

## Two photon absorption spectrum of *p*-dichlorobenzene

I B SINGH, S B RAI and D K RAI

Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221 005, India

MS received 28 November 1994; revised 23 May 1995

**Abstract.** Two photon absorption spectrum of *p*-dichlorobenzene has been studied in the spectral region 497–552 nm (one photon wavelength). Bands involving several frequencies of the excited electronic state not detected in the one photon absorption are seen. The observed two photon spectrum indicates that the electronic transition retains, to a large extent, the salient features of the two photon absorption spectrum of benzene and thus confirms chlorine as weak perturber (in the sense of Goodman and Rava [1]).

**Keywords.** Two photon absorption spectrum; *p*-dichlorobenzene; weak perturber; molecular spectra.

PACS No. 30-10

### 1. Introduction

Two photon absorption studies enable the observation of several features not accessible to direct observation in the usual one photon absorption spectrum [1]. Substituted benzenes, wherein one or more hydrogen atoms are replaced by other atoms or group of atoms, form a related class of molecules whose systematic study has led to a better understanding of many aspects of molecular spectra and hence such molecules have continued to draw the attention of molecular spectroscopist. Recently, we have reported an analysis of a part of the two photon electronic absorption spectrum of *o*-dichlorobenzene (ODCB) in the wavelength region 485–540 nm (one photon wavelength). In the present communication we report the results obtained in a similar study on *p*-dichlorobenzene (PDCB).

Earlier one photon absorption studies on PDCB have been carried out by Wollman [2] and by Conrad-Billroth [3] in the liquid phase and by Sponer [4], Joshi [5] and Anno and Matubara [6] in the vapour phase at low resolution. Rai [7] reported the one photon absorption spectrum of PDCB at a moderately high resolution which enabled him to identify several hitherto unobserved vibrational features. Even though two photon electronic absorption corresponding  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  transition of benzene has been investigated for several mono- and di-substituted benzenes (Goodman and his colleagues [1]), no work on dichlorobenzene has been reported prior to present study.

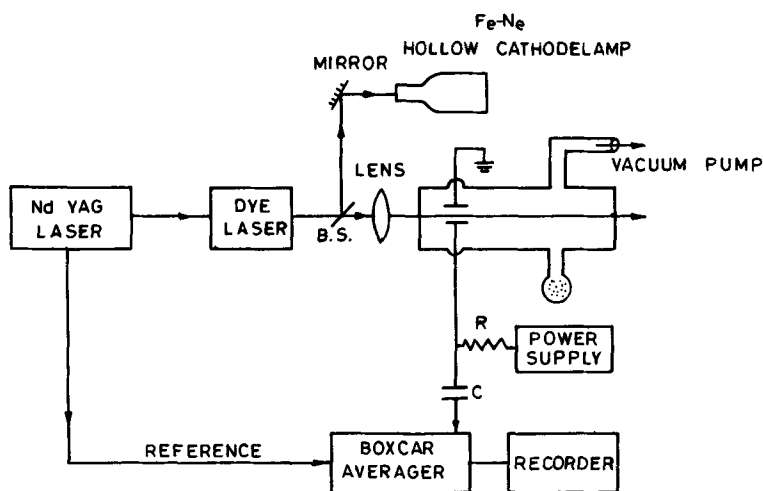
### 2. Experimental

The experimental set up used for recording the two photon spectrum of *p*-dichlorobenzene is essentially the same as described in our earlier paper [8]. In brief it consists of a pyrex cell 4 cm in diameter and 20 cm in length. A small bulb is attached in the middle of the tube to hold sample while the ends are closed with flat glass windows. An outlet is

also provided to connect a vacuum pump to create a proper vacuum in the cell. The electrodes are circular discs of stainless steel 1 cm in diameter and are mounted in the cell facing each other at a mutual separation of 1 cm. The electrodes are at a distance 5 cm from one of the windows. The experimental set up used is shown in figure 1.

