

## Two-photon excitation spectrum of benzonitrile vapour

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**Abstract.** The two-photon excitation spectrum of benzonitrile in the gas phase at about 1 torr has been recorded and analysed in the total energy region of 36300 to 40500  $\text{cm}^{-1}$  using both linearly and circularly polarised light from a Nd-YAG pumped dye laser. The two-photon spectrum consists of strong Franck Condon (FC) transitions bearing a good resemblance to the one-photon spectrum and also vibronic coupling (VC) transitions essentially arising out of the analogue of the benzene  $\nu_{14}$ . By a comparative study of the TP spectra of various other monosubstituted benzenes, it has been inferred that the strong TP spectrum of benzonitrile should be ascribed to a considerable  $\pi$  charge delocalization over the phenyl and nitrile groups.

**Keywords.** Two-photon spectroscopy; benzonitrile.

### 1. Introduction

The last decade has seen the emergence of two-photon spectroscopy as a powerful spectroscopic tool for investigating the excited electronic states of molecules, which are not possible by conventional one-photon excitation (Wunsch *et al* 1977, Mikami and Ito 1975; Robey and Schlag 1978; Vasudev and Brand 1979a, b; Goodman and Rava 1981; Chia and Goodman 1982; Rava and Goodman 1982). The two-photon excitation spectrum is generally obtained by monitoring the fluorescence intensity from the sample excited by the simultaneous absorption of two photons from a tunable dye laser beam focussed on to the sample cell. The two-photon absorption process is feasible with either two identical photons from a single laser beam or two distinguishable photons from two different laser beams. The advantages of two-photon (TP) spectroscopy are: (i) the selection rules for the two-photon absorption are complementary to those of one-photon (OP) absorption. Forbidden transitions in OP spectroscopy may be permitted in TP spectroscopy and vice versa. (ii) the symmetry assignments of excited states can be made on the basis of the absorption intensity for linearly and circularly polarized light even in randomly-oriented samples.

According to the predictions of simple molecular orbital theory, benzene has four low-lying  $\pi\pi^*$  singlet states. They are generally labelled as  ${}^1B_{2u}$ ,  ${}^1B_{1u}$ ,  ${}^1E_{1u}$  and  ${}^1E_{2g}$  [ ${}^1L_b$ ,  ${}^1L_a$ ,  ${}^1B_{ab}$  and  ${}^1C_{ab}$  in Platt's notation] having energies of nearly 4.9, 6, 6.5 and 8 eV respectively with respect to the ground state  ${}^1A_{1g}$ . The first three states arise from the excitation of an electron from the highest occupied molecular orbital ( $e_{1g}$ ) to the lowest unoccupied orbital ( $e_{2u}$ ), while the  $E_{2g}$  state arises from the promotion of the electron to the highest unoccupied  $\pi$ -electron molecular orbital  $b_{2g}$ .

The well-known, much studied symmetry- and parity-forbidden  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  tran-

sition of benzene occurring at 260 nm derives its intensity in both OP and TP spectra through vibronic interactions. While the OP spectrum is built on the vibronic origin from the  $\nu_6$  ( $e_{2g}$ ) vibration (Sklar 1937), the TP spectrum is mainly induced by the  $\nu_{14}$  ( $b_{2u}$ ) vibration and to a lesser extent by  $\nu_{17}$  ( $e_{2u}$ ) and  $\nu_{18}$  ( $e_{1u}$ ) vibrations (Wunsch *et al* 1977; Lombardi *et al* 1976). Monosubstitution lowers the molecular symmetry from  $D_{6h}$  to  $C_{2v}$  symmetry. The lowest-lying  $\pi^* \leftarrow \pi$  transition in monosubstituted benzene derivatives generally falls in the range of 260–320 nm and are essentially derived from the 260 nm band in benzene. The orbitals involved in forming the lowest excited benzene configuration ( $e_{1g}$ ,  $e_{2u}$ ) now in  $C_{2v}$  give rise to four states, two of symmetry  $A_1$  and two of symmetry  $B_2$ . In spite of the fact that transitions to these states are group theoretically permitted, the lowest one is often weak due to the fact that the transition moment is small (Hartford and Lombardi 1971).

