The InfraRed Absorption of Hydrogen Fluoride

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Anharmonicity of CH Vibrations and Product Rule

Applications of the product rule, derived by Teller[1] and the author,[2] have been impaired to some extent by the anharmonicity of hydrogen vibrations which causes discrepancies a little larger than common experimental errors. Anharmonicity is connected by Morse's formula[3] with dissociation energy and the latter is known to be approximately the same for all CH bonds. It may be expected, therefore, that deviations due to anharmonic character of CH vibrations are eliminated with sufficient accuracy if the same correction is applied to vibrations of similar kind.

The anharmonicity factor x may be taken, according to Ellis,[4] as 2.2 percent for an aliphatic and 1.9 percent for an aromatic hydrogen valency vibration. The correction to be applied to the quotient of corresponding valency vibrations of hydrogen and deuterium[5] amounts to $x(2-\sqrt{2})$ = 1.3 percent and 1.1 percent, respectively.

The applications of the product rule to compounds with CD bonds are listed in Table I. The column headed "V" contains the number of D valency vibrations involved, column "B" the number of bending or deformation vibrations. The differences between the calculated and observed product values and the suggested correction for anharmonicity are given in percents.

The average difference in 34 cases involving valency vibrations amounts to 1.62 percent and agrees satisfactorily with the average correction 1.42 percent. The individual discrepancies, considerable though unsystematic, are explained by experimental error. The discrepancies are remarkably less in the cases of totally symmetrical frequencies which, as a rule, can be determined more precisely.

It may be noted that the ten cases involving only a bending frequency seem to indicate a small negative anharmonicity factor. The third-order term in a power series of the potential energy must necessarily result in a positive value of this factor (cf. reference 5). It may be concluded, therefore, that the third-power term is zero or, at least, small. This is precisely what is to be expected in bending vibrations. The two halves of a bending vibration are in some molecules exactly, in others at least approximately alike. So we may expect, indeed, that the odd terms of the potential energy series vanish. The experimental material available will hardly justify a quantitative conclusion.

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[1] Cf. C. K. Ingold et al., J. Chem. Soc. London 971 (1936).
[2] O. Redlich, Zeits. f. physik. Chemie B28, 371 (1935).
[3] P. M. Morse, Phys. Rev. 34, 57 (1929).
[4] J. W. Ellis, Phys. Rev. 33, 27 (1929). Ta-You Wu and A. T. Kiang, J. Chem. Phys. 7, 178 (1939), found 2.1 percent and 1.5 percent for the hydrogen valency vibrations of acetylene.
[5] Cf. C. Manneback, Ann. Soc. Scient. Bruxelles B55, 237 (1935).
[6] G. E. MacWood and H. C. Urey, J. Chem. Phys. 4, 402 (1936). W. S. Benedict, K. Morikawa, R. B. Barnes and H. S. Taylor, J. Chem. Phys. 5, 1 (1937). The average of Raman and infra-red values has been used where both have been determined. The product formulae are, of course, identical in this case with the corresponding equations derived by J. E. Rosenthal, Phys. Rev. 45, 538 (1934).
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[17] Referred to p-C6H4D2 not to C6H6.

TABLE I. *Product values and anharmonicity correction.*

SUBSTANCE	SYM-METRY	V	B	PROD. CALC.	PROD. OBS.	DIFF. %	CORR. %	REF.
CH₃D	A_1	1		1.370	1.354	1.2	1.3	6
	E		1	1.179	1.170	0.8	—	
CH₂D₂	A_1	1	1	1.881	1.823	3.1	1.3	
	A_2		1	1.155	1.181	-2.3	—	
	B_1	1.	1	1.437	1.416	1.5	1.3	
	B_2		1	1.204	1.197	0.6	—	
CHD₃	A_1	1	1	1.833	1.810	1.1	1.3	
	E	1	2	2.046	2.083	-1.8	1.3	
CD₄	A	1		1.414	1.398	1.1	1.3	
	E		1	1.414	1.444	-2.1	—	
	F	1	1	1.788	1.768	1.1	1.3	
C₂D₂	A_1	1		1.414	1.398	1.1	1.3	7
C₂D₄	A_{1g}	1	1	1.998	1.954	2.2	1.3	8
	A_{2g}	1	1	1.666	1.624	2.5	1.3	
	A_{1u}	1	1	1.868	1.827	2.2	1.3	
C₂D₆	A_1	1	1	1.998	1.91	4.5	1.3	9
	A_2	1	1	1.82	1.79	1.7	1.3	
	E	1	2	2.58	2.44	5.4	1.3	
CHCl₃	A_1	1		1.407	1.378	2.1	1.3	10
	E		1	1.398	1.382	1.1	—	
CHBr₃	A_1	1		1.411	1.400	0.8	1.3	11
	E		1	1.406	1.409	-0.2	—	
CH₂Br₂	A_1	1	1	1.986	1.95	2.0	1.3 ·	12
cis-C₂D₂Cl₂	A_1	1	1	1.978	1.915	3.2	1.3	13
trans-C₂D₂Cl₂	A_1	1	1	1.985	1.883	5.1	1.3	
C₂D₄Br₂	A_1	1	2	2.82	2.76	2.1	1.3	14
CD₂O	A_1	1	1	1.936	1.900	1.9	1.3	15
	B_1	1	1	1.662	1.715	-3.2	1.3	
	B_2		1	1.168	1.241	-6.2	—	
o-C₆H₄D₂	B_1	1	1	1.909	1.881	1.5	1.1	16
m-C₆H₄D₂	A_1	1	1	1.975	1.972	0.2	1.1	
p-C₆H₄D₂	A_{1g}	1		1.414	1.397	1.2	1.1	
vic-C₆H₃D₃	A_1	2	1	2.776	2.790	-0.5	2.2	
sym-C₆H₃D₃	E'	1	1	1.959	1.97	-0.6	1.1	
o-C₆H₂D₄	B_1	2	2	3.655	3.572	2.3	2.2	
m-C₆H₂D₄	A_1	3	1	3.901	3.901	0.0	3.3	
p-C₆H₂D₄	A_{1g}		1	1.414	1.442	-2.0	—	17
	B_{1g}		1	1.286	1.283	0.2	—	17
	B_{2g}	1		1.370	1.350	1.5	1.1	17
C₆HD₅	A_1	3	2	5.484	5.291	3.5	3.3	
C₆D₆	A_{1g}	1		1.414	1.402	0.8	1.1	
	E_g^+	1	1	1.998	1.941	2.9	1.1	
	E_g^-		1	1.288	1.280	0.6	—	
	E_u^-	1	1	1.925	1.931	-0.3	1.1	