A freshly purified sample of *p*-dichlorobenzene (reported purity 99.9%) is kept in the bulb of the cell which is dipped into a container of liquid nitrogen while the cell was evacuated to a residual gas pressure of approximately  $10^{-2}$  torr. The liquid nitrogen container is then removed and the *p*-dichlorobenzene vapour fills the cell at a pressure appropriate to the ambient temperature. A DC voltage of 110–150 V was applied across the electrodes from a stabilized power supply (Bertan model No. 205A-O1R). The laser radiation from a dye laser (Quanta Ray model PDL-2 with coumarine 500 dye) pumped by the third harmonic of a Nd:YAG laser (Quanta Ray model DCR-2) was focused at a spot between the two electrodes with the help of a 5 cm focal length convergent lens. The repetition rate of the laser was 10 Hz and pulse width of the dye laser was  $\sim 7$  ns. The dye laser peak output power at 510 nm was 10 mJ/pulse.

Under conditions of tight focusing, the photon density in the region becomes large enough to cause multiphoton absorption. Since the wavelength of the dye laser is appropriate for two photon absorption to the lowest lying singlet excited state of *p*-dichlorobenzene a substantial fraction of these molecules are excited to the excited state. Such excited molecules can be ionized by the absorption of an additional photon resulting in the creation of electron ion pairs. These ions and electrons are collected at the respective electrodes and give rise to an ionization signal. The A.C. signal thus generated was filtered from D.C. by using a capacitance resistance combination. The signal thus obtained is processed through a boxcar averager (EG and G model 164) with a gate width of 5 ns. The bias voltage, laser power and the focusing of the lens were adjusted so that the signal for one of the absorption peaks (near the middle of the tuning



**Figure 1.** Experimental set up used for recording the two photon absorption spectrum of *p*-dichlorobenzene.

## Two photon absorption spectrum

range) was optimum. The resulting absorption spectrum was then recorded with a double pen recorder. The resolution achieved in the experiment is  $1-2\text{ cm}^{-1}$ . A small part of the dye laser beam was sent into a Fe-Ne hollow cathode lamp and the optogalvanic signal of Ne was used to provide standard lines for wavelength calibration of the spectrum. A part of the spectrum along with noise level is shown in figure 2. The measured wavelengths, the frequencies and the relative intensities of the various bands are listed in table 1. We also monitored the signal by varying the laser power. It is marked that the signal is varying linearly with the square of the laser power. This clearly indicates that the signal is due to simultaneous absorption of two photons.

### 3. Results

The reduced point group symmetry  $D_{2h}$  of PDCB results in the transition analogous to the  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  transition of benzene becoming an allowed transition. This results in the appearance of a strong (O-O) band along with intense bands involving the totally symmetric vibrations, namely 1, 2, 6a, 8a and 9a (in Wilson notation). The one photon absorption spectrum of PDCB vapour analyzed by Anno and Matubara [6], Joshi [5] and Rai [7] clearly demonstrates the correctness of this interpretation. The origin band as identified by these authors is at  $35742\text{ cm}^{-1}$ . Since the longest wavelength available with the present dye is  $552.0\text{ nm}$ , we could not observe bands with energy less than  $36240\text{ cm}^{-1}$  and we have taken the value reported by Rai [7] for the position of the (O-O) band.

