

## Electronic spectra of parafluorobromobenzene

SHASHI K SINGH and K N UPADHYA

Department of Physics, Banaras Hindu University, Varanasi 221 005

MS received 15 March 1979; revised 15 February 1980

**Abstract.** The electronic absorption spectrum of parafluorobromobenzene is reported together with its band shape and molecular geometry. The electronic transition is found to be the 2900–2400 Å system and the analysis consistent with other parahetero-halogenated benzenes. The intense bands, including 0–0, are double headed and are *B*-type in nature. *A*-type vibronic bands are also observed although less intense than the *B*-type bands. In all 9 excited states and 5 ground state fundamentals could be assigned.

**Keywords.** Vibrational analysis; band shape; molecular geometry; parafluorobromobenzene.

### 1. Introduction

The electronic absorption spectrum of parafluorobromobenzene (PFBB) molecule still lacks a thorough vibrational assignment. Earlier studies were made with hexane solution (Conrod-Billroth and Forster 1936) and in vapour state (Dima and Tintea 1940). Krishnamachari (1956) investigated the molecule in the vapour state and observed only five fundamentals in 2900–2475 Å system. Varsanyi *et al* (1963) assigned the normal vibration frequencies and discussed their respective modes. Green (1970) carried out infrared studies and suggested a few changes in vibrational assignments. The present work deals with the vibrational analysis and the assignments of the frequencies in the upper state.

### 2. Experimental

The spectrum is photographed on Steinheil quartz spectrograph which has a resolution  $\approx 4 \text{ cm}^{-1}$  in the ultraviolet region ( $\approx 2700 \text{ Å}$ ). The sample was obtained from Koch Light Company and was used without further purification. The absorption cell was 40 cm in length with an attached bulb kept at  $-15^\circ\text{C}$ . The spectrum was recorded on an  $\text{HP}_3$  plate and exposed for 5 hr. Iron spectrum was superposed for identification. A densitometer trace of the absorption bands was also taken. The absorption spectrum could not be photographed on a grating spectrograph of high resolution since it required a powerful xenon lamp as a source of excitation. In order to prevent dissociation of the molecule due to the intense ultraviolet radiation from this lamp a hydrogen lamp source was used to record the spectrum. The poor intensity of the hydrogen lamp prevented the use of grating spectrograph with a long optical path and instead a prism spectrograph was used.

### 3. Description of the spectra and discussion

Several bands were observed in the absorption spectrum of PFBB. The low resolution spectrum has three groups of intense bands with about 70% of intensity. The strong bands are double-headed and separated by a small region of low absorption. There are also bands of good intensity with a single peak.

The vibrational spectrum of parafluorochlorobenzene (PFCB) and PFBB show marked similarities and differ only slightly in atomic mass at the para position and electronegativity. This difference affects only the spacing of rotational levels and not the chemical properties of the two molecules. The parahetero-substituted benzene molecule belongs to point group  $C_{2v}$  and the change of mass at para position leaves the moment of inertia  $I_A$  untouched.

Since  ${}^1B_2 \rightarrow {}^1A_1$  transition is responsible for the absorption system in the ultraviolet region, the transition moment will be polarised along  $y$ -axis. Therefore, the 0—0 band and the other bands involving totally symmetric vibrations show  $B$ -type band structure. If the in-plane bending vibrations of symmetry  $b_2$  are excited, the vibrational moment will be along the  $z$ -axis which is also the symmetry axis of the molecule. These bands are  $A$ -type in nature and show less absorption than the  $B$ -type bands. Bands involving out-of-plane vibrations ( $b_1$  or  $a_2$ ) will have  $C$ -type structure and their presence is less likely.

