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TWO-PHOTON ABSORPTION SPECTROSCOPY OF POLYENES.(U)
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Two-Photon Absorption Spectroscopy of Polyenes

(12)

Final Report

by

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March 1977

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Two-Photon Absorption Spectroscopy of Polyenes

I. Foreward

The question addressed by this project was a basic one concerning the behavior of a class of biologically important molecules under the action of high-intensity laser light. The polyenes were chosen for study because there was reason to suspect from their known structure and spectroscopy that they would have a large non-linear response to the electromagnetic field of an optical laser.

This initial guess has been very nicely borne out. The molecular two-photon absorptivities measured for polyenes in the course of this project are the largest ever measured for any class of molecules. The two-photon spectra of these molecules raise extremely interesting further questions about the structure may play in photosynthesis and in vision.

II. Body of Report

A. Financial

The direct cost monies expended totaled \$55,132. The bulk of this (63.3%) was spent for salaries and fringe benefits for the investigators. A smaller fraction (17.2%) was spent for expendable items, mainly special optical coatings for laser mirrors. Only 12.2% was spent for permanent equipment. Items bought include a teletype for our data acquisition system and analog-to-digital conversion equipment. This grant allowed my lab to undertake work which would have been prohibitively slow without digital data acquisition and impossible without the manpower.

Workers who were supported were

1. Donald M. Friedrich, Ph. D.
2. Ronald P. Drucker, Ph. D.
3. Thomas M. Stachelek, soon to receive his Ph. D.
4. Wm. Martin McClain, P. I.
5. Nobuki Kanamaru, Ph. D.
6. Lawrence Jack, Lab Assistant

B. Scientific

The best way to report the science done on this grant is to quote the abstracts of a number of the papers written by the above-named workers while supported by AROD.

I would like particularly to call attention to the papers co-authored by D. M. Friedrich. These papers contain the first use of polarization methods to identify the absorption peaks of a highly resolved gas-phase spectrum, which promises to be the standard method for all such work in the future.

1. "Polarized two-photon studies of biphenyl and several derivatives", R. P. Drucker and W. M. McClain, *J. Chem. P.* 61, 2609 (1974).

The two-photon absorption spectrum of biphenyl dissolved in CCl_4 is reported, using both the absolute two-photon absorption technique and the two-photon excited fluorescence technique. Polarization methods were used which permit the strong two-photon absorptions to be assigned without resort to any subsidiary vibrational analysis. We find that the lowest singlet of biphenyl is a B state (in group D_2 , with twisted rings); its band stretches from about $33,000\text{-}36,000\text{ cm}^{-1}$, well to the red of the lowest strong one-photon spectroscopy in the $42,000\text{-}45,000\text{ cm}^{-1}$ region. Other A states are also possibly present. Two-photon spectra of 4,4' dichlorobiphenyl, 4,4' difluorobiphenyl, 2,2' bipyridine, 2,2' difluorobiphenyl, and terphenyl are also given and discussed.

2. "Dye laser two-photon excitation study of several o,o'-bridged biphenyls", R. P. Drucker and W. M. McClain, *J. Chem. Phys.* 61, 2616 (1974).

Polarized dye laser two-photon excitation spectra are reported for the following series of o,o'-bridged biphenyls: fluorene, dibenzofuran, dibenzothiophene, carbazole, and phenanthrene. Two-photon polarization selection rules are used to assign the peaks observed. Several new states are reported and a number of tenuous assignments in the literature are confirmed. The spectra of the bridged compounds are compared with the biphenyl two-photon spectrum.

3. "Two-Photon Absorption in 'Double Molecules'", R. P. Drucker and W. M. McClain, *Chem. Phys. Lett.* 28, 255 (1974).

The two-photon excited fluorescence excitation spectrum is reported for naphthalene and 2,2'-binaphthyl, and for fluorene and difluorenyl. These results are compared with the previously reported results for benzene and biphenyl. The exciton approximation predicts that the two-photon spectra of such single and double molecules should resemble each other quite closely, even in cases where the one-photon spectra are quite different. However, this behaviour is not observed in the reported compounds.