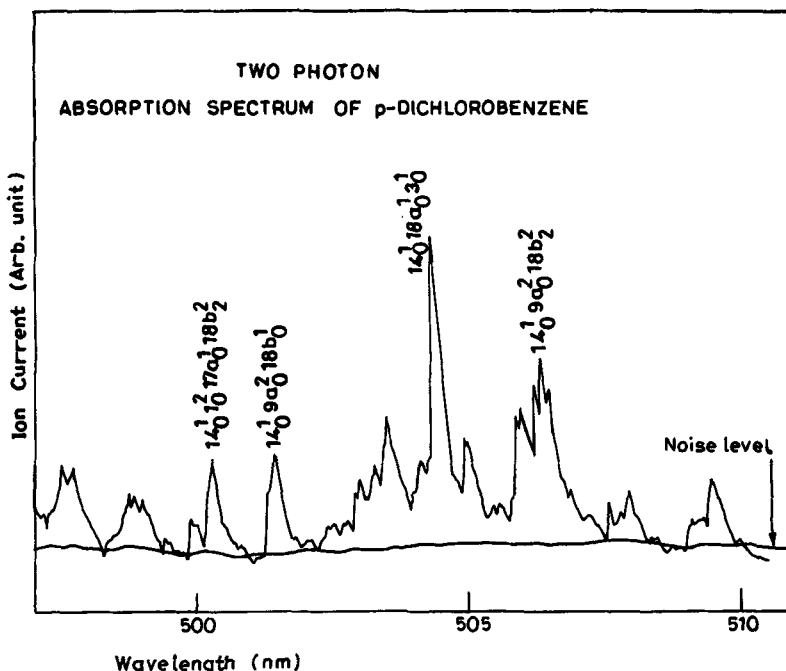


Figure 2a. A part of the two photon absorption spectrum of *p*-dichlorobenzene.

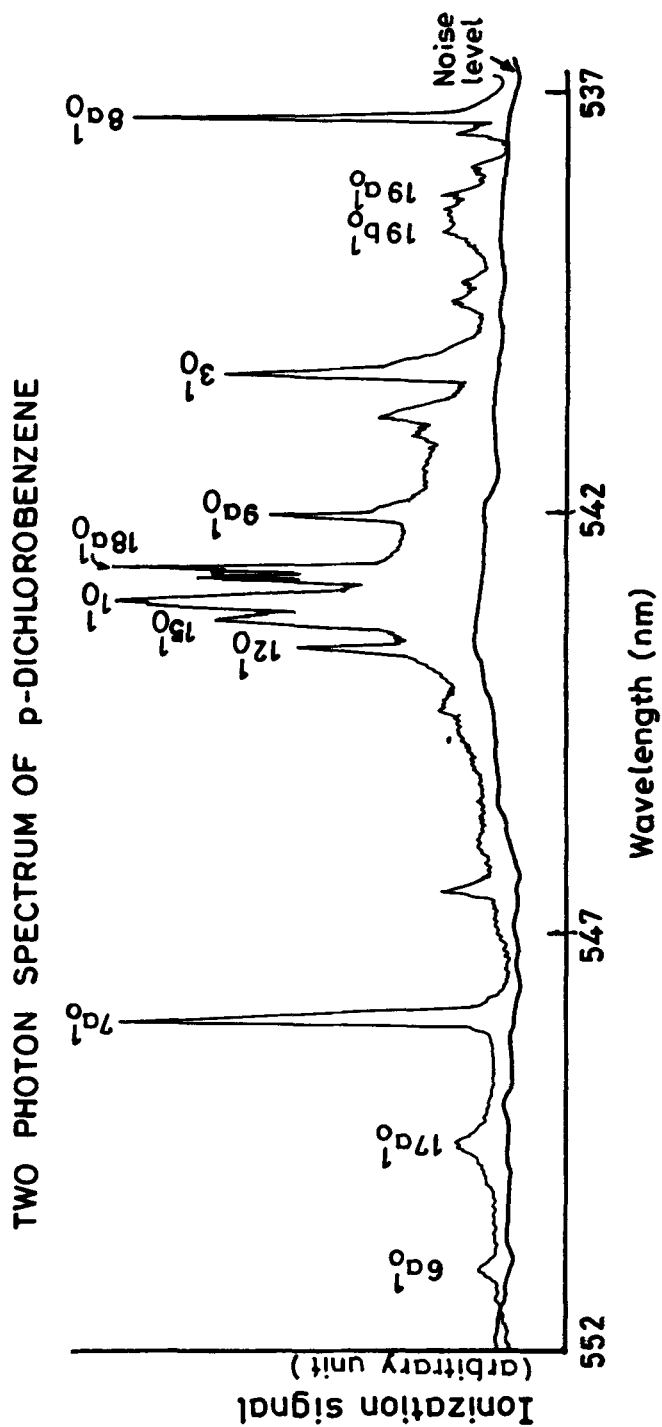


Figure 2b. A part of the two photon absorption spectrum of p-dichlorobenzene.

