Journal of Molecular Structure, 61 (1980) 285—290

TWO PHOTON SPECTROSCOPY OF PYRAZINE AND TRIAZINE

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ABSTRACT

Two photon absorption spectra, detected by fluorescence, phosphorescence, and photoacoustic methods are presented for pyrazine and triazine. Vibronic assignments are made in both systems based on polarization and contour analysis. For pyrazine, origin intensity is observed which suggests the $^1B_{3u}$ state does not possess inversion symmetry. Linear, quadratic, and pseudo-Jahn Teller couplings are discussed for triazine.

INTRODUCTION

Multiphoton spectroscopy has recently received a good deal of attention, particularly with regard to its application to molecular systems (ref. 1). The motivations behind such investigations of typically well studied systems (e.g., benzene and pyrazine) are: new selection rules allow photophysical and photochemical studies of different excited electronic and vibronic states; multiphoton transitions may reach vacuum ultraviolet regions with high resolution and relative ease; it is possible to obtain polarized spectra (with linearly and circularly polarized photons) even in isotropic liquids and gases; using counter propagating beams, Doppler free high resolution gas phase spectra can be observed; intense electric dipole transitions in bulk materials can be more easily studied; and infrared multiphoton photochemistry, photophysics, and isotope separation can be pursued.

As with most laser spectroscopic techniques it turns out to be most useful to use what may be called secondary detection techniques; that is, it is not the loss of photons from the laser beam that is monitored during an experiment, but some ensuing molecular process (i.e., emission of photons, sound or heat pulses, or electrons). In this work we use fluorescence, phosphorescence, and photoacoustic techniques to detect the primary (two photon) absorption process.

The systems studied are 1-10 torr of pyrazine and triazine. Both of these molecules are relatively well studied over the past 25 years because of their general interest for N-heterocyclic photochemistry and photophysics. Triazine

(D_{3h} symmetry--symmetric top) has dipole forbidden (two photon allowed) $^{1,3}E''$ first excited states. Strong vibronic (inter- and intra-state) coupling is expected for both these states. Location of nπ* and ππ* excited states and determination of their geometry is essential for an understanding of the series. Pyrazine (D_{2h} symmetry--asymmetric top) has a $^1B_{3u}$ first excited singlet state which is vibronically allowed in two photon spectra. Aside from the general interest in vibronic structure and geometry of this system, the location of other nπ* states, particularly the two photon allowed $^1B_{2g}$ arising from n-(b_{1u}) and π(b_{3u}) orbitals, has been of long-standing interest and considerable importance.

In the following section is presented a brief discussion of experimental techniques. In Section III, results and their interpretation are given. Analysis of these data is at present somewhat tentative, due to the occurrence of strong intrastate vibronic coupling (linear Jahn Teller - LJT, quadratic Jahn Teller - QJT effects) and interstate vibronic coupling (pseudo Jahn Teller - PJT effect). A more complete and detailed analysis will rely heavily on calculations (similar to those on transition metal hexafluorides - ref. 2) and contour simulations presently in progress.

For this paper we discuss assignments, nature and source of vibronic interactions, and qualitative features of geometry and symmetry that are apparent from the spectra.

EXPERIMENTAL

Samples were vacuum distilled through molecular sieve to remove all traces of water and air. Triazine was fused with potassium prior to distillation. Three different detection methods were employed for these experiments but all had the general design given in Figure 1. Fluorescence detection apparatus was the same as

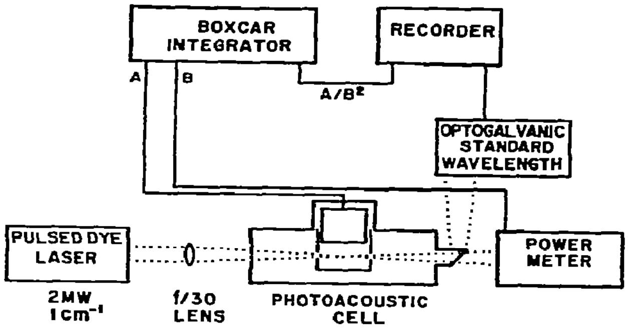

Fig. 1. Experimental apparatus for multiphoton spectroscopy photoacoustically detected. For emission detection, the microphone is replaced with photomultiplier tube.

the photoacoustic depicted with the microphone replaced with a cooled RCA 8850 phototube. Phosphorescence times were long enough to employ digital boxcar techniques with photon counting. Spectra are calibrated to 0.1 cm^{-1} with the optogalvanic effect using an Fe-He hollow cathode lamp.