The strongest band in the spectrum at  $36229.6 \text{ cm}^{-1}$  is assigned the electronic origin. This is a double-headed band and the other one is less intense and lies at the frequency difference of  $7.9 \text{ cm}^{-1}$  on the lower frequency side. Krishnamachari (1956) assigned  $36221 \text{ cm}^{-1}$  as the 0—0 band while Varsanyi *et al* (1963) reported it to be  $36212 \text{ cm}^{-1}$ . We also observed  $36221 \text{ cm}^{-1}$  along with the more intense one of  $36229.6$ . The assignment of the latter as 0—0 band agrees with the band contour analysis and is justified by the presence of sequence structure.

In PFCB Cvitas and Hollas (1970) observed a positive sequence ( $2.7 \text{ cm}^{-1}$ ) due to vibration  $\nu_{30}$  of  $b_2$  symmetry type. We observed  $\nu_{30}''$  ( $218.3$ ) and  $\nu_{30}'$  ( $220.8$ ) with a difference of  $+2.5 \text{ cm}^{-1}$  but a sequence of this difference is not seen probably because of the low resolving power of the instrument. The fundamental  $\nu_{30}$  however superposes with other fundamentals and sequence intervals present in both states. In the analysis of para dibromobenzene (PDBB) Japar (1972) also observed positive sequence in the vicinity of the 0—0 band.

The difference frequencies of PFCB and PFBB are strikingly similar (table 1). The bands involving separation of  $32.4$  and  $86.4 \text{ cm}^{-1}$  are double-headed like the 0—0 band and the peaks are separated by  $7.9 \text{ cm}^{-1}$ . The difference frequency  $32.4$  is observed upto 4 quanta. Cvitas and Hollas (1970), assigned it as the vibration of lowest frequency  $\nu_{20}$  on the basis of its maximum intensity among sequences. In this analysis the transition from one quantum of totally symmetric frequency  $\nu_{11}$  in the upper state to the level of its one quantum in the ground state is assigned as  $11_1^1$  and involves a difference frequency of magnitude  $34.2 \text{ cm}^{-1}$ . Similarly the transition  $20_1^1$  gives a difference frequency of  $27.4 \text{ cm}^{-1}$ . All these frequencies superimpose on all the observed fundamental vibrations.

Table 2 contains the fundamental vibrational frequencies which agree with those given by Krishnamachari (1956) and Varsanyi *et al* (1963) respectively. In the ground state only five fundamentals namely  $126.5$ ,  $218.3$ ,  $282.4$ ,  $316.9$  and  $398.8 \text{ cm}^{-1}$  could be assigned. Their respective infrared values and symmetry species are  $\nu_{20}$   $121(b)_1$ ,

Table 1. Prominent sequence intervals in *p*-fluorobromobenzene analysis.

Sequence head	Interval (cm <sup>-1</sup> )
20 <sub>1</sub> <sup>1</sup>	-27.4 (-32.4)
11 <sub>1</sub> <sup>1</sup>	-34.2
30 <sub>1</sub> <sup>1</sup>	+ 2.5 (+ 2.7)
19 <sub>1</sub> <sup>1</sup>	-86.4 (-88.3)
?	-238.3 (-246.7)
29 <sub>1</sub> <sup>1</sup>	-24.2 (-24.1)

In the parentheses are the corresponding values for *p*-fluorochlorobenzene as given by Cvitas and Hollas (1970).

Table 2. Vibrational frequencies for parafluorobromobenzene in its ground and excited states (used in the analysis).