There are two ways in which a substituent may affect the electronic structure of benzene: (i) inductive effect, in which a substituent may change the potential acting on the  $\pi$  electrons. It has been shown (Murrell 1963) that because of the inductive effect, the intensity of the  ${}^1L_b$  OP spectrum gets enhanced; (ii) mesomeric effect, in which the electrons are transferred between a substituent and the benzene ring resulting in an interaction between the states arising from such a transfer [often referred to as charge transfer (CT) or electron transfer states] and the locally excited states. The energy of a charge-transfer state, in which there is no overlap of donor and acceptor orbitals is given by  $(I-A-C)$  where  $I$  is the ionization potential of the donating group,  $A$  is the electron affinity of the acceptor group and  $C$  is the Coulombic interaction between the donated electron and the positive hole left behind by it. The amount of charge transfer contamination in the locally excited states depends linearly on the perturbation matrix element (given by the resonance integral  $\beta$ ) and inversely on the energy separation between the CT state and locally excited state. Based on the energies of charge transfer configurations, which have a strong influence on the nature of the absorption spectra of the monosubstituted benzenes, the substituents are classified as weak or strong. It has been shown (Goodman and Rava 1981) that the inductive substituents cause a mixing of  ${}^1B_b$  state with  ${}^1L_b$  state and contributes to an enhancement of the intensity of the  ${}^1B_2 \leftarrow {}^1A_1$  OP spectrum, whereas mesomeric substituents, by imparting charge transfer character to the locally-excited states, contribute to the intensity of the  ${}^1B_2 \leftarrow {}^1A_1$  two-photon spectrum.

In this communication, we report the two-photon spectrum of benzonitrile, the first aromatic molecule with a moderately strong  $\pi$  electron acceptor substituent. From an extensive microwave work on a number of isotopic species of benzonitrile (Bak *et al* 1962), it has been inferred that in the electronic ground state the contribution of ionic structures is not significant to account for the geometrical modifications in the ring due the nitrile group. This is in good agreement with the small mesomeric dipole moment of 0.2 debye (Bak *et al* 1962). The 33 normal vibrations of benzonitrile — ( $12a_1 + 11b_2$ ) in-plane and ( $3a_2 + 7b_1$ ) out-of-plane have been characterised by infrared studies (Green and Harrison 1976). The near ultraviolet spectrum of benzonitrile (Hirt and Howe 1948) has confirmed that benzonitrile has a very strong  $O_0^0$  band at  $36516 \text{ cm}^{-1}$  (compared with  $36512 \text{ cm}^{-1}$  recorded by Brand and Knight 1970) and most of the spectral intensity arises from the excitation of totally symmetric vibrations. From a rotational analysis of the  $O_0^0$  band of the  ${}^1B_2 \leftarrow {}^1A_1$  transition, it has been found (Brand and Knight 1970) that the increase in the long axis moment of inertia is greater than the increase about

the short axis. These results have been rationalized by assuming the  $B_2$  state to have a charge transfer character together with local excitation character and it has been concluded that the phenyl group acts as an electron donor in the charge transfer process.

## 2. Theory

In the ground state, benzonitrile has been shown by microwave studies to be a planar molecule having  $C_{2v}$  symmetry (Bak *et al* 1962). If the molecule is chosen to be in the  $yz$  plane with the  $z$  axis along the  $C - C \equiv N$  axis and  $x$  axis perpendicular to the molecular plane, then the one-photon transition moment to the  $B_2$  state is given by

$$M_y = \langle A_1 | \mu_y | B_2 \rangle.$$

The simultaneous absorption of two photons causing an excitation of a molecule from the ground state  $g$  to an excited state  $f$  through an intermediate state  $i$  can be described by a tensor  $S_{gf}$  (McClain and Harris 1977). For the absorption of two identical photons, as it happens in a single laser beam experiment, the tensor becomes symmetric and can be written as

