The CH out-of-plane deformation vibrations of monosubstituted benzenes and effect of substituents on related force constants

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Abstract—Raman spectra of 14 monosubstituted benzenes and eight *p*-deuterated derivatives have been recorded in the region between 2000 and $1600 \,\mathrm{cm^{-1}}$, and the observed bands have been assigned to overtones of the CH out-of-plane deformation vibrations. The results have been utilized to investigate the correlation between the CH out-of-plane deformation frequencies and the electronic properties of the substituent.

For the substituents with no lone pair electrons at the α -atom, the frequencies of the in-phase CH out-of-plane deformation vibration are nearly proportional to Taft's resonance parameter σ_R^0 of the substituent. The change of the out-of-plane force constants giving rise to the observed variations of the out-of-plane fundamentals have been studied.

INTRODUCTION

The force constants for the CH out-of-plane deformation vibrations of monosubstituted benzenes are good measures of the effects of the substituent on the distribution of electrons around the ring [1, 2]. Generally, the normal modes consisting of these vibrations give rise to only weak bands in i.r. and Raman spectra except that a strong or medium i.r. absorption band near $750 \,\mathrm{cm}^{-1}$ arises from the well known umbrella mode, viz. the in-phase motion of all the ring hydrogen atoms. Accordingly, the CH out-ofplane deformation frequencies of a number of monosubstituted benzenes have been estimated from analysis of the i.r. summation bands which give a characteristic pattern of spectra between 2000 and 1600 cm^{-1} [3, 4]. In many cases, however, the observed summation bands are not abundant enough to provide sufficient cross checks of the assignments. Additional criteria are thus required for assigning the CH out-of-plane deformation frequencies of monosubstituted benzenes equivocally.

In this work, we have investigated these summation frequencies in both i.r. and Raman spectra of monosubstituted benzenes and their *p*-deuterated derivatives. By using the fundamental frequencies derived from the analysis of the summation bands, the correlation between the relevant force constants and the electronic properties of the substituent has been investigated.

EXPERIMENTAL

The undeuterated samples of 13 monosubstituted benzenes were obtained from commercial sources, and were purified by distillation or recrystalization. Benzene-*d*, bromobenzene-*p*-*d*, toluene-*p*-*d* and anisole-*p*-*d* were prepared from the corresponding bromo compounds by decomposing the Grignard reagent with heavy water, and were confirmed to give the identical gas chromatogram with the corresponding undeuterated compounds. Benzoicp-d acid was prepared by the oxidation of toluene-p-d in the alkaline potassium permanganate solution and converted to sodium benzoate-p-d. Benzamide-p-d was prepared by the ordinary method with thionyl chloride and aqueous ammonia. The isotopic purity of these materials were estimated to be above 90% by the measurements of NMR or mass spectra. Benzonitrile-p-d was prepared by the method of BAK and NIELSEN [5] and was estimated to have the ratio of deuteration more than 98% by the mass spectra. Nitrobenzene-p-d was prepared by decomposing the diazonium compound of *p*-nitroaniline by hypophosphorous acid- d_3 dissolved in heavy water [6]. Fully ring-deuterated derivatives of nitrobenzene, phenol, benzoic acid, benzonitrile and bromobenzene were obtained from commercial sources and used without further purification. Fully ringdeuterated benzoic acid was used to prepare ring-deuterated sodium benzoate and benzamide.

The i.r. spectra were recorded on a JASCO-A2 grating spectrophotometer with programmed slitwidth in the region between 4000 and 400 cm⁻¹. The crystalline samples were run as Nujol mulls and the liquids were placed between two KBr plates. When the i.r. absorptions of the liquid samples in the region between 2000 and 1600 cm⁻¹ were very weak, 0.1 mm rock salt liquid cell was used. The standard absorptions of polystyrene film were used for the frequency calibration. The Raman spectra between 2000 and 1600 cm⁻¹ were recorded on a JEOL S-1 laser Raman spectrophotometer. The 488.0 nm line of a Coherent 52G Ar⁺ laser was used as the exciting source with an output power of about 180 mW at the sample position. A slitwidth of 14 or 27 cm⁻¹ was used on recording the summation band region. The samples of liquid or solution were sealed in a 1 mm capillary tube or placed in a liquid cell. The samples of crystalline powder were sealed in a capillary or placed in a powder cell.