*Two photon absorption spectrum*

**Table 1.** Prominent two photon bands in *p*-dichlorobenzene and their assignment.

Wavelength of the bands (Å)	$2\nu$ in $\text{cm}^{-1}$	$\Delta\nu$ in $\text{cm}^{-1}$	Intensity	Assignment
5512.6	36280	538	W	$6a_0^1$
5499.6	36366	624	W	$17a_0^1$
5482.7	36478	736	VS	$7a_0^1$
5469.5	36566	824	MW	$17a_0^1 17b_0^1 6a_1^1$
5440.5	36761	1019	MS	$12a_0^1$
5436.9	36785	1043	MS	$15_0^1$
5436.2	36790	1048	VS	$1_0^1$
5433.0	36803	1061	S	$9a_0^1$
5432.7	36814	1072	VS	$18a_0^1$
5426.2	36858	1116	MS	$6a_0^1 17a_0^1$
5414.7	36936	1194	M	$7a_0^1 16b_0^1$
5409.7	36970	1228	S	$3_0^1$
5401.9	37024	1282	W	$7a_0^1 6b_0^1$
5399.4	37082	1340	W	$19b_0^1$
5389.8	37107	1365	W	$19a_0^1$
5381.4	37165	1423	VS	$8a_0^1$
5358.3	37325	1583	VS	$14_0^1$
5309.8	37666	1924	W	$14_0^1 18b_0^1$
5254.2	38064	2322	W	$14_0^1 7a_0^1$
5224.8	38278	2536	M	$14_0^1 18b_0^1 17a_0^1$
5174.7	38651	2909	W	$9a_0^2 7a_0^1 18b_1^1$
5141.5	38898	3156	S	$14_0^1 1_0^1 6a_0^1$
5128.1	39000	3258	M	$14_0^1 19a_0^1 18b_0^1$
5115.7	39095	3353	M	$14_0^1 1_0^1 7a_0^1$
5097.1	39237	3495	MS	$14_0^1 7a_0^2 16b_0^1$
5081.9	39355	3613	W	$14_0^1 1_0^1 10b_1^1$
5078.0	39385	3643	W	$14_0^1 1_0^2 6a_1^1$
5066.2	39477	3735	S	$14_0^1 9a_0^2 18b_2^2$
5052.1	39588	3846	M	$7a_0^2 19b_0^1 6a_0^2$
5048.7	39614	3872	S	$14_0^1 18a_0^1 3_0^1$
5038.2	39696	3954	MS	$14_0^1 9a_0^2 17b_0^2 10b_1^1$
5016.5	39868	4127	MS	$14_0^1 9a_0^2 18b_0^1$
5005.2	39958	4216	M	$14_0^1 1_0^2 17a_0^1 18b_2^2$
4990.0	40079	4337	MW	$14_0^1 9a_0^2 6a_0^1$
4977.5	40180	4438	MW	$14_0^1 9a_0^2 7a_0^1 10b_1^1$

It is well-known that in the corresponding transition in benzene vapour the longest wavelength band observed at the lowest temperature is the one involving the excitation of one quantum of a C–C–C in-plane bending vibration of  $e_{2g}$  symmetry. The ground state magnitude of this frequency is  $608\text{ cm}^{-1}$  (mode 6a in Wilson notation) while the excited ( ${}^1B_{2u}$ ) state magnitude is  $538\text{ cm}^{-1}$ . This vibration is not expected to change drastically when some of the hydrogen atoms in benzene are replaced by chlorine atoms as in PDCB. Moreover, though the transition is now electronically allowed the charge cloud of the molecule does retain to a great extent the same features as in benzene so that the excitation of a single quantum of this vibration could be expected to give rise to a false origin and band structure loaded on to it. This is actually observed.