The Infra-Red Absorption of Hydrogen Fluoride

Imes[1] observed the infra-red absorption spectrum with the characteristic rotational structure of the P and R branches, for monomeric hydrogen fluoride. Because of the presence of water vapor he made no observations at longer wave-lengths. Since hydrogen fluoride is known to be highly associated in the vapor state because of hydrogen bonding, it seemed desirable to investigate the absorption spectrum thoroughly. We have done this with both the prism and grating spectrometer, for hydrogen fluoride in the vapor state and in carbon tetrachloride solution. The results of Imes were of course confirmed. At longer wave-lengths a very strong absorption is observed at higher pressures which we attribute to association. This absorption has several

maxima but the two main ones of equal intensity are at 2.95, and 2.87μ respectively.

The hydrogen fluoride spectrum in an inert solvent is of great interest since hydrogen fluoride has the lowest moment of inertia of any diatomic molecule which gives a rotation-vibration spectrum and some indication of rotational structure might be anticipated in solution. The spectrum as observed in carbon tetrachloride solution shows two very interesting features. In the first place there is no evidence of association, although the solubility is considerable. Water shows no association in carbon tetrachloride solution but water shows no association in the vapor state which is in equilibrium with the solution. Alcohols of course show strong association in carbon tetrachloride solution.

The absorption spectrum in solution as determined by a prism spectrometer appears to resemble, at first glance, the single molecule vapor spectrum, but a closer investigation shows that there are probably three absorption maxima instead of two and that one of these, the middle component is greatly magnified in intensity. A similar spectrum is found for hydrogen chloride. With the grating, evidence of fine structure is found. The complete results of this investigation will be published in the near future.

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[1] Imes, Astrophys. J. **50**, 251 (1919).

Sulfur Bands and an Attempt to Obtain HS Bands

Sometime ago we noticed that the band spectrum of the HS radical had not been observed. We have studied several sulfur compounds attempting to obtain such bands but the recent work of Lewis and White[1] indicates that it will be difficult to produce them in emission.

In every case investigated the sulfur band systems[2] appeared on our plates. The following gases and mixtures were passed through an 8000-volt uncondensed discharge at pressures ranging from 0.1 to 20 mm Hg.

(1) H_2S
(2) $H_2S + H_2$
(3) $H_2 + S$ (at various S concentrations)
(4) $H_2 + H_2S + S$
(5) H_2S_2
(6) $H_2S_2 + H_2$
(7) H_2S_3
(8) $H_2S_3 + H_2$
(9) $S_2Cl_2 + H_2$
(10) $S_2Cl_2 + H_2 + H_2S$
(11) $SOCl_2 + H_2$
(12) $SOCl_2 + H_2 + H_2S$

The spectrum of the $H_2S - O_2$ flame was also studied.

Systems 1 to 4 are obvious attempts while the use of hydrogen disulfide[3] was suggested by the production of intense OH bands from hydrogen peroxide by Dawson and Johnston.[4] Again we observed the usual sulfur bands. The HS band found by Lewis and White[1] at 3237A in absorption falls in a relatively clear portion of the tail of the sulfur band at 3216A. Some of our plates appeared to show a very slight darkening at this point but this indication was not definite enough for analysis.

Our findings attest to the great instability of the HS radical.

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[1] M. N. Lewis and J. U. White, Phys. Rev. **55**, 894 (1939).
[2] See references in H. Spaner, *Molekulspektren* (Julius Springer, Berlin, 1935), Vol. I, p. 61.
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Errata: On Transport Phenomena in the Cage Model of Liquids*

(J. Chem. Phys. **7**, 202 (1939))

Equation (2) should read

$$\eta = \frac{f\sigma}{\Delta v} = \frac{f\sigma}{a(m_+ - m_-)}.$$

In the third line after Eq. (2) read $\pm fqa/2$ instead of $\pm lga/2$. In the eighth line after Eq. (2) read $\pm f$ rather than $\pm l$. The formula in the tenth line after Eq. (2) should read

$$m_+ - m_- = \frac{m_0}{6}(e^{fqa/2kT} - e^{-fqa/2kT}) = \frac{m_0}{6}\frac{fqa}{kT}.$$

Eq. (3) should read

$$\eta = kT\sigma/qD.$$

In the seventh line after Eq. (3) read $q\sigma = V/N$ rather than $g\sigma = V/N$.

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