The i.r. and the Raman spectra of six representative compounds in the summation band region are shown in Fig. 1.

ASSIGNMENT

By disregarding the internal structure of the substituent, monosubstituted benzenes and their *p*-deuterated derivatives may be assumed to have the

 $C_{2\nu}$ symmetry. On this approximation, the fundamentals h and g, in WHIFFEN's notation [3, 7], are in the a_2 species and j, i and f are in the b_1 species. The mode f usually gives rise to a strong i.r. absorption and is well known as the umbrella mode.

The i.r. and the Raman spectra of benzene-d were investigated by BAILEY et al. [8], who reported eight i.r. absorptions and two Raman bands in the region between 2000 and 1600 cm⁻¹. In this work, three polarized Raman bands were newly observed at 1938, 1850 and 1706 cm⁻¹. By referring to the fundamental frequencies already determined, these bands are assigned to the overtones 2h, 2i and 2g in the order of decreasing frequency. All the i.r. absorptions in the summation band region, including a newly observed band at 1748 cm⁻¹ (h + f), are assigned to the combination tones of the out-of-plane fundamentals. The two Raman bands at 1617 and 1605 cm⁻¹ observed by BAILEY et al. were not detected in this work because of interruption of the strong Raman band at 1591 cm⁻¹.

In the summation band region of Raman spectra, bromobenzene shows five bands at 1970, 1930, 1810, 1750 and 1665 cm⁻¹, of which the 1750 cm⁻¹ band cannot be interpreted as any summation bands of the out-of-plane fundamental vibrations. The other bands are assigned reasonably to the overtones 2j, 2h, 2i and 2g in the order of decreasing frequency. On deuteration of the *p*-hydrogen atom, the 1970 and the 1810 cm⁻¹ bands shift to 1904 and 1687 cm⁻¹, respectively, while the 1930 and the 1665 cm⁻¹ bands remain almost unshifted. This spectral change reflects well the behaviors of the corresponding fundamentals [9]. Benzonitrile and anisole give nearly the same pattern of Raman spectra between 2000 and 1600 cm⁻¹ as bromobenzene, showing an extra band at the low frequency side of 2*i*. In Fig. 1, it is recognized well that the i.r. combination bands appear at the midpoints of the corresponding Raman overtone bands.

There have been controversies regarding the assignment of the CH out-of-plane fundamentals of toluene*p-d*. WILMSHURST and BERNSTEIN [10] assigned two i.r. absorptions at 863 and 803 cm⁻¹ to *i* and *j*, respectively, while TIERS and TIERS [11] assigned an i.r. band at 838 cm⁻¹ to *i*. The presently observed Raman spectrum of toluene-p-d- affords definite evidence for the latter assignment, showing three bands assignable to 2h, 2j and 2i at 1930, 1900 and 1675 cm^{-1} , respectively. Furthermore, two i.r. bands at 1783 and 1675 cm⁻¹ are given reasonable assignments to j + i and i + g, respectively, by locating the fundamental *i* around 835 cm⁻¹, but they cannot be interpreted if the 863 cm^{-1} band is assigned to *i*. In contrast to the monosubstituted benzenes mentioned above, nitrobenzene shows only two overtones 2i and 2g in the Raman spectrum in addition to three bands unassignable to any summations of the CH out-of-plane fundamentals. Unfortunately, we failed to record the Raman spectrum of nitrobenzene-p-d because of trace fluorescence which exerts negligible influence on recording spectra in the ordinary condition.

Assignments of the summation bands of the other compounds were made in a similar way, leading to the results given in Tables 1 and 2. The out-of-plane fundamental frequencies, either directly observed or deduced from the summation frequencies, are listed in Table 3. Except for a few cases, the present assignments of the fundamental frequencies agree with those in the literatures [8, 9, 12–21]. By summarizing these analyses,



Fig. 1. Infrared and Raman spectra of representative monosubstituted benzenes and their *p*-deuterated derivatives. Broken line shows the i.r. spectrum of *p*-deuterated derivative.