$$S_{\rho\sigma}^{gf} = \sum_i \frac{1}{(\Delta E_{ig} - \hbar\omega)} [\langle g | \mu_\rho | i \rangle \langle i | \mu_\sigma | f \rangle + \langle g | \mu_\sigma | i \rangle \langle i | \mu_\rho | f \rangle],$$

where the intermediate states  $i$  are other eigenstates.  $\Delta E_{ig}$  is the energy difference between the ground and intermediate states,  $\hbar\omega$  is the laser photon energy,  $\mu_\rho$  and  $\mu_\sigma$  are the appropriate electric dipole component, and  $\rho, \sigma$  are any two axes of the molecule-fixed set,  $x, y, z$ . For a molecule of  $C_{2v}$  symmetry such as benzonitrile,  $S_{\rho\sigma}$  mostly involves only the in-plane  $S_{yz}$  component for a transition to the  $L_b$  state having  $B_2$  symmetry.

$$S_{yz} = \sum_i \frac{1}{(\Delta E_{ig} - \hbar\omega)} [\langle A_1 | \mu_y | i \rangle \langle i | \mu_z | B_2 \rangle + \langle A_1 | \mu_z | i \rangle \langle i | \mu_y | B_2 \rangle].$$

The low-lying, strongly-allowed  $B_{a,b}$  ( $E_{1u}$ ) state of benzene, which splits into  $A_1$  and  $B_2$  states in  $C_{2v}$  symmetry will be the dominant intermediate state and is expected to contribute significantly to the TP intensity. The prominent absorption in the OP spectrum of benzonitrile occurs near  $53000 \text{ cm}^{-1}$  (Kimura and Nagakura 1965) and correspond to the transition that correlate with the  $E_{1u}$  state of benzene.

In two-photon spectroscopy the orientationally averaged two-photon absorptivity  $\delta_{av}$  may be expressed in terms of three invariants (McClain and Harris 1977):

$$\delta_{av} = \delta_F F + \delta_G G + \delta_H H,$$

where  $F$ ,  $G$  and  $H$  are functions of the incident beam polarizations  $e_1$  and  $e_2$ . If common proportionality constants are ignored

$$\delta_F = \sum_{\rho\sigma} S_{\rho\rho} S_{\sigma\sigma}^*, \delta_G = \sum_{\rho\sigma} S_{\rho\sigma} S_{\rho\sigma}^*, \delta_H = \sum_{\rho\sigma} S_{\rho\sigma} S_{\sigma\rho}^*$$

For a measurement using single laser beam  $S_{\rho\sigma} = S_{\sigma\rho}$ , so that  $\delta_G = \delta_H$  and hence only two unique absorptivities  $\delta_F$  and  $\delta_G$  can be determined. Since  $\delta_F$  is a measure of the diagonal elements, it obviously indicates totally symmetric transitions.  $\delta_F = 0$  when transition is to a non-totally symmetric state.  $\delta_G$  being a measure of the sum of the squares of all elements in the transition tensor, can be considered to represent the overall strength of the transition. In a single laser experiment, the independent polarizations are linear and circular and the corresponding absorptivities can be written

$$\langle \delta_{\text{lin}} \rangle = 2 (\delta_F + 2 \delta_G),$$

and 
$$\langle \delta_{\text{cir}} \rangle = 2 (-\delta_F + 3 \delta_G).$$

The value of  $(\delta_F/\delta_G)$  can never exceed 3. The polarization ratio is essentially defined as

$$\Omega = \delta_{\text{cir}}/\delta_{\text{lin}} = \frac{3 \delta_G - \delta_F}{2 \delta_G + \delta_F}.$$

The range of value for  $\Omega$  is  $0 \leq \Omega \leq 3/2$ .

