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Two-Photon Excitation Spectra of Polycyclic Aromatic Hydrocarbonst

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Two-photon excitation spectra of several polycyclic aromatic hydrocarbons are presented and compared to the corresponding one-photon results. The specific molecules are chosen to demonstrate the range of selection rule changes that are possible, and the sensitivity that the spectra show toward alkyl substitution patterns.

KEY WORDS: Fluorescence, lasers, PAH.

INTRODUCTION

Two-photon spectroscopy is a nonlinear optical phenomenon involving the simultaneous absorption of two quanta from a radiation field. Such excitation provides a variety of new capabilities for fluorescence based analytical techniques. First, there are major changes in the selection rules which govern the strength of various transitions.¹ Thus, excitation spectra may be generated which complement the normal one-photon results. Second, unlike one-photon polarization studies which must be performed with single crystals, two-photon excitation often allows the identification of transition symmetry for randomly oriented samples.² Third, two-photon induced fluorescence has been shown to have unique analytical capabilities, such as quantifying molecular species in the presence of high and/or varying matrix absorbance,³ or selective excitation of molecules based on excited state symmetry.⁴

[†]Presented at the 10th Symposium on the Analytical Chemistry of Pollutants, Dortmund GFR, May 28-30, 1980.

In this paper attention will be focused on the first analytical capability. The spectra of fluorene, *p*-bis(0-methylstyryl)benzene (bis-MSB), phenanthrene and naphthalene will be compared to demonstrate the range of selection rule changes that are possible between one- and two-photon excitation. In addition, the spectra for a series of methylnaphthalenes will be presented to demonstrate the sensitivity of the two-photon process to substitution patterns.

EXPERIMENTAL

Chemical

Fluorene, bis-MSB, and phenanthrene were Eastman scintillation grade; naphthalene was Baker scintillation grade; and all methylnaphthalenes were Aldrich gold label. The cyclohexane used as the solvent was Burdick and Jackson glass distilled.

The quality of the spectral data was optimized by utilizing solution concentrations near 0.1 M.

Instrumental

Single frequency excitation was obtained using a Coherent CR-669-21 actively stabilized ring dye laser system. Output powers of greater than 1 W of single-mode free-running radiation are attainable with an effective line-width of less than 1 MHz rms, using rhodamine 6G dye pumped by all lines of a Coherent Model CR-8 supergraphite argon ion laser. The tuning range was 570 to 620 nm with a maximum power of 1.3 W of stable single-mode 578 nm radiation with 8.0 W of pump power. The selected mode for each desired wavelength of radiation was locked and monitored with a Tropol Spectrum Analyzer Model 240 interferometer and Model 251 controller.

Excitation powers were measured using a Coherent Model 210 power meter or a Laser Precision Corporation Model RK-5100 radiometer.

The laser beam was focused into the sample cell, with the focal plane close to the collection side of the cell to reduce reabsorption effects. The fluorescence emission was collected by a quartz lens (*f*/1.5) focused into the slit of an ISA DH-10 double monochromator. The entrance and exit slits were 2 mm, giving a spectral bandpass of 8 nm.

The fluorescence was detected by an EMI 9558 13-stage photomultiplier tube cooled to -20°C . This signal was digitized using a Pacific Photometric Model 124 digital photometer. A schematic of the experimental arrangement is shown in Figure 1.

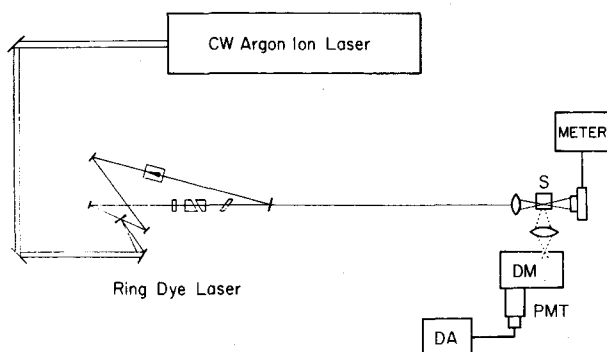


FIGURE 1 Schematic of experimental arrangement: DA, digital picoammeter; DM, double monochromator; METER, optical power meter; PMT, cooled photomultiplier; and S, sample.

