Bending Force Constants for Halogenated Ethylenes

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Force constants have been calculated for the out-of-plane bending motions of the vinyl halides and for *cis-* and *trans-* 1,2-dichloroethylene. Published vibrational assignments have been followed for the most part, but several changes were found necessary. A generally consistent set of force constants was obtained in which the values are also similar to those for the methyl halides.

WHILE bending force constants in general have received less attention than stretching force constants, they are important in establishing the assignments of the lower fundamental vibration frequencies. In thermodynamic calculations the lower frequencies take on primary significance. In this investigation, an attempt has been made to evaluate the force constants for the non-planar vibrations in certain halogenated ethylenes, and to find some correlation among them for this series of compounds.

Complete assignments of fundamental vibration frequencies for the vinyl halides have been made by Torkington and Thompson[1,2] on the basis of their own infra-red spectra. These assignments appear to be straightforward and unambiguous except in the case of vinyl fluoride. Here some anomalies occur that are not yet satisfactorily explained. The fluoride, furthermore, is the only one of these substances for which Raman data are lacking. Wu[3] and Herzberg[4] have summarized the data on the dichloroethylenes.

The calculations were carried out by the method of Wilson[5] for which the following coordinates were chosen:

θ_1 = angle of wag of CH_2 group (angle between extension of $C=C$ bond and HCH plane).
θ_2 = angle of wag of CHX group.
θ_3 = angle of twist of groups at opposite ends of $C=C$ bond.

The elements of the reciprocal kinetic energy matrix then take the following form for the vinyl halides:

$$G_{11} = 2\epsilon^2\mu_H + \mu_C(4\epsilon^2 + 4\epsilon\rho + 2\rho^2);$$
$$G_{12} = G_{21} = -\mu_C\rho(3\epsilon + \eta + 2\rho);$$
$$G_{13} = G_{31} = 0;$$
$$G_{22} = \epsilon^2\mu_H + \eta^2\mu_X + \mu_C(\epsilon^2 + \eta^2 + 2\rho^2 + 2\epsilon\eta + 2\epsilon\rho + 2\eta\rho);$$
$$G_{23} = G_{32} = (\epsilon^2\mu_H - \eta^2\mu_X)/\sqrt{3};$$
$$G_{33} = \epsilon^2\mu_H + \tfrac{1}{3}\eta^2\mu_X,$$

where the μ's refer to reciprocal masses, and ϵ, ρ, and η are the reciprocals of the $C-H$, $C=C$, and $C-X$ bond distances, respectively. The $C-C$ and $C-H$ bond lengths (1.353 and 1.071A) are taken to be those in ethylene, as determined by Gallaway and Barker.[6] These authors report a bond angle of 119° 55' for $H-C-H$ in ethylene, whereas electron diffraction measurements on vinyl chloride by Brockway, Pauling, and Beach[7] indicate a $C-C-Cl$ angle of $122\pm2°$.

TABLE I. Non-planar frequencies and force constants of vinyl halides.

	C_2H_3F	C_2H_3Cl	C_2H_3Br	C_2H_3I
$C-X$ distance, A	1.36	1.69	1.85	2.03
Frequencies (cm^{-1})				
ω_1	924 (860)	940	940	946
ω_2	860 (732)	895	902	909
ω_3	715 (715)	622	497	435
Assumed force constants				
F_{11} (from ethylene)	0.37	0.39	0.39	0.39
F_{12} ($=F_{21}$) (ethylene)	0.045	0.054	0.054	0.054
F_{13} ($=F_{31}$)	0.00	0.00	0.00	0.00
Calculated force constants				
F_{22}	0.48	0.43	0.36	0.32
F_{23} ($=F_{32}$)	−0.21	−0.10	0.03	0.09
F_{33}	0.90	0.82	0.64	0.60

[1] P. Torkington and H. W. Thompson, J. Chem. Soc. 303 (1944).
[2] P. Torkington and H. W. Thompson, Trans. Faraday Soc. 41, 236 (1945).
[3] T. Y. Wu, Phys. Rev. 46, 465 (1934).
[4] G. Herzberg, *Infra-Red and Raman Spectra* (D. Van Nostrand Company, New York, 1945), p. 330.
[5] E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939) and 9, 76 (1941). See also A. G. Meister and F. F. Cleveland, Am. J. Phys. 14, 13 (1946).
[6] W. S. Gallaway and E. F. Barker, J. Chem. Phys. 10, 88 (1942).
[7] L. O. Brockway, L. Pauling, and J. Y. Beach, J. Am. Chem. Soc. 57, 2693 (1935).