A spectrum is usually recorded for both kinds of polarisation and the excited state symmetry is assigned by comparing the ratio with  $\Omega$  predicted by tensors of different possible excited state symmetries (McClain and Harris 1977).

The band system representing the  ${}^1B_2 \leftarrow {}^1A_1$  electronic transition of monosubstituted benzenes can be classified into two parts: one part, often referred to as electronically allowed system and other an electronically forbidden but vibrationally induced part. The allowed system exhibits a  $B_2$  tensor pattern, while the forbidden system exhibits an  $A_1$  tensor pattern and the inducing vibrations are of  $b_2$  species. 'Forbidden' transitions can be identified by near vanishing intensities under circular polarisation of the laser beam.

### 3. Experimental

The experimental set up for the study of two-photon excitation spectrum of benzonitrile is shown in figure 1. A sample of benzonitrile (E. Merck) was repeatedly chilled and thawed to expel any dissolved air before being filled into a cylindrical quartz cell (18 cm  $\times$  2 cm). The third harmonic 355 nm laser pulse from a Moletron Nd-YAG (MY 35) laser was used to pump a Moletron (DL 18) dye laser. The pulsed (10 sec<sup>-1</sup>), linearly polarised dye laser beam was focussed in to the quartz

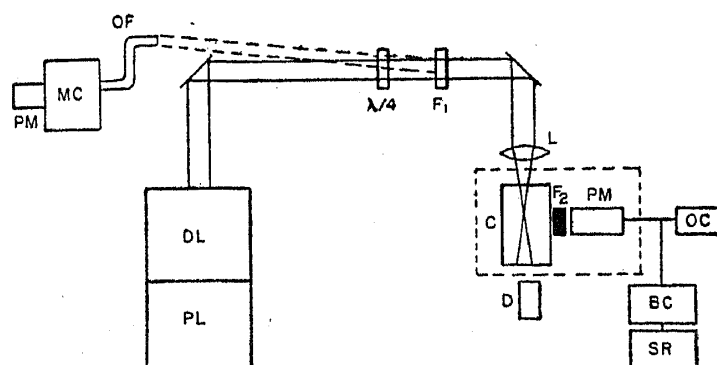


Figure 1. Experimental set-up for recording the two-photon fluorescence excitation spectrum. PL: Nd-YAG laser. DL: dye laser.  $\lambda/4$ : quarter wave plate.  $F_1$ : filter. L: achromatic lens. D: beam dump. C: quartz cell.  $F_2$ : corning filter CS 7-54. PM: photomultiplier tube. BC: box car averager. SR: strip chart recorder. OC: oscilloscope. OF: optical fiber MC: monochromator.

Table 1. Prominent bands in the two-photon excitation spectrum of benzonitrile.