A Cary 17D spectrophotometer was used to obtain the one-photon absorption spectra.

Procedures

To obtain an uncorrected two-photon excitation spectrum, the monochromator was adjusted to an emission maximum and the signal was measured as a function of dye laser wavelength. Since the molecules studied have no features finer than 5 nm in width, the dye laser was stepped in 2 nm increments. At each of these wavelengths adjustments were made to produce single frequency operation. To correct the spectrum for laser intensity variations, the average power of the excitation beam was squared and divided into the photometer reading. Although the entire procedure was manual, automation of the instrument should be quite simple.

RESULTS AND DISCUSSION

Choice of excitation source

In two-photon excited fluorescence spectroscopy using a single source, the detected response must be corrected for the square of the incident intensity. Thus the rate of absorption is given by

$$A = C \langle I(t)^2 \rangle$$

where C is a group of constants, $I(t)$ is the instantaneous intensity, and the brackets represent a time average. Since $I(t)$ is usually difficult to determine, some measurable parameter related to it is usually employed. The most common choice is the average intensity, $\langle I \rangle$, of the beam. The resultant rate expression is then given by

$$A = Cg^2(0)\langle I \rangle^2$$

where $g^2(0)$ is the second order coherence of the beam.

Two-photon spectra have been obtained using many types of lasers including both pulsed or cw excitation. Unfortunately most such devices share a common drawback in that the value of $g^2(0)$ either varies from pulse to pulse and/or with wavelength, making any correction difficult. For the work reported in this paper we chose to utilize a single-mode laser where $g^2(0)$ is always unity. As a result, accurate two-photon excitation spectra can be obtained by dividing the fluorescence response by the average intensity squared. For relative two-photon spectra, this simplifies to a correction using the average power squared, since the laser beam diameter at the focus within the sample can be kept constant while scanning the excitation wavelength.⁵

Allowed/allowed transitions

As mentioned previously, there are major differences in the development of selection rules for one- and two-photon spectroscopy. The most clear-cut distinction occurs when the molecule has a center of symmetry. For this case, one-photon absorption occurs between states of opposite parity ($g \leftrightarrow u$) while two-photon absorption occurs between states of identical parity ($g \leftrightarrow g$ or $u \leftrightarrow u$). For molecules without a center of symmetry the distinction is less clear and must be ascertained on a case-by-case basis. The worst situation occurs when one particular transition is allowed by both methods of excitation and there are no nearby states with changing selection rules to modify the spectrum. The 32–35 kK region of fluorene provides such an example. As can be seen in Figure 2, the one- and two-photon spectra are nearly identical with only an ~ 0.2 kK shift in the principle band and some minor peak height changes in the 34–35 kK region. Although this is the closest agreement between spectra that we have observed, there is no reason to assume that a larger spectral range would maintain the same degree of similarity. The strength of the two-photon transition was not quantitatively determined, but was observed to be strong. The one-photon transition had $\epsilon \sim 10,000$ which could also be labeled strong.

