

Ultra-violet absorption spectrum of methyl benzene sulfinate

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The ultraviolet absorption spectrum of methyl benzene sulfinate in the vapour state and in solution have been studied. The observed fundamentals and their assignments are reported

1. INTRODUCTION

The ultraviolet absorption spectrum of methyl benzene sulfinate has been recorded in the range $\lambda 2720$ – $\lambda 2120\text{\AA}$ and analysed. The spectrum was also recorded in isoctane solution and the f values obtained. Since the data on the ground state vibrational frequencies of the molecule is not available in the literature, the infrared absorption spectrum is also recorded and analysed.

2. EXPERIMENTAL

The vapour and solution spectra were recorded with a DK2A Beckman spectrophotometer with 1 to 10 cm cells at room temperature and the vapour phase spectra was also recorded with a large quartz spectrograph with 10 to 150 cm cells at 0°C to 150°C . Ilford R-40 plates were used. The accuracy of measurements has been estimated to be $+5\text{ cm}^{-1}$ for sharp bands and $\pm 10\text{ cm}^{-1}$ for broad or diffuse bands. The f values of the solution spectrum were computed and is described elsewhere (Shashidhar & Rao 1975).

The infrared spectrum of this molecule was recorded using a Perkin Elmer model 225 spectrophotometer in the range 200 – 4000 cm^{-1} . For recording the spectrum in the regions 200 – 650 cm^{-1} and 650 – 4000 cm^{-1} CsI and NaCl optics were used respectively. Methyl benzene sulfinate being solid it was mixed in Nujol and in tetrachloroethylene and pastes of sufficient concentration were prepared. A little amount of these pastes were enclosed between the windows to obtain the desired absorption.

3. RESULTS AND DISCUSSION

The ultraviolet absorption spectrum of this molecule lies in the region $\lambda 2720$ – $\lambda 2120\text{\AA}$.

The infrared frequencies are given in table 1. The analysis of the infrared spectrum were made by comparison with the related molecules like benzene sulfonyl chloride, benzene sulfonyl bromide (Ham *et al* 1960). The characteristic

Table I Fundamental vibrational frequencies (in cm^{-1}) of methyl benzeno sulfinate

Wave number	Intensity	Assignment
265	m	α'' C-S-C deformation
310	s	α'' C-C out of-plane bending
405	m	α'' C-C out of-plane bending
445	s	α' C-C in-plane bending
610	w	α' C-C in-plane bending
530	s	α'' SO ₂ deformation
685	s	α'' C-C out of-plane bending
695	s	α' C-S stretching
745	s	α'' C-H out of-plane bending
785	s	α'' C-H out of-plane bending
925	s	α'' C-H out of-plane bending
955	s	α'' C-H out of-plane bending
960	vs	α'' C-H out of-plane bending
995	s	α' C-C stretching
1020	m	α' C-H in-plane bending
1035	m	α'' CH ₃ rocking
1070	s	α' C-H in-plane bending
1085	s	α' SO ₂ -CH ₃ stretching
1140	s	α' C-H in-plane bending
1160	m	α' C-H in-plane bending
1175	m	α' SO ₂ symmetric stretching
1280	s	α' C-H in-plane bending
1325	m	α' C-C stretching
1365	s	α' SO ₂ asymmetric stretching
1375	s	α' CH ₃ symmetric bending
1405	m	α' CH ₃ asymmetric bending
1445	s	α' C-C stretching
1465	m	α' C-C stretching
1585	ms	α' C-C stretching
2950	m	α' CH ₃ symmetric stretching
3005	m	α' CH ₃ asymmetric stretching
3010	m	α' C-H stretching
3040	w	α' C-H stretching
3085	w	α' C-H stretching

vs = very strong, s = strong, ms = medium strong,
m = medium, w = weak.

