

Electronic spectra of paramethoxy benzyl alcohol and parachloro benzyl cyanide

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Abstract. The electronic absorption spectra of paramethoxy benzyl alcohol (PMBA) and parachloro benzyl cyanide (PCBC) are described. The broad features of the spectra of the molecules are consistent with allowed transition for C_{2v} symmetry. However, the solid state and glass matrix spectra of PMBA at 77K indicate possible deviation from planarity in the structure of the molecule. In PCBC, it is pointed out that intensity borrowing may be responsible for the large intensity of the vibrationally-induced part of the spectra, in which non-totally symmetric vibrations are excited.

Keywords. Solid phase spectrum; glass matrix spectrum; intensity borrowing; paramethoxy benzyl alcohol; parachloro benzyl cyanide.

1. Introduction

Complete vibrational assignments of paramethoxy benzyl alcohol (PMBA) and parachloro benzyl cyanide (PCBC) molecules were recently described (Chakravorti *et al* 1982). This paper concerns recording and analysis of hitherto unreported electronic absorption spectra of PMBA in the vapour and solid states and in an isobutyl alcohol rigid glass at 77K and of PCBC in the solid phase and in an ethanol rigid glass at 77K. Both are para-disubstituted benzene molecules with one or more large substituents. In PMBA, both substituents (OCH_3 and CH_2OH) are electron releasing while in PCBC, one substituent (Cl) is electron releasing and the other (CH_2CN) is electron withdrawing. In interpreting the results attention has been paid to probable structure and symmetry of the molecules, with which the symmetry of vibrational modes involved in an electronic transition is known to be intimately related.

2. Experimental

The compounds PMBA and PCBC were of purum grade and were obtained from Fluka AG (Switzerland) and E. Merck (Germany) respectively. They were used after repeated vacuum distillation. Isobutyl alcohol and ethanol of spectroscopic purity were supplied by BDH (London). Experimental arrangements were the same as described elsewhere (Mallick and Banerjee 1974).

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3. Interpretation of the results

In making vibrational assignments of the ring vibrations, the molecules were assumed to belong to symmetry species C_{2v} (Chakravorti *et al* 1982). If the assumption is valid, then with recommended choice of axes (Mulliken 1955) the π -electronic transition would be ${}^1B_2 \leftarrow {}^1A_1$ corresponding to ${}^1B_{2u} \leftarrow {}^1A_{1g}$ of benzene with dipole moment in the plane of molecules and along Y direction *i.e.* perpendicular to C_2 axis. The expected vibrational structure of the electronic spectra of such molecules is well established. The spectra should exhibit a strong O, O band and progressions of totally symmetric (a_1) vibrations. Non-totally symmetric vibrations (b_2 type) may couple with the transition but only weakly.

3.1 PMBA

The f -value of the transition, which is allowed, is measured in cyclohexane solution and found to be 2.59×10^{-2} . The O, O band in the vapour spectrum is identified with the band 35539 cm^{-1} . Modes 1 and 12 of benzene, which are substituent sensitive in para-substituted benzenes, yield two trigonal modes (Chakravorti *et al* 1982) assigned as ν_9 (851 cm^{-1}) and ν_{10} (818 cm^{-1}). The excited state frequency 820 cm^{-1} may be reasonably correlated with ν_9 . The excited state vibration 313 cm^{-1} represents the a_1 component of the $\alpha(\text{CCC})$ mode 6 of benzene, the corresponding ground state vibration being 374 cm^{-1} (ν_{11}). These two vibrations are the most prominent in the vapour spectrum. Another a_1 vibration 1127 cm^{-1} is also observed in the band at 36646 cm^{-1} (table 1), which is broad due to the presence of a second unresolved band $0 + 313 + 820$. The spectrum shows presence of one nontotally symmetric planar b_2 vibration which appears in the weak band at 36877 cm^{-1} .

The two excited state a_1 vibrations related to ν_{11} and ν_9 , observed in the vapour spectrum, are also strongly excited in the spectra of PMBA in the solid phase and in isobutyl alcohol glass matrix at 77K (tables 2 and 3). The solid state spectrum consists of sharper bands and a b_2 vibration 198 cm^{-1} couples

Table 1. Absorption bands of PMBA vapour.

Wave no in cm^{-1} and intensity	Assignment
35143 wb	0 - 376
35519 w	0, 0
35832 m	0 + 313
36339 m	0 + 820
36646 sb	0 + 1127; 0 + 313 + 820
36877 w	0 + 1358
37122 wb	0 + 2 \times 820
37484 wb	0 + 820 + 1127

Table 2. Absorption bands of PMBA in isobutyl alcohol rigid glass and in solid phase at 77K.

Isobutyl alcohol rigid glass at 77K		Solid at 77K	
Wave number in cm^{-1} intensity	Assignment	Wave number in cm^{-1} and intensity	Assignment
35164 m	0 - 0	35127 m	0 - 0
35275 s	0 + 111	35227 sb	0 + 100
		35325 vs	0 + 190
35501 vs	0 + 337	35451 vs	0 + 324
35987 vs	0 + 823	35948 m	0 + 821
36326 vs	0 + 1162; 0 + 337 + 823	36277 vs	0 + 1150; 0 + 324 + 821
36713 vs	0 + 2 \times 823	36713 vs	0 + 2 \times 821
37136 svb	0 + 337 + 2 \times 823; 0 + 823 + 1162	37095 vs	0 + 324 + 2 \times 821; 0 + 821 + 1150
		37510 s	0 + 3 \times 821
		37925 mb	0 + 324 + 3 \times 821; 0 + 2 \times 821 + 1150
		38259 m	0 + 4 \times 821

Table 3. Correlation between ground and excited state frequencies of PMBA in cm^{-1} .