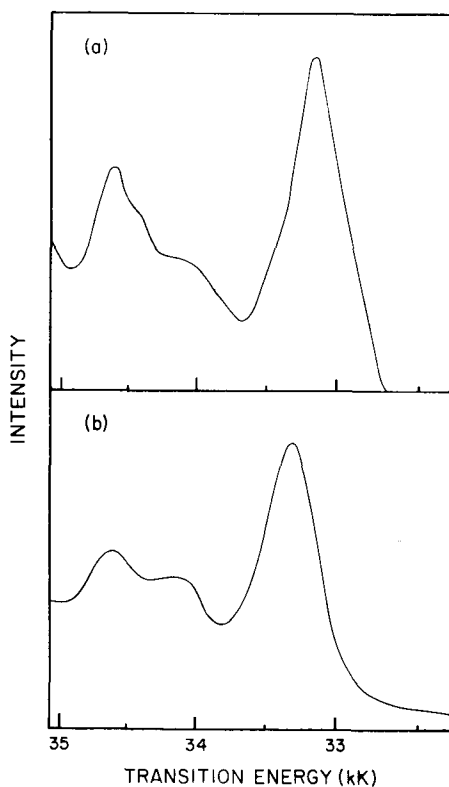


FIGURE 2 Fluorene excitation spectra. (a) Two-photon, and (b) one-photon.

Allowed/forbidden transitions

For identifying a compound the ideal situation would be represented by excitation spectra derived from mutually exclusive sets of transitions. This would be expected to occur most often in molecules containing a center of symmetry. An excellent example for the 32–35 kK region is bis-MSB. Figure 3 shows a very small region of the overall range of absorbing wavelengths which starts near 25 kK and extends down into the middle ultraviolet. The one-photon transition is represented only by a smooth monodirectional curve since the single band maximum occurs at 29 kK. Although the data are incomplete, the two-photon transition seems to peak near 34.5 kK. In both cases the bands are very broad, ~ 5 kK, and featureless. The two-photon transition is the strongest we have ever

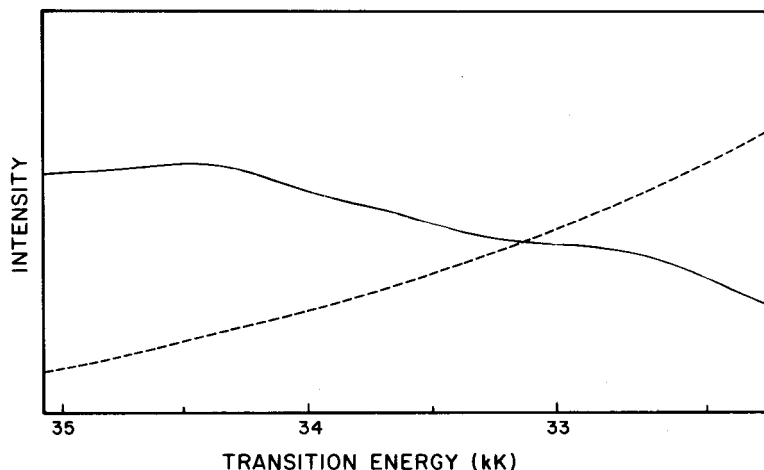


FIGURE 3 Bis-MSB excitation spectra. — Two-photon, and --- one-photon.

observed. This correlates quite well with the very large one-photon molar absorptivity of $\epsilon \sim 60,000$.

Phenanthrene is an example of a non-centrosymmetric molecule having transitions with both allowed and forbidden character. As can be seen from Figure 4, the one photon spectrum has a strong band near 34.2 kK ($\epsilon \sim 15,000$) and a weak vibronic progression from 33 kK on toward the red ($\epsilon \sim 300$). On the other hand, the two-photon excitation is strong near 33 kK, drops to almost zero at 33.3 kK and then slowly rises toward higher frequencies. Note the absence of any clear evidence for the presence of the one-photon 34.2 kK band in the two-photon spectrum.