Table 2 Spectral data of methyl benzoate sulfinate

Lower frequency transition		
(a) In vapour phase $\nu(\text{cm}^{-1})$	Relative intensity	Assignment
36855	w	0,0 -311
36978	w	0,0 -198
37017	w	0,0 -3 × 49
37065	m	0,0 -2 × 49
37117	s	0,0 -49
37166	s	0,0
37244	w	0,0 +179 -2 × 49
37345	w	0,0 +179
37453	m	0,0 +287
37528	m	0,0 +661 -311
37741	w	0,0 +2 × 287
37827	m	0,0 +661
37997	w	0,0 +661 +179
38114	s	0,0 +948
38235	ma	0,0 +1069
38394	m	0,0 +948 +287
38569	w	0,0 +948 +287 +179
38696	w	0,0 +2 × 287 +948
38784	w	0,0 +948 +661
38883	w	0,0 +1069 +661
38958	w	0,0 +1069 +948 -198
39060	m	0,0 +2 × 948
39175	m	0,0 +1069 +948
39328	m	0,0 +2 × 1069
39474	w	0,0 +948 +1069 +287
39689	w	0,0 +3 × 948 -311
40005	w	0,0 +3 × 948
40315	w	0,0 +3 × 948 +287
40636	w	0,0 +4 × 948 -311
40945	w	0,0 +4 × 948
(b) In isooctane solution $\nu(\text{cm}^{-1})$	ϵ	Assignment
36985	798	0,0
37950	956	0,0 +965
38900	717	0,0 +2 × 965
39865	475	0,0 +3 × 965
40820	315	0,0 +4 × 965
$f_s = 0.00799 \pm 0.0002$		
Higher frequency transition		
In vapour phase $\nu(\text{cm}^{-1})$	In isooctane solution $\nu(\text{cm}^{-1})$	ϵ
47050 i	46350	8135
$f = 0.0562 \pm 0.002$		

contours were used to identify the species. The assignments were made by assuming C_s symmetry for the molecule. Out of 48 normal modes of vibration 33 are of a' type and 15 are of a'' type.

The band system lying in the region $\lambda 2710$ – 2410\AA (lower frequency transition) consists of some what narrow bands and are degraded to the red and this corresponds to the $A_{1g} \rightarrow B_{2u}$ transition of benzene. The study of temperature effect on band system has facilitated the choice of the band at 37166 cm^{-1} as the 0, 0 band. With this band as 0, 0, the bands with separations 198, 311 cm^{-1} towards the longer wavelength side are assigned as the ground state fundamentals, while the strong bands with shifts 179, 287, 661, 948 and 1069 cm^{-1} from the 0, 0 band towards the shorter wavelength side are identified as the excited state vibrational frequencies. On the basis of these ground and excited state fundamentals all the observed bands of this molecule can be interpreted. The excited state fundamentals 948 and 1069 cm^{-1} are progression forming and they may respectively correspond to the modes ring A_1 and $7a(A_1)$ (following the nomenclature of Randle & Whiffen 1955). The other two excited state fundamentals 179 and 287 cm^{-1} corresponding to the ground state fundamentals 198 and 311 cm^{-1} may respectively correspond to the modes $11(B_2)$ and $6a(A_1)$. The excited state fundamental 661 cm^{-1} , which combines with the frequencies 948 and 1069 cm^{-1} may correspond to the mode $12a(A_1)$. In addition, difference frequency 49 cm^{-1} has been observed and this may correspond probably due to v-v transition of some nontotally symmetric vibrations.

In absorption spectra of this compound in solution of isoctane, the strong band at 36985 cm^{-1} has been chosen as the 0, 0 band (lower frequency transition). It is interesting to note that the absorption spectrum of this compound in solution retain the vibrational structure observed in the corresponding vapour spectrum.

The spectra in the higher frequency transition both in the vapour and solution phase were recorded with the spectrophotometer. This may correspond to the 1980\AA band of benzene.

The spectral data for this compound both in the lower and higher frequency transitions are given in table 2.

References

- Ham N. S., Hambly A. N. & Laby R. H. 1960 *Aust. J. Chem.* **13**, 443.
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