$\lambda$ (Å)	$\nu$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )	Symmetry of the tensor	Intensity	Assignment
5476.8	36517	0	$B_2$	VS(100)	origin
5421.6	36889	372	$B_2$	MW	?
5416.0	36927	410	$B_2$	M	$6a_0^1$
5373.3	37221	704	$B_2$	W	$12_0^1$
5340.1	37452	935	$B_2$	{S(70)	$1_0^1$
5336.7	37476	959	$B_2$		$18a_0^1$
5304.9	37701	1184	$B_2$	M	$7a_0^1$
5283.6	37853	1336	$A_1$		
5252.0	38081	1564	$A_1$	S(50)	$14_0^1$
5241.3	38158	1641	$B_2$		$1_0^1 12_0^1$
5238.0	38183	1666	$B_2$		$18a_0^1 12_0^1$
5210.4	38385	1868	$B_2$	MW	$1_0^2$
5208.2	38400	1884	$B_2$	MW	$12_0^1 7a_0^1$
5206.0	38417	1901	$B_2$	MW	$1_0^1 18a_0^1$
5203.0	38439	1922	$B_2$	W	$18a_0^2$
5198.0	38476	1959	$A_1$	W	$14_0^1 6a_0^1$ (?)
5181.2	38601	2084		W	
5177.2	38631	2114	$A_1$	W	
5175.6	38643	2126	$B_2$		$1_0^1 7a_0^1$
5163.3	38735	2218	$A_1$	W	seq. of $14_0^1 12_0^1$ (?) $14_0^1 12_0^1$ (?)
5158.3	38772	2255	$A_1$	W	
5151.6	38823	2306	$A_1$		
5145.5	38869	2352	$B_2$	W	$7a_0^2$
5126.9	39011	2494	$A_1$	MS	$14_0^1 1_0^1$
5123.6	39035	2518	$A_1$	MS	$14_0^1 18a_0^1$
5094.2	39260	2743	$A_1$	W	$14_0^1 7a_0^1$
5043.5	39655	3138	$A_1$	W	
5036.8	39708	3191	$A_1$	VW	$14_0^1 1_0^1 12_0^1$
5033.4	39735	3218	$A_1$	VW	$14_0^1 18a_0^1 12_0^1$
5004.2	39966	3449	$A_1$	VW	$14_0^1 1_0^2$
4998.2	40014	3497	$A_1$	VW	$14_0^1 18a_0^2$

The intensity of the lines is denoted by VW = very weak, W = weak, MW = medium weak, M = medium, MS = medium strong, S = strong, VS = very strong.

absorption cell by an achromatic quartz lens (F. L. = 50 mm). Dyes coumarin 7 (in DMF) and coumarin 500 (in methanol) were used to scan the range 4900-5500 Å. The dye laser was operated in the fifth order and the wavelength was scanned at 3 Å/min. The range of the energy per pulse for recording the spectrum was 100-600  $\mu$ j and was periodically monitored by a Scientech 362 energy meter. Two-photon fluorescence intensity was monitored by an IP 28 photomultiplier with 6 mm thick Corning filter CS 7-54 to cut out the scattered laser light. The signal was averaged by a box car averager (PAR 162/164) and recorded on a strip chart recorder. The calibration of the laser wavelength was effected with a Carl-Zeiss 0.5 metre monochromator by using mercury and sodium lines. The calibration was cross-checked by recording the two-photon excitation spectrum of benzene for which measurements are available to an accuracy better than  $\pm 2$   $\text{cm}^{-1}$  (Wunsch *et al* 1977). Circular polarization of the laser beam was achieved by using a  $\lambda/4$  plate. The frequencies of benzonitrile quoted in table 1 correspond to the peak of the absorption lines and is believed to be accurate to  $\pm 4$   $\text{cm}^{-1}$  in OP energy.

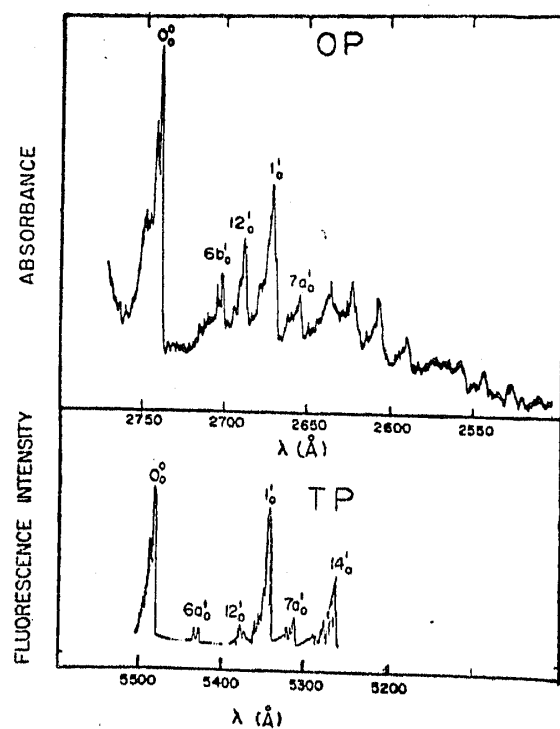
The one-photon absorption spectrum of benzonitrile ( $\sim 1$  torr) was recorded (using Cary 17 D spectrophotometer) with a cylindrical quartz cell of 12 cm path length.