Forbidden/forbidden transitions

In many cases a transition which is forbidden by a selection rule will appear in a spectrum as a low intensity set of vibronic bands. This occurs because a particular vibration can deform the molecule into a shape belonging to a symmetry group where that particular electric transition is allowed. Because of selection rule differences, a transition forbidden with both types of excitation can have dissimilar one- and two-photon vibronic band patterns due to different deformation shape requirements. The classic example of such a transition occurs in the 32–35 kK region of the naphthalene spectrum. Unfortunately, a nearby allowed transition in the one-photon case so dramatically alters the spectrum that this particular point is difficult to demonstrate with the raw data.⁶ To visually enhance any similarity of the two curves, Figure 5 shows this region of the

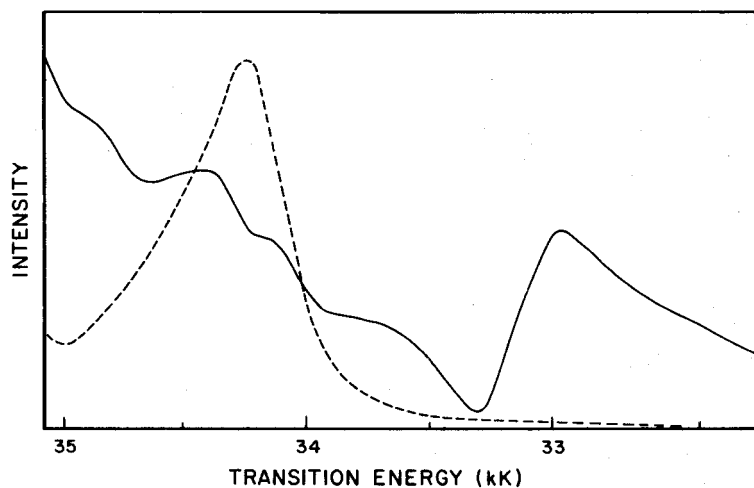


FIGURE 4 Phenanthrene excitation spectra. — Two-photon, and --- one-photon.

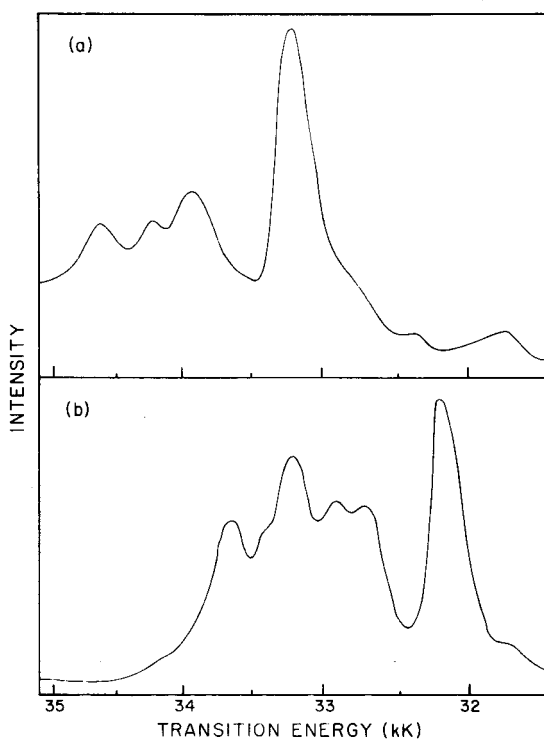


FIGURE 5 Naphthalene excitation spectra. (a) Two-photon, and (b) one-photon (background removed).

spectrum with the strong one-photon transition subtracted from the total absorbance. After such mathematical treatment of the data it is easy to see that the positions and spacing of the vibronic bands have changed. Again, these spectral differences are caused by the specific vibrations required to properly deform the molecule into a shape permitting electronic excitation. The strength of this transition is weak with both one-photon ($\epsilon \sim 300$) and two-photon excitation.