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x	2j	j+h	2h	j+i	h+i	2 i	h+g	i+g	2g	i+f
D		1957	1938	1910	1897	1850	1817	1775	1706	1707
снз	1963	1941	1931	1869	1855	1792	1797	1740	1683	1621
Br	1970	1943	1930	188 1	1862	1810	1789	1730	1665	1639
оснз	1958	1933	1919	1859		1775	1781	1707		
CN	1985	1970	1948		1901	1840	1813	1770	1689	1684
COOH		1976		1935		1877	1820			1744
с ₂ н ₅	1965	1943	1930	1881	1866	1810	1802	1742	1683	1650
^{NH} 2	1947	1928	1922		1836	1759	1776	1696		
ОН	1959	1934	1918	1865	1848	1778	1776	1708		
NO2		1973		1924	1906	1860	1807	1771	1685	1728
COONa				1908	1894		1811	1768		
CF3		1967	1940	1914	1895	1845	1815	1766		
NCS			1935	1886	1864	1814	1784	1727		1643
COONH ₂		1955		1911	1892			1810		

Table 1. Summation frequencies^{*} (cm⁻¹) and assignments of C_6H_5 -X

* The overtone and the combination frequencies were taken respectively from Raman and i.r. spectra.

it is concluded that monosubstituted benzenes show usually four overtone bands in Raman spectra, 2jaround 1960 cm⁻¹, 2h around 1930 cm⁻¹, 2i around 1810 cm⁻¹ and 2g around 1680 cm⁻¹. On deuteration of *p*-hydrogen atom, 2j and 2i undergo low-frequency shifts by about 50 and 100 cm⁻¹, respectively, while 2h and 2g remain unshifted in accordance with the behaviors of the fundamentals. These analyses of the Raman overtone bands are very useful to confirm the fundamental frequencies of the CH out-of-plane deformation vibrations when they are uncertain or unobserved in the fundamental frequency region.

The out-of-plane fundamental frequencies of six fully ring-deuterated compounds are listed in Table 4. For benzonitrile- d_5 , we revised the assignment of the fundamentals g and v by JAKOBSEN [22]. The fundamentals f and v of phenol- d_5 were assigned by BIST *et al.* [23]. The other frequencies in Table 4 were those newly observed in this work. In analogy with the case of undeuterated and the *p*-deuterated compounds, the modes f and v of fully ring-deuterated monosubstituted benzenes gave rise to fairly strong i.r. bands, while the modes j, h, i, g and w were attributed to weak i.r. bands unassignable otherwise. Since no summation bands involving excitation of the out-of-plane vibrations of benzene- d_5 ring are observed in either the i.r. or the Raman spectrum, their assignments are not so confidential as those given in Table 3.

x	2h	j+h	2 j	h+g	j+i	2i	i+g	2g
CH ₃	1930	1910	1900	1804	1783	1675	1675	
Br	1926	1909	1904	1788		1687	1670	1663
осн _з	1910	1900		1778		1675	1660	
CN	1950	1933	1929	1815		1742	1704	1687
COOH		1949		1826				
NO2		1941		1806			1710	
COONa		1922		1810				
COONH2		1931		1812			1719	

Table 2. Summation frequencies* (cm⁻¹) and assignments of *p*-*d*-C₆H₄-X

* See footnote of Table 1.

Table 3. Fundamental frequencies

	j	h	i	g	f	v	w	ref.
Monodeuterobenzene	981	970*	926	847	781	700		[8]
Toluene	978	961	893	839	723	698	407	[12]
Toluene-p-d	950*	961	834	839	707	607	407	[13]
Bromobenzene	988	963	903	832	735	681	409	[9]
Bromobenzene-p-d	951	963	844	832	705	604	409	[9]
Anisole	979*	960*	887	820	757	692		[14]
Anisole-p-d	940*	960	842	820	718	600		
Benzonitrile	996*	974	926	843	757	685	414	[15]
Benzonitrile-p-d	962	974	866	843	729	613	414	
Benzoic acid	996*	980*	939*	840*	808	682		
Benzoic-p-d acid	968*	980	883	840	780	610		
Nitrobenzene	998*	975	936	838	79 1	675	399	[16]
Nitrobenzene-p-d	966*	975	878	838	761	606	399	
Sodium benzoate	987*	973*	921	838*	820	678	399	[17]
Sodium benzoate-p-d	944*	973	867	838	795	600	399	
Benzamide	985	966	922	847	807	684		
Benzamide-p-d	960	966	867	B47	779	608		
Aniline	972	961	880	825	754	690	415	[18]
Phenol	981	962	889	824	753	686	408	[19]
Benzotrifluoride	992	970	924	840	768	691		[20]
Phenylisothiocyanate	979	967*	902	825	749	684		[21]
Ethylbenzene	980	965	905	842	747	696		[14]