#### 4. Results

The one-photon absorption spectrum of benzonitrile is shown in the upper part of figure 2. It may be seen that the origin band around 2740 Å is the strongest. In the two-photon spectrum shown in the lower part of the same figure, it may be seen that the most intense band  $0_0^0$  occurring at  $2\bar{\nu}$  (36518  $\text{cm}^{-1}$ ) is nearly identical to the value of the origin band reported for OP spectrum and hence it is obvious that it is the two-photon spectrum of benzonitrile.

The fundamentals observed in the two-photon spectrum which belong to symmetric  $a_1$  modes are  $6a_0^1$  (+ 410  $\text{cm}^{-1}$ ),  $12_0^1$  (+710  $\text{cm}^{-1}$ ),  $1_0^1$  (+935  $\text{cm}^{-1}$ ),  $18a_0^1$  (+ 958  $\text{cm}^{-1}$ ) and  $7a_0^1$  (+ 1184  $\text{cm}^{-1}$ ). All these fundamentals also appear in combinations. The indexing of the normal modes follows Wilson's convention (Wilson *et al* 1955). Excepting the FC mode  $6a_0^1$ , all the  $a_1$  modes can be correlated with the OP spectrum. Sequence bands contribute a significant fraction of total intensity of many bands and are stacked towards the red side as in other benzenoid systems. For the  $0_0^0$  band (figure 3), the sequence bands were measured at  $-1 \times 10$ ,  $-1 \times 23$ ,  $-2 \times 23$ ,  $-1 \times 77$ ,  $-1 \times 110$ ,  $-1 \times 127$ ,  $-1 \times 158$   $\text{cm}^{-1}$ , etc, a few of which should be expected to correspond to  $-1 \times 40$ ,  $-2 \times 40$ ,  $-3 \times 40$   $\text{cm}^{-1}$  observed in OP spectrum (Hirt and Howe 1948). In table 1 are shown some of the important bands observed in the two-photon spectrum along with their behaviour under polarization.

The only active intense VC mode in the TP spectrum of benzonitrile is the analogue of benzene  $\nu_{14}$ , occurring at 5252 Å (figure 4). It shows a polarization behaviour suitable for  $b_2$  vibration—namely a sharp reduction in intensity under circular polarization. Further it occurs at about 1565  $\text{cm}^{-1}$  above the band origin, similar to that found in other mono-substituted benzenes. Hence the assignment of  $14_0^1$  to this band seems to be correct. This band system is also heavily studded with sequences, prominent among which occur at  $-1 \times 40$ ,  $-2 \times 40$  and  $-3 \times 40$   $\text{cm}^{-1}$



ONE AND TWO - PHOTON SPECTRA OF BENZONITRILE VAPOUR

Figure 2. One- and two-photon spectra of benzonitrile vapour ( $\sim 1$  torr). The TP spectral bands were recorded at a constant energy of  $100 \mu\text{j}$ .