RESULTS AND DISCUSSION

Pyrazine

We begin discussion of results with pyrazine because they are more simple to analyze. Figure 2 shows a portion of the two photon spectrum of pyrazine photoelectrically detected. Well developed, rather broad contours obtain. The major fluorescence signal is due to CN (cyanyl) emission. This diatomic radical is created photochemically following pyrazine two photon absorption. The large signal at about 32,000 cm^{-1} is due to two photon absorption of ground state CN followed by fluorescence. Polarized higher resolution photoacoustically detected spectra presented in Figure 3 (which do not evidence CN) show totally symmetric peaks due to b_{3u} vibrations ($16^{1}6^{1}_{0}$ and 11^{1}_{0}). This figure shows origin intensity which is unpolarized. Spectra taken at 100°C do not show any increase or variation in this intensity relative to other features; thus it is probably not sequence structure. We tentatively conclude that this is origin intensity and therefore the molecule has lost its inversion symmetry in the $^{1}B_{3u}$ state.

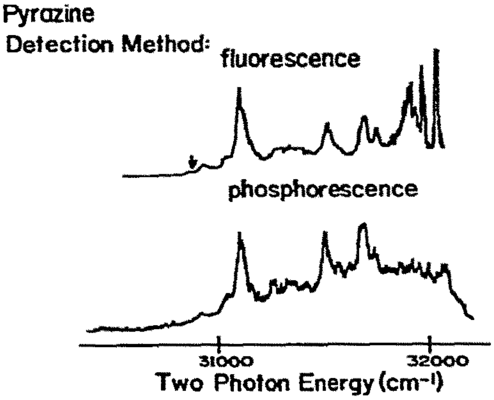

Fig. 2. Pyrazine two photon spectra of $^{1}B_{3u}$ state. Photoelectrically detected; origin marked with arrow.

A thorough search for the $^{1}B_{2g}$ state 1000 cm^{-1} to lower energy than the 0-0 transition of $^{1}B_{3u}$ and up to 2000 cm^{-1} to higher energy than the 0-0 gave no hint of this two photon allowed state.

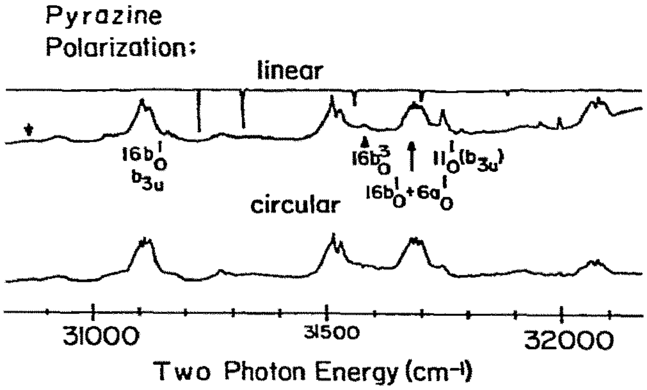

Fig. 3. Same as Figure 2 but polarized and photoacoustically detected, origin marked with arrow.

Triazine

Triazine represents a far more complicated situation than does pyrazine due to strong Jahn Teller coupling (e.g., e' modes ν_6 and ν_8) and strong pseudo Jahn Teller (e.g., e' modes and e'' modes ν_{10} and ν_{16}). This situation obtains, of course, because of the degenerate electronic state E'' and the increased density of the excited electronic manifold (A_1'', A_2'', E'' $n\pi^*$ states and A_1', A_2', E' $\pi\pi^*$ states).

Figure 4 presents a comparison of the one and two photon spectra of this molecule. Notice in particular that there is little overlap between the two spectra even though D_{3h} selection rules indicate many coincidences should be present. Most importantly, however, the E'' (perpendicular) origin is observed and assigned based

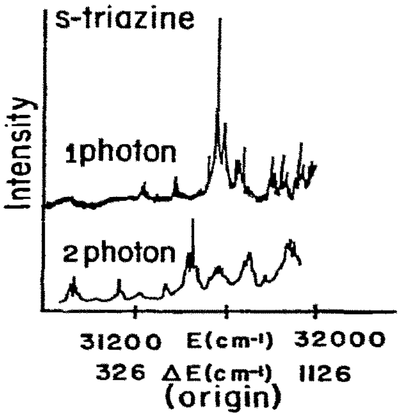

Fig. 4. Sym-triazine E'' spectra.