Raman	Ground state			Excited state		Symmetry species*
	IR	UV	Vapour	Solid at 77	Glass at 77K	
-	120	-	-	100	111	b_1 (ν_{20})
226	-	-	-	198	-	b_2 (ν_{30})
374	-	376	313	324	337	a_1 (ν_{11})
851	-	-	820	821	823	a_1 (ν_9)
1204	1182	-	1127	1150	1162	a_1 (ν_6)
1249	1260	-	-	-	-	a_1 (ν_5)
-	1428	-	1358	-	-	b_2 (ν_{24})

* Discussion in the text

with the transition. Both the solid state and rigid glass spectra are characterised by the appearance of an excited state frequency *ca* 111 cm^{-1} corresponding to the out of plane b_1 vibration 120 cm^{-1} (ν_{20}) in the ground state (Chakravorti *et al* 1982) representing an X - sensitive mode. Since such b_1 vibration should be forbidden in a ${}^1B_2 \leftarrow {}^1A_1$ transition, it is possible that the molecule may be distorted from planar structure in the solid phase and also in isobutyl alcohol matrix at 77K. Similar conclusions drawn in the case of benzene (Kanda and Shimada 1961; Kanda *et al* 1961) and 1,3,5-trimethoxy benzene (Chakravorti *et al* 1979 may) be noted.

3.2 PCBC

The computed *f*-value in cyclohexane solution is 2.9×10^{-3} . This shows that

Table 4. Absorption bands of PCBC in ethanol glass and solid phase at 77K.

Ethyl alcohol rigid glass		Solid at 77K	
Wave number in cm^{-1} and intensity	Assignment	Wave number in cm^{-1} and intensity	Assignment
36379 m	0, 0	36155 m	0, 0
		36406 s	0+251
		36713 s	0+558
37152 vs	0+773	36944 s	0+789
37442 vw	0+1063	37219 mb	0+1064
37653 m	0+1274	37442 s	0+1287
		37526 msh	0+1371
		37611 m	0+1456
37913 vw	0+1534; 0+2 \times 773	37710 m	0+1555; 0+2 \times 789
		37839 m	0+251+1456
		37968 m	0+789+1064
		38055 w	0+2 \times 558+789
38142 s	0+1763 (?)		
38381 w	0+773+1274	38200 w	0+789+1287
38667 w	0+3 \times 773; 0+1063+1274	38464 s	0+1064+1287; 0+3 \times 789
		38569 ssh	0+3 \times 558+789
38881 vw	0+2 \times 1274	38718 msh	0+2 \times 1287
		38854 w	0+1287+1456
		39235 m	0+4 \times 789

Table 5. Correlation of ground and excited state vibrational frequencies of PCBC in cm^{-1} .

Ground state		Excited state		Symmetry species *
Raman	IR	Rigid Glass at 77K	Solid at 77K	
—	260 or 358	—	251	b_2 (ν_{29}) or (ν_{30})
637	635	—	558	b_2 (ν_{28})
808	800	773	789	a_1 (ν_9)
1069	1070	1063	1064	a_1 (ν_7)
1322	1314	1274	1287	b_2 (ν_{25})
—	1485	—	1371	a_1 (ν_4)
1583	1578	—	1456	b_2 (ν_{23})
1600	1615	1534	1555	a_1 (ν_3)

*Discussion in text.

the electronic transition though allowed by symmetry is of weaker nature than that in PMBA. The vapour phase spectrum of this compound is not well structured and the vibronic analysis of electronic bands had to be confined to the solid phase and ethanol glass matrix spectra at 77K. As shown in table 4 the O, O band is identified at 36379 cm^{-1} and 36155 cm^{-1} in the spectra due to the rigid glass and the solid respectively. An upper state a_1 vibration 789 cm^{-1} is the most prominent and is excited several quanta in the spectra. Two other a_1 vibrations 1064 and 1371 cm^{-1} are also involved in the transition. One notable feature is a b_2 vibration of frequency 558 cm^{-1} (tables 4 and 5) which represents the $\alpha(\text{CCC})$ mode derived from the e_{2g} mode 6 of benzene. This vibration is quite prominent and several quanta of it appear in combination with the 789 cm^{-1} vibration. A few other bands arising from excitation of b_2 vibrations 251 , 1287 and 1456 cm^{-1} appear with considerable intensity. Several combinations of these are observed in the spectra. The excitation of these b_2 vibrations which constitute the so-called 'forbidden part' is quite high and may be attributed to intensity borrowing, effected through vibronic mixing of the B_2 state concerned in the $B_2 \leftarrow A_1$ transition with an upper A_1 state derived from E_{1u} state of benzene by excitation of b_2 vibration (Herzberg 1966; Mallick and Banerjee 1977). It was pointed out by Chakravorti *et al* (1977) that vibronic mixing of states is facilitated by crystal forces in the solid phase. However, in the case of the molecule PCBC, all the vibrations are planar (a_1 or b_2) and as such there is no indication of deviation from planar structure either due to crystal fields in the solid phase or in the ethanol matrix at 77K.

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