

compared to any other band even at very low vapour pressures. The spectrum has been analysed in terms of eleven excited state frequencies (180, 195, 360, 590, 712, 805, 930, 1075, 1185, 1345 and 1525 cm^{-1}).

The most prominent vibrational frequencies in the excited electronic state are 1346, 1345 and 1345 cm^{-1} in *o*-, *m*- and *p*-compounds respectively and these have been assigned to the C=O stretching mode.

The order of shift for the (0,0) bands in A units is *o*- > *m*- > *p*-, which is the same as given by Morton and Stubbs⁷ in the case of *o*-, *m*- and *p*-hydroxybenzaldehydes.

The authors record their thanks to Prof. N. L. Singh for encouragement. One of us (V. B. Singh) is grateful to C.S.I.R., New Delhi, for financial assistance.

Department of Spectroscopy, V. B. SINGH.
Banaras Hindu University, I. S. SINGH.
Varanasi-5, September 2, 1967.

1. Padhye, M. R. and Viladkar, B. G., *Indian J. Pure Appl. Phys.*, 1963, 1, 51.
2. — and —, *J. Sci. Industr. Res.*, 1960, 19 B, 49.
3. Jai-wal, R. M. P., *Indian J. Pure Appl. Phys.*, 1964, 2, 232.
4. Borino, G. B. and Manzoni, R., *Atti Accad. Sci. Inst. Bologna, Classe Sci. Fis.*, 1934, 9, 1; 7.
5. Kahovec, L. and Kohlrausch, K. W. F., *Z. Physik. Chem.*, 1937, 38 B, 119.
6. Singh, V. B. and Singh, I. S. (Unpublished work).
7. Morton, R. A. and Stubbs, A. L., *J. Chem. Soc.*, 1940, p. 1347.

VIBRATIONAL SPECTRUM OF 1-METHYL 9, 10-ANTHRAQUINONE

THE visible emission spectra of anthraquinone and some of its monosubstituted derivatives studied during the course of the present investigations^{1,2} have necessitated a knowledge of their vibrational frequencies in greater detail than obtained from their electronic spectra. These informations can be obtained from the Raman and infrared spectra of the compounds. Attempts made in this direction for substituted anthraquinones are meagre being confined to some selective regions of spectra. The infrared spectra of the compound in the C-H stretching and C-H out-of-plane bending regions have been recorded³ with a view to study the shift in these frequencies by ring-additions. The C-O stretching vibrations have been studied by Josien and Deschamps.⁴ However, no vibrational assignments of the observed frequencies have been made so far. Therefore, it was thought worthwhile to suggest the assignments of various frequencies observed in the present

infrared spectrum along with the Raman frequencies, the laser trace of which has been made available to us through the courtesy of Dr. Haber of Cary Instruments Lab., California, U.S.A.

The Eastman grade sample of 1-methyl 9, 10 anthraquinone was sublimed before use. The infrared spectrum was recorded with a Perkin-Elmer Spectrophotometer equipped with NaCl optics employing KBr technique. The concentration of the compound was varied between 1% and 2.5%.

TABLE I
Fundamental vibrational frequencies of
1-methyl 9, 10-anthraquinone

Raman cm^{-1}	(Solid) Int.	Infrared cm^{-1}	(Solid) Int.	Assignments
273	(1)			a'' C=O bending o.p.
290	(1½)			a'' skeletal deformation o.p.
335	(2)			a' C—CH ₃ bending i.p.
372	(½)			a'' skeletal deformation o.p.
440	(1)			a' C=O bending i.p.
455	(8)			a' skeletal deformation i.p.
652	(½)	653 (3)		a'' skeletal deformation o.p.
		655 (1)		C—H ₃ wagging
		691 (1)		a' skeletal deformation i.p.
696	(7)	702 (10)		a' ring breathing
716	(1)	716 (2½)		a' C—CH ₃ stretching
750	(½)	743 (1)		a'' skeletal deformation o.p.
		806 (½)		a'' C—H bending o.p.
		810 (2½)		"
850	(1)	849 (½)		"
		890 (3½)		a' C—H bending i.p.
		925 (1½)		a'' C—H bending o.p.
941	(½)	942 (6)		a' skeletal deformation i.p.
963	(3½)	970 (5)		a'' C—H bending o.p.
		982 (1½)		"
1012	(1)	1009 (1)		C—CH ₃ rocking
1043	(2½)	1041 (2)		a' C—H bending i.p.
1142	(2)	1142 (2½)		"
1180	(4½)	1178 (2)		"
1222	(3)	1222 (1)		"
		1260 (4½)		"
1281	(1)	1282 (9)		"
1325	(1)	1326 (9)		a' C—C stretching
1380	(1)	1352 (2½)		C—CH ₃ bending (symmetric)
		1412 (2)		a' C—C stretching
1430	(½)	1436 (1)		"
1450	(½)	1452 (1)		C—CH ₃ bending (asymmetric)
		1473 (1)		a' C—C stretching
1595	(6)	1597 (8)		"
1667	(10)	1671 (10)		a' C—O stretching
		2864 (½)		C—H stretching in CH ₃ group (symmetric)
		2950 (½)		C—H stretching in CH ₃ group (asymmetric)
3032	(1½)	3026 (1)		a' C—H stretching
3070	(2)	3062 (1)		"
3096	(½)	3104 (½)		"