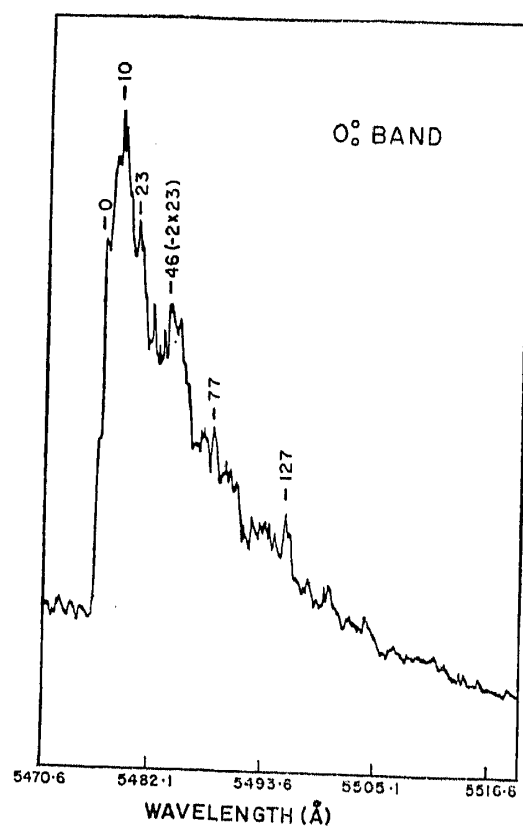


Figure 3.  $O_0^0$  band of benzonitrile with a few sequence bands.

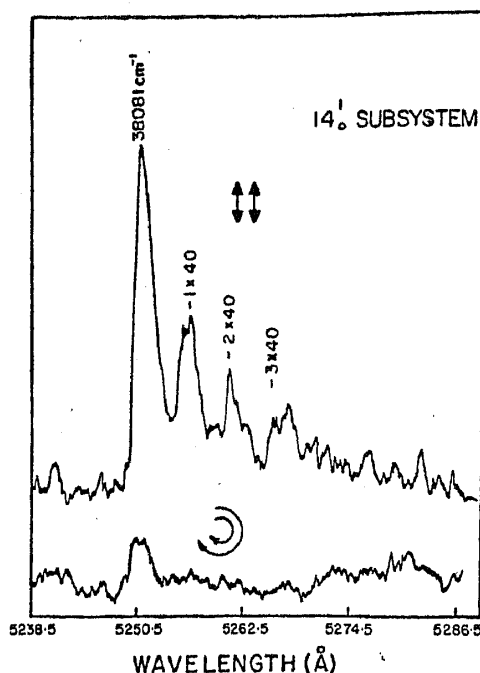


Figure 4. The two-photon spectrum of the analogue of benzene  $14_0^1$  subsystem using linearly (upper) and circularly polarized laser beam. The Strong sequence structures at multiples of  $-40 \text{ cm}^{-1}$  are also included.

and can be reasonably ascribed (Hirt and Howe 1948) to the out-of-plane bending ( $170 \text{ cm}^{-1}$ ) of the nitrile tail. The  $a_1$  fundamentals discussed above also appear in combination with  $14_0^1$  and exhibit a similar polarization behaviour appropriate of a  $b_2$  vibration. No other vibronically-induced subsystem could be observed in the TP spectrum of benzonitrile.

The intensity ordering of the vibronic fundamentals in the TP spectrum of benzonitrile is  $0_0^0 > 1_0^1 (18 a_1^1) > 14_0^1 > 7a_0^1 > 6a_0^1 > 12_0^1$  and has a strong similarity to the TP spectrum of its isoelectronic analogue phenyl acetylene (Chia and Goodman 1982).

A band around  $0_0^0 + 370 \text{ cm}^{-1}$  has been observed in the OP spectra of some monosubstituted benzenes (Hirt and Howe 1948) including benzonitrile. A clear transition was observed at  $370 \text{ cm}^{-1}$  in the TP spectrum of benzonitrile, which shows a polarization behaviour expected of a  $B_2$  tensor pattern (figure 5). It is not the  $-40 \text{ cm}^{-1}$  sequence of the  $6a_0^1$  transition ( $410 \text{ cm}^{-1}$ ) as there are no accompanying structures at  $-2 \times 40$  etc.

Table 2 indicates the relative intensities of the various  $a_1$  modes observed in the one- and two-photon spectra. It may be noted that the intensities of  $7a_0^1$  and  $12_0^1$  are reversed in the two cases. Further the  $6a_0^1$  mode is missing in the OP spectrum.