* Estimated from the frequencies of the summation bands.

FREQUENCY CORRELATION

On examining the correlation between the CH outof-plane deformation frequencies of monosubstituted benzenes and the electron attractivity of the substituent, it was found convenient to classify monosubstituted benzenes into two groups, I and II, distinguishable from each other by the behavior of the umbrella mode f. The frequency of this mode is highly sensitive to the electronic property of the substituent of which the atom attached directly to the ring (α -atom) is associated with no lone pair electrons (group I). Contrarily, the mode f has an almost constant frequency around 750 cm⁻¹ for the substituents with the α -atom of the second row elements being associated with at least one lone pair (group II). Group II may be extended to include the α -atom of the other elements if the effect of its mass on the frequency of the mode f is corrected on the basis of the mass-frequency correlation reported by MARGOSHES and FASSEL [24]. In Fig. 2, the frequencies of the mode f are plotted against TAFT's resonance parameter σ_R^0 , which is taken as a measure of the electron attractivity of the substituent [25, 26]. On replacing the observed frequencies of deutero-, chloro-, bromo- and iodobenzenes by 750 cm⁻¹, the points for the two groups of the compounds are clearly represented by two straight lines which intersect each other on the abscissa.

MARGOSHES et al. pointed out that the force constants for the CH out-of-plane deformation increase on the

<u>x</u>	j	h	i	ġ	f	v	W
CN		789	769	656	640	558	
СООН	850				610	540	
NO2	846		772	657	611	53 9	
COONa	839	790		658	608	538	355
CONH ₂	840				620	544	
он	812		717	660	623	551	

Table 4. The out-of-plane fundamental frequencies (cm^{-1}) of C_6D_5 -X



Fig. 2. Correlation between Taft's σ_R^0 and the frequency of the fundamental vibration f. Circles and squares represent the observed and the mass-corrected frequencies, respectively.

decrease of the π -electron density at the apex carbon atom [1]. Consequently, the high-frequency shifts of the mode f on the increase of σ_R^0 of the compounds in group I is attributable to the transfer of the π electrons from the ring to the substituent. On the other hand, the behavior of the compounds in group II may be elucidated by referring to the i.r. band intensities of the modes f and v of various monosubstituted benzenes reported by HIGUCHI et al. [27]. According to these authors, the CH bond moments derived from the i.r. intensities of the compounds in group II increase with the red shift of the benzenoid band in the u.v. absorption spectra while those of the compounds in group I do not depend on the position of the u.v. absorption maximum. Furthermore, the amount of the red shift of the benzenoid band given rise to by the substituent is roughly proportional to $|\sigma_R^0|$ [28]. In consequence the effect of π -electron density on the force constants of the compounds in group II may be cancelled by the excess work required to produce a

dipole moment in the direction perpendicular to the ring plane.

NORMAL COORDINATE ANALYSIS

With the purpose to generalize the correlation between the force constants and the frequency of the mode f and to incorporate the other CH out-of-plane deformation modes in it, we carried out a normal coordinate analysis of the out-of-plane vibrations of a model monosubstituted benzene. Initially, the force constants were taken from the valence force field for benzene proposed by LA LAU and SNYDER [29], but a few off-diagonal terms connecting the CH out-of-plane deformation coordinates at the *para* and *meta* positions of each other were dropped according to our recent study on bromobenzene [9]. In a preliminary calculation, this revision was found necessary for fitting the frequencies of monosubstituted benzenes with strongly electronegative substituent.

