

Raman and infrared spectra of tere-phthalaldehyde

R A YADAV, RAMAKANT, P C MISHRA and I S SINGH
Spectroscopy Laboratory, Department of Physics, Banaras Hindu University,
Varanasi 221 005, India

MS received 3 October 1981; revised 14 December 1981

Abstract. The laser Raman spectrum of tere-phthalaldehyde powder has been recorded on a Jobin Yvon HG 2S spectrophotometer with a ~ 100 mW Argon-Ion laser. The infrared spectrum of the solid substance has been recorded on a Perkin-Elmer 621 spectrophotometer in the region $300-4000\text{ cm}^{-1}$ using KBr and nujol mull techniques. The observed frequencies have been assigned in terms of the fundamentals, overtones and combinations assuming D_{2h} point-group symmetry.

Keywords. Infrared spectrum; Raman spectrum; vibrational assignment.

1. Introduction

Benzaldehyde and its mono-substituted derivatives have been the subject of extensive studies. Consequently, sufficient data on the vibrational frequencies of mono-substituted derivatives of benzaldehyde are available in the literature. The infrared spectrum of phthalaldehyde has been studied by Pinchas (1957) and Lal *et al* (1971). Srivastava *et al* (1972) have analysed the infrared spectrum of iso-phthalaldehyde. But neither the Raman nor the infrared spectrum of tere-phthalaldehyde seems to have been reported in the available literature so far. In the present investigation we report the results and analysis of the Raman and infrared spectra of tere-phthalaldehyde.

2. Experimental

The chemical, of pure grade, was obtained from Fluka Co. and was used without any further purification. The substance is solid at room temperature.

The infrared spectrum (figure 1) was recorded on a Perkin-Elmer 621 spectrophotometer in the region $300-4000\text{ cm}^{-1}$ using KBr and nujol mull techniques.

The Raman spectrum (figure 2) of powdered substance was recorded on a Jobin Yvon HG 2S spectrophotometer using a ~ 100 mW Argon-Ion laser source. Due to high level of fluorescence emission, the measurement of depolarization was not possible.

3. Results and discussion

The molecule tere-phthalaldehyde would belong to D_{2h} point group, if the two CHO groups are taken to be coplanar with the phenyl ring and are assumed to be mutually

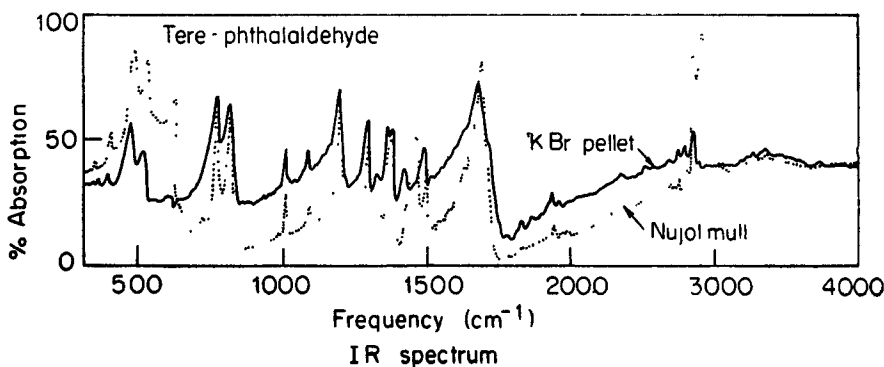


Figure 1.

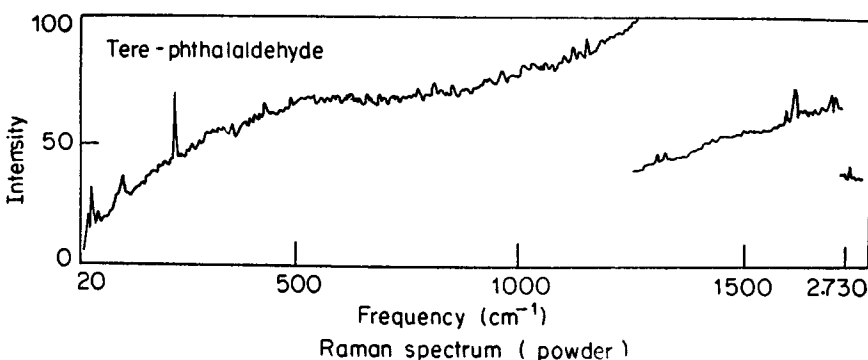


Figure 2.

non-interacting. Forty-two normal modes of vibrations are distributed among the various species as:

$$8a_g + 2b_{1g} + 4b_{2g} + 7b_{3g} + 3a_u + 7b_{1u} + 7b_{2u} + 4b_{3u}$$

but thirty normal modes of vibrations of the molecule $p\text{-X C}_6\text{H}_4\text{X}$ are distributed among the species of the D_{2h} point group as:

$$6a_g + 1b_{1g} + 3b_{2g} + 5b_{3g} + 2a_u + 5b_{1u} + 5b_{2u} + 3b_{3u}$$

Thus the two CHO groups would give rise to 12 normal modes of vibrations as:

$$2a_g + 1b_{1g} + 1b_{2g} + 2b_{3g} + 1a_u + 2b_{1u} + 2b_{2u} + 1b_{3u}.$$

The vibrations of species a_g and b_g 's are Raman active (vibrations of species a_g being polarized and those of b_g 's being depolarized) and the vibrations of the species b_u 's are infrared active, whereas the vibrations of the species a_u are inactive.