For simplicity, 120° has been used for all bond angles in these calculations. The experimental value of 1.69A given by Brockway, Pauling, and Beach,[7] for the C−Cl distance is accepted. This represents a shortening of the bond compared with 1.76A in CCl_4, and a corresponding relationship is assumed to exist in the other halides, i.e., the =C−X length is decreased with respect to that of −C−X. This is corroborated in the case of vinyl iodide, in which the C−I length is reported by Huggill, Coop, and Sutton[8] as 2.03A, while in CI_4 it is 2.12A (Finbak and Hassel[9]). The C−X distances are included in Table I.

In these calculations the force constant for CH_2 wagging, F_{11}, and the interaction constant, F_{12}, were assigned the values obtained from ethylene.[10] This proved satisfactory in all cases except vinyl fluoride, where the noticeably lower value of ω_1 (compared with ethylene and the other halides) made it necessary to lower these constants slightly. All constants are expressed in "atomic weight-angstrom" units, which for angle bending constants is (ergs/radian²)×1.698 ×10^{+11}. The frequencies and constants are listed in Table I. In parentheses are given Torkington and Thompson's[2] assignment for vinyl fluoride.

In an attempt to confirm the F_{22} value for C_2H_3Cl, some calculations were made of the out-of-plane force constants in the cis- and trans-forms of 1,2-dichloroethylene. The appropriate equations are readily derived by the same methods. In spite of some uncertainties in the assignments of these frequencies,[3,4] it is believed that the results obtained provide some measure of verification for the vinyl chloride wagging constant. The choice and classification of the frequencies is given by Table II, which also shows the force constants obtained from them.

These molecules have higher symmetry than the vinyl compounds, so that the non-planar motions may be further subdivided. The B_2 "unsymmetrical" wagging frequency in cis-1,2-dichloroethylene, and the B_g "symmetrical" wagging frequency in trans-1,2-dichloroethylene are both (by symmetry) free from interaction

[8] J. A. C. Huggill, I. E. Coop, and L. E. Sutton, Trans. Faraday Soc. 34, 1518 (1938).
[9] C. Finbak and O. Hassel, Zeits. f. physik. Chemie 36B, 301 (1937).
[10] J. E. Kilpatrick and K. S. Pitzer, to be published.

TABLE II. 1,2-dichloroethylenes.

Vibration	Frequency (cm⁻¹)	Force constant
cis-		
B_2 (unsym. wagging)	694	0.45
A_2 (sym. wagging)	876	0.36*
A_2 (torsion)	406	0.78
(A_2 interaction constant)		−0.08
trans-		
B_g (sym. wagging)	765	0.36
A_u (unsym. wagging)	820	0.45†
A_u (torsion)	270	0.87
(A_u interaction constant)		−0.17
deutero-trans-		
B_g (sym. wagging)	657	0.36

* Assumed from B_g (sym.) in trans-.
† Assumed from B_2 (unsym.) in cis-.

with the other non-planar vibrations. This leads to a rather simple and direct evaluation of these force constants, which in the case of the trans-molecule can also be checked with the deuterated compound. Then if the "symmetrical" wagging constant in trans- is accepted for the corresponding motion in cis-, and the "unsymmetrical" wagging constant in cis- is accepted similarly for trans-, the torsional and interaction constants for the A_2 and A_u vibrations may be calculated and a set of values consistent with the most probable frequencies obtained. The greatest uncertainties in the assigned frequencies are in the A_u vibrations of trans-1,2-dichloroethylene. While Wu[3] and Herzberg[4] both suggest 620 cm⁻¹ for the "unsymmetrical" wagging vibration of this group, it gives too low a force constant. Wood and Stevenson[11] have used 820 cm⁻¹ for this frequency in connection with studies of the cis-trans isomerization, and the present calculations seem to confirm the latter value. The A_u torsional frequency is too low to be observed. The 620 cm⁻¹ band, left unassigned by the choice of 820 cm⁻¹ for the A_u wagging fundamental, may now be assumed to be a combination of two low frequencies. One of these must be the 350 cm⁻¹ C−Cl planar bending, leaving a difference of 270 cm⁻¹. This is taken as the twisting fundamental.

