times the laser frequency minus a vibrational Stokes shift is observed. This is interpreted as hyper-Raman scattering enhanced by the strong 1¹A₉ → 2¹A₉ resonances. 6) Using the low temperature isolated molecule conditions
that obtain in free-jet expansions it should be possible to combine linear and non-linear spectroscopies to obtain a detailed picture of intramolecular relaxation processes in these systems.

V - REFERENCES