4. "Polarization and Assignment of the Two-Photon Excitation Spectrum of Benzene Vapor", D. M. Friedrich and W. M. McClain, *Chem. Phys. Lett.* 32, 541 (1975).

(4) The two-photon excitation (TPE) of benzene fluorescence in the vapor phase at 60 torr is reported for the total-energy region from $38,086 \text{ cm}^{-1}$ to $42,441 \text{ cm}^{-1}$ using both circular and linear polarized light from a nitrogen-pumped dye-laser. The theory of the polarization dependence of the vibronic transitions in benzene is briefly reviewed, and it is seen how transitions involving vibrations of b_{1u} symmetry are expressly forbidden for this type of TPE experiment in which the two photons are identical. Five vibronic origins with distinctive rotational contours and polarization dependence are identified in the TPE spectrum. The $\nu_{14}(b_{2u})$ vibronic origin at 1570 cm^{-1} (above the electronic origin of the ${}^1B_{2u}$ state) stands out very prominently in the linear polarized spectrum, but nearly disappears in the circular polarized spectrum. This striking polarization dependence indicates a significant contribution of A_{2u} electronic states to the intermediate states of this TPE vibronic transition. The relatively great strength of the ν_{14} band may be due to vibronic borrowing by the b_{2u} mode from the ground electronic state (A_{1g}).

5. "The Effect of Spatial and Temporal Laser Beam Characteristics on Two-Photon Absorption", R. L. Swofford and W. M. McClain, Chem. Phys. Lett. 34, 455 (1975).

We present calculations which indicate possible sources of error in the determination of two-photon absorptivity introduced by the choice of experimental conditions. Both the direct absorption experiment and the two-photon excitation experiment are considered. We include the effects of beam alignment, diffraction-limited focusing, and pulse width variation on the observed two-photon absorptivity.

6. "Rotational Contours and Isotope Effects in the Two-Photon Excitation of Benzene Vapor", J. R. Lombardi, D. M. Friedrich and W. M. McClain, Chem. Phys. Lett. 38, 213 (1976).

Rotational contour calculations up to $J = 100$ are compared to experiment for the line $14_0^1(b_{2u})$ in the vibronic two-photon excitation of ${}^1B_{2u}$ benzene. The results require reassignment of modes 19 (e_{1u}) and 15 (b_{2u}) to frequencies 1330 cm^{-1} and 1143 cm^{-1} in C_6H_6 (1209 cm^{-1} and 811 cm^{-1} in C_6D_6). Previously unassigned line families in C_6D_6 are attributed to the carbon-heavy isotope ${}^{13}C_1{}^{12}C_5D_6$.

7. "Two-Photon Excitation Spectra of the Low Energy Excited States of Diphenylhexatriene and Diphenyloctatetraene", G. R. Holtom and W. M. McClain, Chem. Phys. Lett. 44, 436 (1976).

All-trans diphenylhexatriene and diphenyloctatetraene in solution show a very strong two-photon absorption beginning at about the same energy as the one-photon spectrum. This supports the postulated presence of a low-lying 1A_g electronic state.

8. "Detection and Assignment of the 'Phantom' Photochemical Singlet of Trans-Stilbene by Two-Photon Excitation", T. M. Stachelek, T. A. Pazoha, W. M. McClain and R. P. Drucker, J. Chem. Phys. __, xxxx(1977).

We have made a complete polarization study of the two-identical photon excitation (TIPE) spectrum of stilbene in solution in the energy region $34,400 \text{ cm}^{-1}$ to $45,000 \text{ cm}^{-1}$ which shows a strongly allowed two-photon transition with a maximum at $41,000 \text{ cm}^{-1}$. The upper state of this transition is of over-all symmetry A_g . We believe that the electronic part of the upper state is also of A_g symmetry and that it is identifiable with the "phantom" singlet state postulated by Saltiel and by Orlandi and Siebrand as the major pathway for cis-trans photoisomerization of this molecule.