i.p. = in-plane; o.p. = out-of-plane.

The molecular symmetry D_{2h} of 9,10-anthraquinone reduces to C_s when a CH_3 group replaces a hydrogen atom in 1-position. In addition, CH_3 group is assumed to lie in the plane of the molecule. Of the seventy-five normal modes of vibrations, 51 are symmetrical with respect to the plane of the molecule (a' type vibrations) while 24 are antisymmetrical (a'' type vibrations). In assigning the various frequencies to different modes of vibrations, assistance has been taken from the parent molecule⁵ and some related compounds.⁶⁻⁸ The assignments of the fundamental frequencies observed both in Raman and infrared spectra are shown in Table I.

The authors are thankful to Prof. N. L. Singh for the encouragement. They are also grateful to Dr. H. S. Haber of Cary Instruments Lab., California, U.S.A., for kindly supplying them the laser trace of Raman spectrum of the compound. One of them (S. N. S.) is thankful to U.G.C. for financial assistance.

Dept. of Spectroscopy,
Banaras Hindu Univ.,
Varanasi-5, August 22, 1967.

S. NATH SINGH.
R. S. SINGH.

MOLECULAR CONSTANTS OF CIS AND TRANS N_2F_2

THE cis and trans structure of N_2F_2 has been very well established recently.^{1,2} The infrared spectrum of the compound was first taken by Sanborn³ who also reported the valence force constants of the trans and 1,1-difluorodiazine conformations. But in the light of the latest assignment by King and Overend⁴ and structural information a reinvestigation of the force field has become necessary. In the present note, along with the force field (GVF and UBF), the generalised mean square amplitudes of vibration and coriolis coupling coefficients, which are important in electron diffraction and vibration-rotation interaction investigations respectively, are reported. The conventional Urey-Bradley force field has been modified by incorporating a trans-interaction term as described by Scherer and Overend.⁵ The force constants, generalised mean-square amplitudes and coriolis coupling coefficients are given in Tables I, II and III respectively.

TABLE I
Force constants of cis and trans N_2F_2
(md/Å)

Force constants	General valence		Urey-Bradley	
	cis	trans	cis	trans
f_R	11.0000	11.0000	9.9190	10.4000
f_r	4.4695	4.5270	4.1100	4.3610
f_a	0.9875	0.9595	0.6256	0.9120
f_T	0.6808	0.2973	0.6808	0.2973
f_{rr}	0.1915	-0.1500
f_{rR}	0.6902	0.2000
f_{aa}	0.1805	0.0205
f_{ra}	0.1180	0.2506
$f_{ra'}$	0.0000	0.0989
f_{Ra}	0.9605	0.4354
k_{12}	0.0000	0.1019
$F_{\alpha\gamma}$	0.4321	0.1132
$F_{\gamma\gamma}$	-0.6506	-0.3427

TABLE II

Generalised mean-square amplitudes (\AA^2) of cis and trans N_2F_2 at 300° K.

Atom pair	cis				trans			
	$\langle \Delta z^2 \rangle$	$\langle \Delta x^2 \rangle$	$\langle \Delta y^2 \rangle$	$\langle \Delta z \Delta x \rangle$	$\langle \Delta z^2 \rangle$	$\langle \Delta x^2 \rangle$	$\langle \Delta y^2 \rangle$	$\langle \Delta z \Delta x \rangle$
N=N	0.001606	0.002279	0.002904	0.000000	0.001582	0.003588	0.000000	0.000012
N-F	0.002383	0.003697	0.001769	-0.000501	0.002268	0.004267	0.005413	0.000315
N...F	0.003492	0.002455	0.001000	0.000416	0.004112	0.003098	0.005413	0.000192
F...F	0.007248	0.001178	0.001296	0.000000	0.007288	0.000673	0.000000	0.000974