## 5. Discussion

In recent years, the two-photon spectra of a number of mono-substituted benzenes have been reported (Vasudev and Brand 1979a, b; Goodman and Rava 1981; Chia and Goodman 1982; Rava and Goodman 1982). The substituents so far studied are halogens,  $\text{CH}_3$ ,  $\text{OH}$ ,  $\text{CCH}$  and  $\text{NH}_2$ , and they all have been known to be  $\pi$  electron donors (Pross and Radom 1981). The donors have occupied orbitals of  $\pi$  symmetry with relatively high energy, and donor strength decreases as their ionization potential



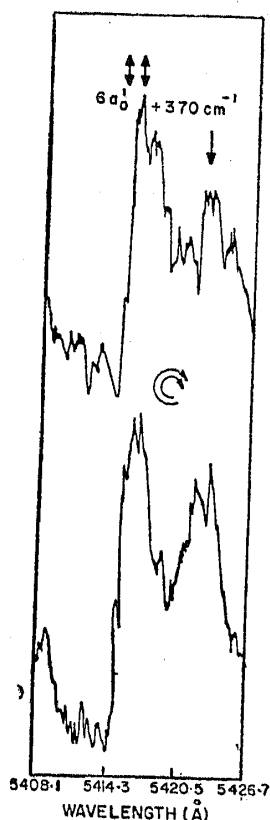


Figure 5. Two-photon spectrum of the  $6a_0^1$  and an unassigned  $O_0^0 370 \text{ cm}^{-1}$  band using linear and circular polarization of laser beam.

Table 2. The  $a_1$  modes: relative intensity of 1—0 transitions.

	One-photon	Two-photon	
	0—0	0—0	$14_0^1$
Origin	100	100	100
$6a$ (410)	NO	16	10
$12$ (704)	30	10	25
$1$ (935)	50	70	30
$18a$ (959)			20
$7a$ (1184)	13	20	10

NO: not observed

increases (Murrell 1963). For example, fluorine (I. P: 15.8 eV) is the weakest donor among the halogens since the ionization potential varies as  $F > Cl > Br > I$ . Hence the two-photon spectrum of fluorene is very much similar to benzene with weak FC modes and a strong VC mode. Since the  $14_0^1$  band in various monosubstituted benzenes is believed to be of approximately equal intensity (Rava and Goodman 1982) its strength *vis-a-vis* the intensities of FC mode  $\nu_1$  and  $0_0^0$  band in the two-photon spectra is a measure of the mesomeric strength of the substituent. It may be seen that in the two-photon spectrum of aniline (Rava and Goodman 1982) the FC modes are predominant compared to the VC mode and the TP spectrum bears a strong resemblance to the OP spectrum.

The electron acceptors have low-lying vacant  $\pi$  orbitals and the acceptor strength increases with the electron affinity of these orbitals (Murrell 1963). It is known that

nitrile group is a strong acceptor (Pross and Radom 1981). Benzonitrile has a strong one-photon and two-photon spectra and in both cases the intensities of origin and the ring breathing  $\nu_1$  band are stronger than the VC modes. Its isoelectronic analogue phenyl acetylene, on the other hand, has a weak OP spectrum (meaning the FC modes are weaker than the VC mode) (King and So 1971) and a strong TP spectrum (meaning that the FC modes are stronger than the VC mode  $14_0^1$ ) (Chia and Goodman 1982). The TP spectrum of phenyl acetylene (Chia and Goodman 1982) is very similar to that of benzonitrile. The intensity of the TP spectrum of phenyl acetylene has been ascribed to the importance of charge transfer states resulting from the acetylene-ring\* promotion and it has been concluded that the  $\pi$  electrons are strongly delocalised over the ring and acetylene portions. In benzonitrile, the results of the OP spectrum indicate that the charge transfer states result from ring-nitrile\* promotion. Since the FC part is almost similar in the OP and TP spectra of benzonitrile, we conclude that the electrons are delocalised over the benzene ring and nitrile moiety. In other words CN is a strong mesomeric substituent and the strong coupling treatment is likely to be applicable for this molecule.

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