The internal coordinates were defined according to LA LAU and SNYDER, and the G matrices were constructed on the basis of the molecular geometry and atomic masses of fluorobenzene [30]. The reason for our choosing this molecule as the representative model of monosubstituted benzenes is that the substituent is monoatomic and, according to the mass-frequency correlation [24], the frequency of the mode f at the point of intersection of the two lines in Fig. 2, 750 cm^{-1} , corresponds to the mass of fluorine. Actually, by using the G matrix of fluorobenzene together with the transferred force constants [29], the frequency of the fundamental f, v_f , was calculated to be 750 cm⁻¹. This frequency is thus regarded as the intrinsic value of v_f attributable to the substituent which exerts no electronic influence on the ring, v_f^0 . The intrinsic frequencies of the other fundamentals, v_x^0 , x = g, h, i, ...,including those of the *p*-deuterated and the fully ringdeuterated compounds, were estimated by plotting the observed frequencies against v_f as shown in Fig. 3 and fitting them to the regression equation in the form

$$v_x = v_x^0 + a_{xf}(v_f - v_f^0).$$



Fig. 3. Frequency correlations between the fundamental f and the other out-of-plane fundamentals. The circles and the broken lines show the observed and the calculated frequencies, respectively, of the b_1 fundamentals, and the squares and the solid lines show those of the a_2 fundamentals.

	j	h	i	g	f	v	w
v x ⁰	983.1	963.7	905.9	834.7	750.0	686.7	406.7
^a xf	0.1083	0.2311	0.4487	0.0102	1.0	0.0721	-0.0263
vx ⁰	952.1		847.9		719.5	606.0	
^a xf	0.0911		0.4006		1.0158	-0.0191	
vx ⁰	824.2	769.5	750.2	660.2	616.2	546.4	361.4
^a xf	0.3652	0.3938	0.5154	-0.2142	-0.0039	-0.0869	-0.0485
	$\frac{\nabla v^{0}}{\nabla x}$ $\frac{a}{xf}$ $\frac{\nabla v^{0}}{x}$ $\frac{a}{xf}$ $\frac{\nabla v^{0}}{x}$ $\frac{a}{xf}$	$ \begin{array}{cccc} $	$\begin{array}{c cccc} j & h \\ \nu_{x}^{0} & 983.1 & 963.7 \\ a_{xf} & 0.1083 & 0.2311 \\ \nu_{x}^{0} & 952.1 \\ a_{xf} & 0.0911 \\ \nu_{x}^{0} & 824.2 & 769.5 \\ a_{xf} & 0.3652 & 0.3938 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 5. The intrinsic fundamental frequencies,* v_x^0 , and the coefficients, a_{xf}

* In cm^{-1} .

† Dimensionless.

Besides the frequencies in Tables 3 and 4, the data for the following compounds were collected from the literature and were used in the regression: fluorobenzene [7], $-d_5$ [31], chlorobenzene [7], $-d_5$ [32], iodobenzene [7], $-d_5$ [33], benzoyl chloride [34], styrene [35], $-d_8$ [35], acetophenon [36], $-d_5$ [36], benzenesulphonamide [37], $-d_5$ [37], benzenesulfonyl chloride [37], $-d_5$ [37], thionylaniline [21], phenylisocyanate [21], sodium benzenesulfonate [38], $-d_5$ [38], phenyisocyanide [39], $-d_5$ [39], toluene- d_5 [40], bromobenzene-

Table 6. Force constants and their variations on the change of the fundamental f

Type*	к _h 0†	K'hf×10 ² +
н _µ о	0.4537	0.0156
н _µ ^m	0.4537	0.0
н _и р	0.4537	0.0320
н _м	0.4279	0.0
H _z ^o	0.2717	0.0290
H ₂	0.2717	0.0
fu	-0.0667	0.0010
f _{µM} o	-0.0555	-0.0586
f m µM	-0.0115	-0.0240
f ^P µM	0.0074	-0.0646
fzo	-0.0511	0.0
f _{µz} o	-0.1615	0.0
$f_{\mu z}^{m}$	0.0139	0.0

* The notations for force constants were taken from Ref. [29]. The superscripts o, m and p on the diagonal term, H, show the position with regard to the substituent and those on the off-diagonal term, f, show the relative position of the two coordinates involved.