Class	Vibration Green (1970)	Description (approx) Green (1970)	Ground state fundamentals (cm <sup>-1</sup> )		Excited state fundamentals Literature		(cm <sup>-1</sup> ) Present work
			Green (1970)	Present I.R. Raman Work	Krishnamachari (1960)	Present work	
<i>a</i> <sub>1</sub>	$\nu_1$	$\nu(\text{CH})$	3076	3077			
	$\nu_2$	$\nu(\text{CH})$					
	$\nu_3$	$\nu(\text{CC})$	1587	1586			
	$\nu_4$	$\nu(\text{CC})$	1485	1485			
	$\nu_5$	Br-sens	1064	1228p	1230		1225.6
	$\nu_6$	$\beta_{-}(\text{CH})$	1156	1155p	—		1136.1
	$\nu_7$	Br-sens	1064	1065p	—		1013.4
	$\nu_8$	$\beta_{-}(\text{CH})$	1012	1013p			
	$\nu_9$	Br-sens		810p	788		{ 784.8 790.6
	$\nu_{10}$	Br-sens	596	596p	530		510.0
	$\nu_{11}$	Br-sens	290	290p	282.4	251	248
<i>a</i> <sub>2</sub>	$\nu_{12}$	$\gamma(\text{CH})$	945				
	$\nu_{13}$	$\gamma(\text{CH})$	804				
	$\nu_{14}$	$\phi(\text{CC})$					
<i>b</i> <sub>1</sub>	$\nu_{15}$	$\gamma(\text{CH})$	931				
	$\nu_{16}$	$\gamma(\text{CH})$	824				
	$\nu_{17}$	$\phi(\text{CC})$	689	689 dp			
	$\nu_{18}$	$\phi(\text{CC})$	495	497			
	$\nu_{19}$	Br-sens	323	323 dp	316.9		234.7
	$\nu_{20}$	Br-sens	121		126.5		99.1
<i>b</i> <sub>2</sub>	$\nu_{21}$	$\gamma(\text{CH})$	3076				
	$\nu_{22}$	$\gamma(\text{CH})$	3046				
	$\nu_{23}$	$\gamma(\text{CC})$	1587	1586			
	$\nu_{24}$	$\gamma(\text{CC})$	1400				
	$\nu_{25}$	$\beta(\text{CH})$	1290	1289			
	$\nu_{26}$	Kekule	1277	1289			
	$\nu_{27}$	$\beta(\text{CH})$	1086	1090			
	$\nu_{28}$	$\alpha(\text{CCC})$	624	627			
	$\nu_{29}$	Br-sens	415	416	398.8		
	$\nu_{30}$	Br-sens	223	224	218.3		220.8

$\nu_{30}$  223( $b_2$ ),  $\nu_{11}$  290( $a_1$ ),  $\nu_{19}$  323( $b_1$ ) and  $\nu_{29}$  415( $b_2$ ). The electronic transitions in which vibration frequencies  $\nu_{20}$  and  $\nu_{19}$  are involved, show weak bands. The reason is that these two frequencies are due to out-of-plane vibrational modes and hence the resulting transition moments will not be in the plane of the molecule. On the basis of theoretical consideration  $\nu_{29}$  will give  $A$ -type bands showing single peak. The densitometer trace of the band (398.8  $\text{cm}^{-1}$ ) shows a similar structure and hence it is assigned due to  $\nu_{29}$ . The difference between the observed and infrared values of  $V_{29}$  may be due to uncertainty in measurement because of weak intensity.

The most active frequency in the upper state is 784.8  $\text{cm}^{-1}$  and assigned as the totally symmetric ring breathing vibration  $\nu_9$ . In the neighbourhood of 784  $\text{cm}^{-1}$  one more band whose intensity is less than the former is observed at a separation of 790.6  $\text{cm}^{-1}$  from the 0-0 band. But the diffuse nature of these bands, probably some kind of a perturbation of vibrational levels, is a possibility. Similar observations in PFCB analysis were made by Thakur (1968) who explained it as due to the coriolis interaction between the levels due to  $\nu_9$  and  $\nu_{16}$  modes. In the present case both the vibrations at 784.8  $\text{cm}^{-1}$  and 790.6  $\text{cm}^{-1}$  are observed in double quanta and separately form combinations, while in PFCB only the unperturbed excited state frequency  $\nu_9$  appears in higher quanta as well as in combinations. It is presumed that the assignment of 784.8  $\text{cm}^{-1}$  gives a series of progressions of good intensity with all the difference frequencies and fundamentals. The fundamental 510  $\text{cm}^{-1}$  in the upper state is due to the medium strong double-headed band at 36739.6  $\text{cm}^{-1}$ . The two peaks of this band are separated by 7.6  $\text{cm}^{-1}$  and its structure is exactly similar to the 0-0 band. This band with a  $B$ -type band structure can be related only to a totally symmetric vibration. Varsanyi *et al* (1963) assigned it to mode  $\nu_{10}$  which is a bromine-sensitive vibration of magnitude 596.0  $\text{cm}^{-1}$  which is totally symmetric. Vibration corresponding to 510 is not observed in PFCB, perhaps due to the extremely weak intensity. In this case  $\nu_{10}$  appears forming combinations with other fundamentals and with difference frequencies and appreciable intensity. In mixed para heavy dihalogenated benzenes the breathing mode  $\nu_9$  loses its character and becomes a planar c-c-c triangular bending vibration.