on its contour which was matched with computer simulation. Again, CN emission can be used to detect the absorption photoelectrically; photoacoustic detection shows small intensity differences between the two techniques. Detailed polarization studies (Figure 5) allow e'' modes 10_0^1 (430 cm^{-1}) and 16_0^1 (300 cm^{-1}) to be

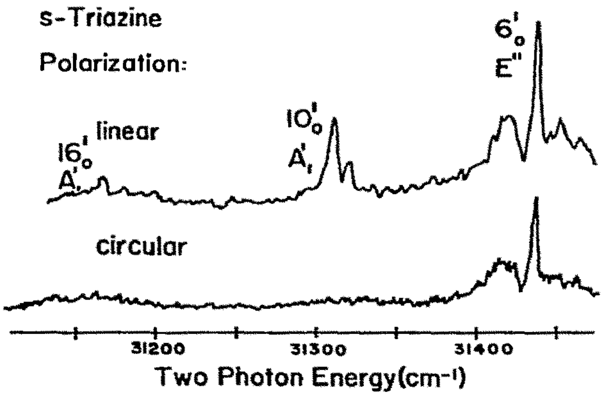

Fig. 5. Polarized, photoacoustically detected portion of triazine spectrum.

identified. These have been shifted from their ground state values (340 and 1031 cm^{-1}) and split due to PJT coupling with ππ* states of A_1', A_2', or E' symmetry.

The origin and 6_0^1 (e') at 550 cm^{-1} have the same contour (Figure 6) and polarization behavior and are identified as E'' vibronic components of JT active modes.

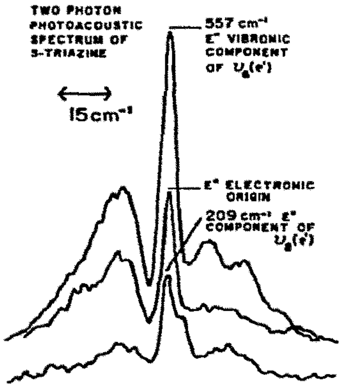

Fig. 6. Comparison of three E'' vibronic features (E'' x e') in the triazine spectrum.

When compared to the one photon spectra in Figure 4, the other 6_0^1 component (A_2) is located at 670 cm^{-1}. Such a splitting is inconsistent with LJT coupling in sign and can only arise through: a) PJT coupling; b) QJT coupling; c) strong mixing of e' modes. The precise mechanism for such strong higher order effects is presently under consideration but is not without precedent (refs. 3, 4).

Finally the feature at 200 cm^{-1} (Figure 6) is similar to the origin and 6_0^1 (E'') in contour and polarization behavior leading one to assign it as an e' vibration. A tentative assignment for this feature is 8_0^1 (ν_8'' (e') 1570 cm^{-1}). Such a large change in frequency upon excitation would be due to PJT coupling as is found in $^3B_{1u}$ 8_0^1 of C_6H_6 (refs. 3,4)(ν_8' 340 cm^{-1} while ν_8'' 1595 cm^{-1}). The PJT coupling would take place with E'', A_2'', or A_1'' D_{3h} $n\pi^*$ electronic states. Again this assignment must be viewed as tentative pending completion of confirming vibronic coupling and contour calculations.

CONCLUSIONS

It is clear from the discussion, as well as the presented figures, that phosphorescence, fluorescence, and photoacoustic detection are all applicable to two photon spectroscopy. Different detection techniques emphasize different aspects of molecular photophysical and photochemical processes. For pyrazine it is possible to observe two photon spectra by all three techniques but for fluorescence detection cyanyl (CN) emission was the major component of the signal. A number of vibrations are assigned based on polarized spectra and known coincidences. Apparent non-hot band intensity at the origin of the $^1B_{3u}$ state indicates that this state may have lost its inversion symmetry. The E'' origin of the first excited singlet state of triazine was located and assigned. Vibronic states 16_0^1 (e'') and 10_0^1 (e'') were identified by polarization studies; both modes are shifted and split by PJT coupling with $\pi\pi^*$ states. JT active e' modes were assigned: 6_0^1 (E'' component) is placed at 560 cm^{-1} with its 6_0^1 (A_2'' component) partner at 660 cm^{-1}; and 8_0^1 (E'' component) highly perturbed is tentatively suggested to lie at about 200 cm^{-1} above the ^{1}E'' origin.

ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research, and Army Research Office-Durham.

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NOTE ADDED IN PROOF

Further photoacoustic and fluorescence measurements on pyrazine indicate the contour and intensity of both the origin region and 16_0^1 are temperature dependent. It is thus likely that the origin region intensity is at least partially hot band related. Further experiments and computer fits are in progress.