† K_h^0 in mdyn Å/rad², K_{hf} in mdyn Å·cm/rad². Å = 10^{-10} m, mdyn = 10^{-8} N.

 d_5 [9] and benzotrifluoride- d_5 [20]. The resulting best estimates of the v_x^{0} 's and the a_{xf} 's are listed in Table 5. These empirical values of the intrinsic frequencies were confirmed to agree well with the calculated ones for the initial force constants. The changes of force constants accompanying the unit change of v_f , viz.

$$K_{hf}' = dK_h/dv_f.$$

were then calculated by the method of least squares with a slightly modified normal equation,

$$\mathbf{\tilde{J}WJK}_{f}^{\prime} = \mathbf{\tilde{J}Wa}_{f}$$

where \mathbf{a}_f and \mathbf{K}'_f are column vectors of a_{xf} 's and K'_{kf} 's, respectively.

After several trials of selecting the force constants to be adjusted, seven constants were picked up finally as the minimum and indispensable parameters to elucidate the essential feature of the frequency correlation. The force constant variations thus obtained are shown together with the corresponding initial values in Table 6, where the torsional constant for the C-C bonds between the substituted carbon and the ortho carbon atoms is denoted by H_z^o and those for the other C—C bonds by H_z . It is worth noting that H^m_μ may be kept constant while H^o_{μ} and H^p_{μ} should increase on the high-frequency shift of the fundamental f. This trend is consistent with the conclusion of KAKIUTI et al. based on a simplified treatment of the CH out-of-plane vibrations [2, 41], and confirms the negative correlation between the CH out-of-plane deformation force constants and the π -electron density of the apex carbon atoms [1]. The stronger dependence of H^p_{μ} on v_f than H^o_{μ} is supported by a CNDO/2 calculation of monosubstituted benzenes by Howe [42], according to whom the π -electron density at the *o*-carbon atoms of monosubstituted benzenes with electron-attractive substituents is larger than that at the p-carbon atom.

In order to confirm the reliability of the force constant variations K'_{hf} , the out-of-plane normal frequencies were calculated for each of the four sets of linearly changing constants,

$$K_h = K_h^0 + K_{hf}' \Delta v_f,$$

where Δv_f was taken to be 70, 40, 10 and -20 cm^{-1} . The resulting changes of the calculated frequencies are shown by the solid and the broken lines in Fig. 3. Except for the mode g of the fully ring-deuterated compounds, the calculated frequencies follow well the observed trend of the frequency correlation, although a slight curvature of some of the lines implies that the frequencies are not exactly linear functions of the force constants. In the case of strongly electron-donating substituents ($\Delta v_f = -20 \text{ cm}^{-1}$), the calculated vibrational modes f and v are nearly pure in-phase CH outof-plane deformation and ring puckering vibrations, respectively. On the increase of v_t , the mixing of these two vibrations becomes more and more significant, and eventually about 30% of the original amplitude of the ring puckering is transferred to the fundamental f when $\Delta v_f = 70 \text{ cm}^{-1}$. This result is consistent with the well known fact that the i.r. intensity of the fundamental f diminishes on the increase of its frequency [1].

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REFERENCES

- [1] R. D. KROSS, V. A. FASSEL and M. MARGOSHES, J. Amer. Chem. Soc. 78, 1332 (1956).
- [2] Y. KAKIUTI, Nippon Kagaku Zasshi 80, 250 (1959).
- [3] D. H. WHIFFEN, Spectrochim. Acta 7, 253 (1955).
- [4] C. W. YOUNG, R. B. DUVALL and N. WRIGHT, Analyt. Chem. 23, 709 (1951).
- [5] B. BAK and J. T. NIELSEN, Z. Electrochem. 64, 560 (1960).
 [6] A. MURRAY and D. L. WILLIAMS, Organic Syntheses
- with Isotopes, p. 1592, Interscience (1958).
- [7] D. H. WHIFFEN, J. Chem. Soc. 1350 (1956).
- [8] C. R. BAILEY, R. R. GORDON, J. B. HALE, N. HERZFELD, C. K. INGOLD and H. G. POOLE, J. Chem. Soc. 299 (1946).
- [9] T. UNO, A. KUWAE and K. MACHIDA, Spectrochim. Acta 33A, 607 (1977).
- [10] J. K. WILMSHURST and H. J. BERNSTEIN, Can. J. Chem. 35, 911 (1957).
- [11] G. V. D. TIERS and J. H. TIERS, J. Chem. Phys. 20, 761 (1952).
- [12] N. FUSON, C. GARRIGOU-LAGRANGE and M. L. JOSIEN, Spectrochim. Acta 16, 106 (1960).