The other bands showing  $B$ -type structures are 0+248.1, 0+496.4, 0+1013.4, 0+1033.7, 0+1136.1 and 0+1225.6 of which 496.4  $\text{cm}^{-1}$  and 1033.7  $\text{cm}^{-1}$  are explained as the combinations of  $9_0^1 11_1^0$  and  $9_0^1 11_0^1$  respectively, both with the resulting symmetry  $a_1$ , while others are assigned to different  $a_1$ -type fundamentals. One more possible assignment for 496.4  $\text{cm}^{-1}$  is  $2 \times 248.1$  which also gives the symmetry  $a_1$ . The medium strong band 37455.2  $\text{cm}^{-1}$  is assigned as 0+1225.6 corresponding to the totally symmetric  $C-F$  stretching mode  $\nu_5$  (1228  $\text{cm}^{-1}$ ). This negligible drop in frequency is a characteristic of the  $C-F$  stretching which is also visible in other fluorine-substituted benzenes. The undiscernible drop in the frequency refers to equal band length of  $C-F$  in both the states.

#### 4. Molecular geometry in the excited state

Para fluorobromobenzene is assumed to have a planar benzene-type ring structure in its ground state. Studies with a large number of substituted benzenes confirm that no remarkable change takes place in the shape and size of the phenyl ring.

The geometry of a molecule for its equilibrium configuration in the excited electro-

nic state is decided from the study of rotational structure of the (0, 0) band. In those cases where the structure is not resolved, Franck Condon analysis helps in understanding the changes in geometry due to the electronic excitation from ground to the excited state. This method is based on observing the bands due to non-totally symmetric vibrations. It requires an accurate vibrational analysis.

From the present analysis totally symmetric frequencies  $\nu_5$ ,  $\nu_6$ ,  $\nu_7$ ,  $\nu_8$ ,  $\nu_9$ ,  $\nu_{10}$  and  $\nu_{11}$  explain most of the bands. Of these,  $\nu_9$  the ring breathing mode, forms progression. It is thus clear that there are minimum changes in the geometry of the molecule from ground  $^1A_1$  to the upper  $^1B_2$  electronic state.

### References

- Allen P W and Sutton L E 1950 *Acta. Crystallogr.* **3** 46  
Conrod-Billroth H and Forster G 1936 *Z. Phys. Chem.* **33** 311  
Cvitas T and Hollas J M 1970 *Mol. Phys.* **18** 261  
Duma G A and Tintea H 1940 *Bull. Sect. Sci. Acad. Roy.* **23** 34  
Green J H S 1970 *Spectrochim. Acta* **A26** 1503  
Japar S M 1972 *Can. J. Phys.* **50** 1402  
Krishnamachari S L N G 1956 *Indian J. Phys.* **30** 487  
Thakur S N 1968 *Spectra and structural studies of molecules under high resolution*, Ph.D. Thesis  
Banaras Hindu University  
Varsanyi G, Holly S and Farago T 1963 *Spectrochim. Acta* **19** 669