The symmetrical and unsymmetrical wagging constants for the dichloroethylenes should be approximately $F_{22}-F_{12}$ and $F_{22}+F_{12}$, respectively, from vinyl chloride. While the agreement with these combinations from vinyl chloride is

[11] R. E. Wood and D. P. Stevenson, J. Am. Chem. Soc. 63, 1650 (1941).

not very close, it is about what one might expect. Likewise, the torsion constants of the *cis-* and *trans*-molecules differ somewhat. However, the pattern of constants shows such general consistency as to lend considerable support to their validity.

To examine the trend of the force constants in passing through the series of vinyl halides, it is informative to see whether or not a similar trend exists in some comparable series. The methyl halides afford such a comparison, and the force constants for bending of the $H-C-X$ angles in these molecules are given by Crawford and Brinkley.[12] Their values, expressed in terms

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[12] B. L. Crawford, Jr. and S. R. Brinkley, Jr., J. Chem. Phys. 9, 69 (1941).

of our units are as follows:

	CH_3F	CH_3Cl	CH_3Br	CH_3I
k	0.41	0.31	0.28	0.24

The relative values of k may be properly compared with those of F_{22} in the vinyl compounds (see Table I). In both series, it is observed that progression from the fluoride to successively heavier halides leads to successively lower force constants.

We are aware that our assignment for vinyl fluoride will make it difficult to explain the published spectrum completely; however, any other assignment gives unreasonable force constants. Further investigation is needed here.

The Differential Entropy of Dilution in Aqueous Solutions of Amino Acids

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The relative partial molal entropy of water, $\bar{S}_1 - \bar{S}_1^0$, in aqueous solutions of seven amino acids is calculated from existing data. For all solutions, $\bar{S}_1 - \bar{S}_1^0 = km^2$ approximately; k is positive for glycine solutions and negative for solutions of the two alanines and four aminobutyric acids. The $\bar{S}_1 - \bar{S}_1^0$ values are determined largely by the size and structure of the hydrocarbon part of the amino acid and only to a minor degree by its dipole moment. Positive $\bar{S}_1 - \bar{S}_1^0$ values are interpreted as indicating a structure breaking effect of glycine on water; negative $\bar{S}_1 - \bar{S}_1^0$ values indicate a structure strengthening effect which increases with size of the hydrocarbon residue. The data are consistent with the recent discussion of Frank. Heat capacity and viscosity values for some of these solutions qualitatively show expected behavior.

STUDIES of the heats of dilution of aqueous solutions of amino acids[1-3] have shown that the dipole moment is not the main factor determining the thermodynamic properties of these solutions. The quantity Φ_{L_2} (apparent relative molal heat content) is negative for glycine, has positive values for α-alanine and shows a further increment for α-amino-*n*-butyric acid, although the dielectric increments for these three substances are approximately equal;[4] in contrast, α-amino-*n*-butyric and γ-aminobutyric acids show nearly identical Φ_{L_2} values up to 1.2 m although the dielectric increment of the γ-acid is more than twice as large as that of the α-acid. The hydrocarbon residue is evidently an important factor. Its influence may be exerted through hydrocarbon-hydrocarbon, hydrocarbon-dipole, and hydrocarbon-solvent interactions.

An examination of the differential entropies of dilution $(\bar{S}_1 - \bar{S}_1^0)$ of aqueous electrolyte solutions[5] permitted an attempt to correlate the sizes, shapes, and hydrogen bonding powers of ions with changes in the structure of water in

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[1] W. E. Wallace, W. F. Offutt, and A. L. Robinson, J. Am. Chem. Soc. 65, 347 (1943).

[2] Data for α- and β-alanine, L. S. Mason, H. Benesi, and A. L. Robinson, J. Am. Chem. Soc., to be published.

[3] Data for four aminobutyric acids, L. S. Mason and A. L. Robinson, J. Am. Chem. Soc., submitted for publication.

[4] E. J. Cohn and J. T. Edsall, *Proteins, Amino Acids, and Peptides* (Reinhold Publishing Corporation, New York, 1943), p. 146.

[5] H. S. Frank and A. L. Robinson, J. Chem. Phys. 8, 933 (1940). A recent paper by G. W. Stewart, J. Chem. Phys. 11, 72 (1943) is a particular interest in this connection.