- [13] Y. KAKIUTI and J. OGURA, Bull. Chem. Soc. Japan, 34, 899 (1961).
- [14] J. H. S. GREEN, Spectrochim. Acta 18, 39 (1962).
- [15] J. H. S. GREEN, Spectrochim. Acta 17, 607 (1961).
- [16] J. H. S. GREEN and D. J. HARRISON, Spectrochim. Acta 26A, 1925 (1970).
- [17] J. H. S. GREEN, W. KYNASTON and A. S. LINDSEY, Spectrochim. Acta 17, 486 (1961).
- [18] J. C. EVANS, Spectrochim. Acta 16, 428 (1960).
- [19] J. C. EVANS, Spectrochim. Acta 16, 1382 (1960).
- [20] R. D'CUNHA and V. B. KARTHA, Can. J. Spectrosc. 20, 18 (1975).
- [21] C. V. STEPHENSON, W. C. COBURN, JR and W. S. WILCOX, Spectrochim. Acta 17, 933 (1961).
- [22] R. J. JAKOBSEN, Spectrochim. Acta 21, 127 (1965).
- [23] H. D. BIST, J. C. D. BRAND and D. R. WILLIAMS, J. Molec. Spectrosc. 24, 402 (1967).
- [24] M. MARGOSHES and V. A. FASSEL, Spectrochim. Acta 7, 14 (1955).
- [25] R. W. TAFT, J. Phys. Chem., Ithaca 64, 1805 (1960).
- [26] R. T. C. BROWNLEE, R. E. J. HUTCHINSON, A. R. KATRITZKY, T. T. TIDWELL and R. D. TOPSOM, J. Amer. Chem. Soc. 90, 1757 (1968).
- [27] S. HIGUCHI, K. NAKAMORI, S. TANAKA and H. KAMADA, Nippon Kagaku Zasshi 89, 565 (1968).
- [28] C. N. R. RAO, Chem. Ind. 666 (1956); 1239 (1957).
- [29] C. LA LAU and R. G. SNYDER, Spectrochim. Acta 27A, 2073 (1971).
- [30] K. RADCLIFFE and D. STEELE, Spectrochim. Acta 25A, 597 (1969).
- [31] D. STEELE, E. R. LIPPINCOTT and J. XAVIER, J. Chem. Phys. 33, 1242 (1960).
- [32] T. R. NANNEY, R. T. BAILEY and E. R. LIPPINCOTT, Spectrochim. Acta 21, 1495 (1965).
- [33] T. R. NANNEY, E. R. LIPPINCOTT and J. C. HAMER, Spectrochim. Acta 22, 737 (1966).
- [34] S. CHATTOPADHYAY and J. JHA, Indian J. Phys. 42, 610 (1968).
- [35] W. D. MROSS and G. ZUNDEL, Spectrochim. Acta 26A, 1109 (1970).
- [36] W. D. MROSS and G. ZUNDEL, Spectrochim. Acta 26A, 1097 (1970).
- [37] T. UNO, K. MACHIDA and K. HANAL, Spectrochim. Acta 24A, 1705 (1968).
- [38] T. UNO, A. KUWAE, Y. SAITO and K. MACHIDA, Bull. Chem. Soc. Japan 48, 2231 (1975).
- [39] R. A. NALEPA and J. D. LAPOSA, J. Molec. Spectrosc. 50, 106 (1974).
- [40] A. P. HITCHCOCK and J. D. LAPOSA, J. Molec. Spectrosc. 54, 223 (1975).
- [41] Y. KAKIUTI, H. SAITO and T. YOKOYAMA, J. Molec. Spectrosc. 32, 247 (1969).
- [42] G. R. HOWE, J. Chem. Soc. (B), 984 (1971).