The weak band at a separation of  $538\text{ cm}^{-1}$  (on the shorter wavelength side) from the (O–O) band is ascribed to the excitation  $6a_0^1$ . This mode is the Raman active component of the above mentioned  $e_{2g}$  vibration of benzene. The other component of this doubly degenerate vibration (in benzene) is seen as another weak band at a separation of  $624\text{ cm}^{-1}$  from the (O–O) band. This is ascribed to the 17a mode and is infrared active.

A relatively intense band is seen at  $0 + 736\text{ cm}^{-1}$ . This frequency is ascribed to the 7a mode involving the C–Cl stretching. The corresponding frequency ( $748\text{ cm}^{-1}$ ) in the ground state of the molecule is seen prominently in Raman spectrum.

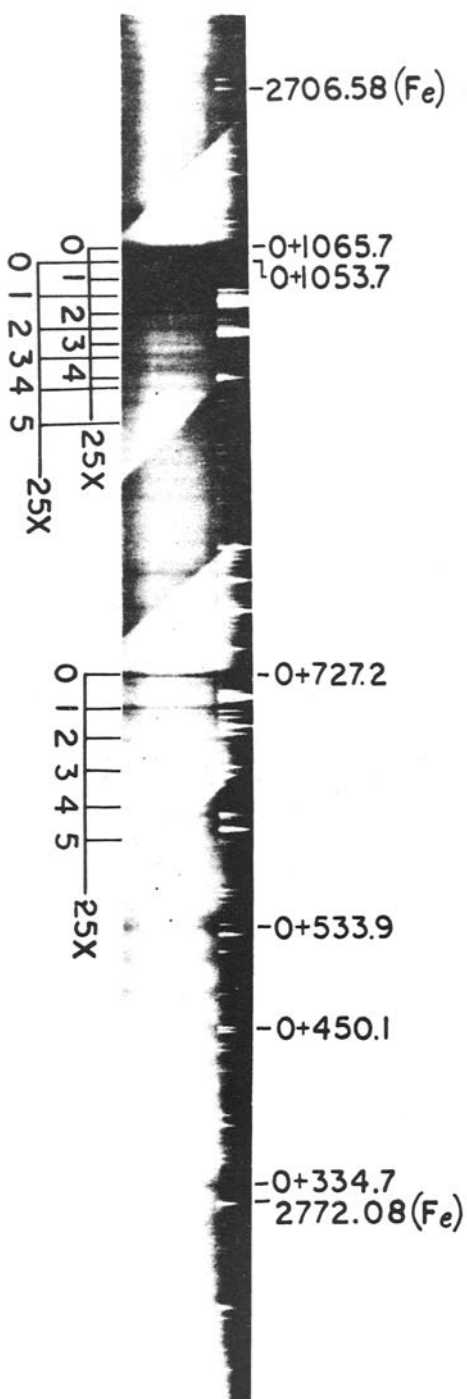
A group of five bands is seen at  $36761, 36785, 36790, 36803$  and  $36814\text{ cm}^{-1}$  with separation from the O–O band of  $1019, 1043, 1048, 1061$  and  $1072\text{ cm}^{-1}$ , respectively. The bands are assigned as  $0 + 12_0^1, 0 + 15_0^1, 0 + 1_0^1, 0 + 9a_0^1$  and  $0 + 18a_0^1$ . Of these the bands at a separation of  $1048\text{ cm}^{-1}$  is the most prominent and is ascribed to the excitation of the totally symmetric ring breathing frequency (some of these bands may also involve sequence bands buried under the succeeding bands).