Changes with alkyl substitution

In general alkyl substitution would be expected to produce a red shift and follow substitution pattern rules analogous to those given for one-photon spectral changes. For fluorene, 2-methyl substitution red shifts the one-photon spectrum about 0.45 kK and the two-photon spectrum about 0.3 kK. No major changes are produced in the band shape. For naphthalene, 1- and 2-methyl substitution red shifts both the one- and two-photon spectra an average of 0.3 kK. As can be seen from Figure 6, this shift is also accompanied by significant changes in the band shape. Such sensitivity could be expected because of the forbidden, vibronic nature of

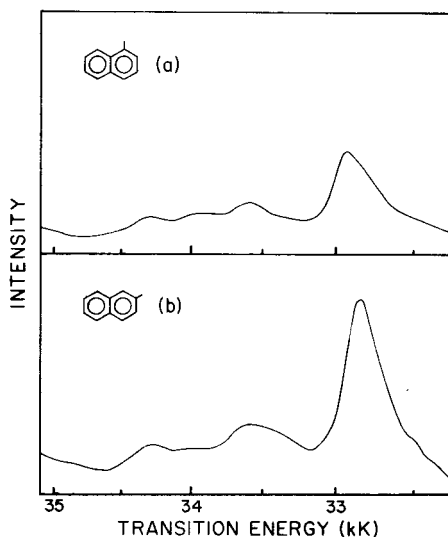


FIGURE 6 Two-photon excitation spectra of methylnaphthalenes. (a) 1-methylnaphthalene, and (b) 2-methylnaphthalene.

the transition. 1,3- and 3,5-dimethyl substitution red shifts the one-photon spectra an average of 0.7 kK and the two-photon spectra an average of 0.6 kK. Again, Figure 7 shows that the red shift is accompanied by changes in the band shape. For both mono- and di-methyl substitution, a close examination of the corresponding one-photon spectra has also revealed a band shape sensitivity. However, because of the intense allowed transition at 34.8 kK these differences are difficult to visualize without first performing a background subtraction similar to that utilized for Figure 5.

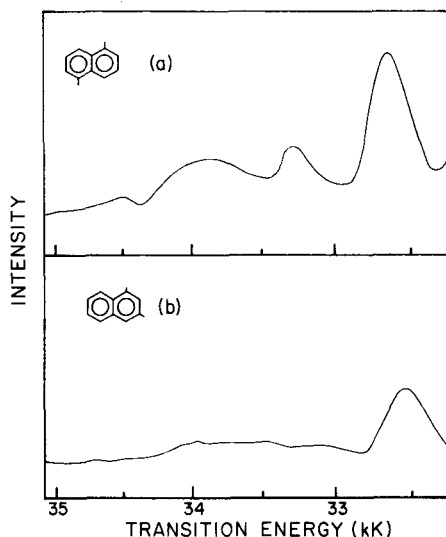


FIGURE 7 Two-photon excitation spectra of dimethylnaphthalenes. (a) 1,5-dimethylnaphthalene, and (b) 1,3-dimethylnaphthalene.

Improvements to the technique

The presented spectra demonstrate the extent to which two-photon excitation can complement the one-photon results ordinarily used as an aid in identifying polycyclic aromatic hydrocarbons. The primary drawbacks to the present instrumentation are the laborious procedure used to obtain the data and the expense of the ring dye laser. The first of these problems can be quickly eliminated through the use of a minicomputer to automate all of the measurements. The second drawback can be accomplished by the use of an ordinary cw dye laser coupled with a chemical reference compound. With this arrangement it will be possible to de-

termine relative values of $g^2(0)$ as the laser parameters are varied. Such an approach has already been shown to produce excellent results for naphthalene,⁵ and when combined with the automation should be easy to implement.

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References

1. W. Kaiser and C. Garrett, *Phys. Rev. Lett.* **7**, 229 (1961).
2. W. M. McClain, *Acc. Chem. Res.* **7**, 129 (1974).
3. M. J. Wirth and F. E. Lytle, *Anal. Chem.* **49**, 2054 (1977).
4. M. J. Wirth, presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1979. Abstract No. 602.
5. M. C. Johnson and F. E. Lytle, *J. Appl. Phys.* **51**, 2445 (1980).
6. M. J. Wirth and F. E. Lytle, "Two-Photon Excited Molecular Fluorescence" in *New Applications of Lasers to Chemistry*, Vol. 85, ACS Symposium Series 85 (1978).