The molecule tere-phthalaldehyde consists of two parts (i) phenyl ring and (ii) CHO groups. Therefore, it must show the characteristic frequencies of both the parts. Two CHO groups, being in para-position, are so widely separated that the interaction between their internal vibrations can be ignored. Therefore, the internal vibrations of the two CHO groups would have nearly equal frequencies.

Phenyl ring as well as CHO group vibrations being separately discussed by earlier workers, need no further discussion.

Assignments have been made on the basis of magnitudes and relative intensities of the observed frequencies in the Raman and infrared spectra. Assistance has also been taken from the assignments made for related molecules (Brown 1967; Garg 1953-54; Lal *et al* 1971, 1973; Padhye and Viladkar 1960; Pinchas 1957; Singh and Singh (1967, 1968a, b, 1969-70), Srivastava *et al* (1969, 1969-70, 1972). Varsanyi's (1969) convention of the heavy and light substituents has also been taken into account.

Most of the observed frequencies have been assigned as fundamentals. In assigning the combination frequencies the infrared frequencies observed in the nujol mull are preferred as compared to those observed in the KBr (if there is a choice).

The observed frequencies along with their relative intensities in the Raman and infrared spectra and tentative assignments are presented in table 1.

Table 1. Observed frequencies and their proposed assignments.

Raman powder Freq. (cm ⁻¹)	Rel. int.	Infrared		Nujol mull		Proposed assignments (7)
		KBr pellet Freq. (cm ⁻¹)	Rel. int.	Rel. int.	Rel. int.	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
38	23					libration (*)
46	32					libration (*)
60	24					libration (*)
112	38					CHO torsion
231	77					C-CHO o.p. bending
				346	47	C-CHO o.p. bending
360	63					C-CHO i.p. bending
		392	40	396	61	C-C-C o.p. bending
432	71					C-C-C i.p. bending
		463	73	475	100	C-CHO i.p. bending
491	74					C=O o.p. bending
		508	54	521	96	C=O o.p. bending
		608	27	616	78	C-C-C i.p. bending
661	76					C-C-C i.p. bending
668	77					C-C-C o.p. bending
		760	91	767	72	C-H o.p. bending
776	77					C-C stretching (ring breathing)
808	82					C=O i.p. bending
		804	82	815	69	C=O i.p. bending
851	80					C-H o.p. bending
		929	27			C-H o.p. bending
967	87					C-H o.p. bending
		1000	56	1006	32	C-H i.p. bending
		1083	56	1088	27	C-H i.p. bending
		1114	52	1106	20	0+491+616
1124	97					C-CHO stretching (*)
		1140	54	1151	28	0+346+808
1153	100					C-H i. p. bending
		1190	95	1196	83	C-CHO stretching
		1292	76	1298	66	C-H i.p. bending (CHO group)

Table 1. (Contd.)

(1)	(2)	(3)	(4)	(5)	(6)	(7)
1299	50					C-H i.p. bending (CHO group)
1309	50					C-H i.p. bending
		1327	41	1333	24	C=C stretching
		1358	72	1365	56	0+521+851
		1375	70	1375	59	C=C stretching
		1421	45	1425	29	0+808+616
						0+231+1196
		1488	58	1492	40	C=C stretching
1592	69					C=C stretching
1606	79					C=C stretching
		1679	100	1690	97	C=O stretching
1689	76					C=O stretching
1700	75					0+2×851
		1777	13	1783	2	0+1309+475
		1827	12	1831	8	
		1940	30	1940	18	0+815+1124
						0+1606+346
		1963	24	1967	13	0+1196+776
						0+967+1006
		1992	44	1988	13	0+1492+491
		2333	42	2335	27	0+1190+1153
		2362	42	2354	27	0+661+1690
		2500	45	2497	29	0+808+1690
						0+1299+1196
						0+1375+1124
		2692	49	2687	37	0+1309+1375
2732	42					C-H stretching (CHO group)
		2750	56	2754	38	C-H stretching (CHO group)
		2796	78	2804	43	0+1690+1124
		2854	57	2854	43	0+1690+1153
		3054	48	3056	44	C-H stretching
		3087	47	3084	44	C-H stretching
		3233	53			0+491+2754
		3307	53			0+1690+1606
		3358	57	3365	51	0+1679+1689
		3458	54			0+3087+360

N.B. 1. i.p. = in-plane, o.p. = out of plane, Rel. int. = Relative intensity, * = Our proposal.

Acknowledgements

The authors are very grateful to the Director, RSIC, IIT, Powai, Bombay, for permission to use Jobin Yvon HG 2S spectrophotometer. They are also thankful to Prof.

G B Singh, for permission to use Perkin-Elmer 621 spectrophotometer. One of the authors (RAY) is thankful to CSIR, New Delhi, for financial assistance.

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