The band observed at  $37325\text{ cm}^{-1}$  has the largest intensity in the whole spectrum. Its separation from the O–O band is  $1583\text{ cm}^{-1}$ . This frequency is one of the characteristic features in the two photon spectrum of benzene derivatives and is assigned as  $14_0^1$ . It is due to C–C stretching vibration. This frequency being the most active is involved in a large number of bands, in combination with several other frequencies, which dominate the whole structure. Some of the strong combination bands where this  $\nu_{14}$  fundamental is involved are  $14_0^1 1_0^1 6a_0^1$  at  $38898\text{ cm}^{-1}$ ,  $14_0^1 9a_0^1 18b_0^1$  at  $39477\text{ cm}^{-1}$ ,  $14_0^1 18_0^1 3_0^1$  at  $39614\text{ cm}^{-1}$  etc. Some other fundamental vibrations which appear with slightly lower intensity have the magnitude  $1228\text{ cm}^{-1}$ ,  $1340\text{ cm}^{-1}$ ,  $1365\text{ cm}^{-1}$  and  $1427\text{ cm}^{-1}$ . These bands are assigned to  $3_0^1$  (of  $b_{3g}$  species),  $19a_0^1$  (of  $b_{2u}$  species),  $19b_0^1$  (of

**Table 2.** Intensity of different vibrations with respect to  $\nu_{14}$  in *o*- and *p*-dichlorobenzenes.

Vibration $\nu_x$	ODCB Molecule $I(\nu_x)/I(\nu_{14})$	PDCB Molecule $I(\nu_x)/I(\nu_{14})$
7a	1/6	1/2.2
18a	1/2.5	1/2.2
1	1/2.5	1/2.2
12	1/6	1/4

*Two photon absorption spectrum*



**Figure 3.** A part of the one photon absorption spectrum of *p*-dichlorobenzene (taken from ref. [7]).

$b_{1u}$  species) and  $8a_0^1$  (of  $a_g$  species) modes respectively. Sequence bands are seen to accompany several of the main bands with separation  $-26$ ,  $-31$  and  $-86\text{ cm}^{-1}$ . Table 1 gives the complete assignment of the observed bands. Some of the bands appear prominently in the two photon spectra of *o*- as well as in *p*-dichlorobenzene. The intensities of these bands with respect to  $\nu_{14}$  in the two molecules are compared in table 2.

We have also compared our two photon spectrum with one photon spectrum reported by Rai [7]. A part of the one photon spectrum is also given in figure 3. Some of the prominent bands observed in our two photon spectrum (viz.  $O_0^0 + 1061\text{ cm}^{-1}$ ;  $O_0^0 + 1048\text{ cm}^{-1}$ ,  $O_0^0 + 736\text{ cm}^{-1}$ ,  $O_0^0 + 538\text{ cm}^{-1}$  etc) are clearly seen in one photon spectrum also.

### Acknowledgement

Authors are grateful to CSIR for financial assistance.

### References

- [1a] L Goodman and R P Rava, *Adv. Chem. Phys.* **54**, 177 (1983)
- [1b] L Goodman and R P Rava, *J. Chem. Phys.* **74**, 4826 (1981)
- [2] W Wollman, (Unpublished work quoted in reference 5)
- [3] H Conrad Billroth, *Z. Phys. Chem.* **1319**, 76 (1932)
- [4a] H Sponer, *Rev. Mod. Phys.* **14**, 224 (1942)
- [4b] H Sponer and J S Kirby Smith, *J. Chem. Phys.* **9**, 667 (1941)
- [5] B D Joshi, *J. Sci. Res.* **6**, 133 (1955-56)
- [6] T Anno and I Matubara, *J. Chem. Phys.* **23**, 796 (1955)
- [7] J N Rai, Ph D thesis, Banaras Hindu University, India, (1967)
- [8] I B Singh, S B Rai and D K Rai, *J. Mol. Spectrosc.* **163**, 364 (1994)