

Evaluation of Force Constants of Tetrahedral Hydrides from Raman and Infrared Data

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expected to exceed the ordinary thermal dilatation only for observation times which are short compared with the decay time of the excited state. It thus might be observable in not too short-lived transitions. We feel however that the information yielded by such experiments would not be worth the experimental difficulties in studying this effect.

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Evaluation of Force Constants of Tetrahedral Hydrides from Raman and Infrared Data

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The force constants of 4 molecules and 4 ions of the type XH_4 belonging to the T_d symmetry have been calculated by Wilson's $\mathbf{F}-\mathbf{G}$ matrix method, using Raman and infrared data. Using a modified Urey-Bradley field, the force constants between nonbonded atoms were calculated separately and substituted in the main equations. Anharmonicity was not taken into account.

1. INTRODUCTION

THE most convenient method for obtaining the normal frequencies of a molecule is the one utilizing the symmetry coordinates, first introduced by Wilson.¹ These symmetry coordinates must be such that they transform according to the characters of the vibration type concerned and also must be normalized and orthogonal. In this group-theoretical method the elements of a matrix \mathbf{F} related to the potential energy, and the elements of a matrix \mathbf{G} related to the kinetic energy, are obtained. From these matrices the equations giving the vibrational frequencies in terms of the force constants are deduced.

The group-theoretical method of obtaining the force constants in the molecules discussed in this paper is given below. The present values of the force constants in some cases are compared with those computed by a previous worker, who had obtained them by a slightly different method.

2. THEORETICAL CONSIDERATIONS

The molecules and ions of the type XH_4 discussed in the present investigation have been proved to have the symmetry T_d . Consequently, from the relevant character table and applying the selection rules, it can be seen that such a structure will give rise to one non-degenerate type a_1 vibration, one doubly degenerate type e vibration, and two triply degenerate type t_2 vibrations. All are allowed in the Raman spectrum, but only the t_2 vibrations are allowed in the infrared spectrum. The relevant symmetry coordinates and other details have been worked out by Meister and Cleve-

land,² using four force constants in the expression for the potential energy, since there are only four distinct frequencies for each molecule. The force constants used by them were f_d (representing the force between the X and H atoms), f_α (that associated with the bending), $f_{\alpha\alpha}$ (representing that due to the interaction between bending and bending), and $f_{d\alpha}$ (that due to the interaction between bending and stretching); d is the equilibrium bond distance and α is the interbond angle.

Using those results, Venkateswarlu and Sundaram³ calculated those four force constants for a number of tetrahedral molecules and radicals, including two hydrides. However, in the case of SiH_4 , imaginary values were found for all force constants except f_d .⁴ On applying Venkateswarlu and Sundaram's method to other tetrahedral hydrides, the present author found imaginary values for the force constants of all the molecules and ions discussed in this paper, except GeH_4 . This is clearly the result of the choice of an inadequate potential function.

In trying to solve this problem, the present author worked out the \mathbf{F} and \mathbf{G} matrices for the most general harmonic potential function in the same way as Meister and Cleveland did for the more approximate potential function. The results are given in the following.

(i) \mathbf{F} -Matrix Elements

For type a_1 vibration,

$$F_{11} = f_d + 3f_{d\alpha}.$$

² A. G. Meister and F. F. Cleveland, *Am. J. Phys.* **14**, 13 (1946).

³ K. Venkateswarlu and S. Sundaram, *J. Chem. Phys.* **23**, 2365 (1955).

⁴ Actually they seem to have made a numerical error, because they list real values while the correct results according to their method undoubtedly are imaginary.

¹ E. B. Wilson, Jr., *J. Chem. Phys.* **7**, 1047 (1939); **9**, 76 (1941).

For type e vibration,

$$F_{11} = d^2(f_{\alpha} + f_{\alpha\alpha'} - 2f_{\alpha\alpha}),$$

and for type t_2 vibrations,

$$\begin{bmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{bmatrix} = \begin{bmatrix} d^2(f_{\alpha} - f_{\alpha\alpha'}) & \sqrt{2}d(f_{d\alpha} - f_{\alpha\alpha'}) \\ \sqrt{2}d(f_{d\alpha} - f_{\alpha\alpha'}) & (f_d - f_{dd}) \end{bmatrix}.$$

Here $f_{\alpha\alpha'}$ represents the small interaction between bending and bending in the case where the two angles concerned have no common bond, f_{dd} represents the interaction between stretching and stretching, and $f_{d\alpha}$ is the force constant representing the interaction between stretching and bending when there is no common bond.

(ii) G-Matrix Elements

For type a_1 vibration,

$$G_{11} = \mu_y.$$

For type e vibration,

$$G_{11} = 3\mu_y/d^2,$$

and for type t_2 vibrations,

$$\begin{bmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{bmatrix} = \begin{bmatrix} \left(2\mu_y + \frac{16}{3}\mu_x\right)/d^2 & -\frac{8\mu_x}{3d} \\ -\frac{8\mu_x}{3d} & (\mu_y + \frac{4}{3}\mu_x) \end{bmatrix}.$$

From the above matrices, the secular equations for the three types of vibration are:

for a_1 type,

$$\lambda_1 = F_{11}G_{11} = (f_d + 3f_{dd}) = 4\pi^2 c^2 \nu_1^2$$

for e type,

$$\lambda_2 = F_{11}G_{11} = (f_{\alpha} + f_{\alpha\alpha'} - 2f_{\alpha\alpha}) \cdot 3\mu_y = (2\pi c \nu_2)^2,$$

and for t_2 vibrations it is

$$\lambda^2 - \lambda[F_{11}G_{11} + 2F_{12}G_{12} + F_{22}G_{22}] + \begin{vmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{vmatrix} \cdot \begin{vmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{vmatrix} = 0.$$

$$\begin{aligned} \therefore \lambda^2 - \lambda \left[(f_{\alpha} - f_{\alpha\alpha'}) \left(2\mu_y + \frac{16}{3}\mu_x \right) \right. \\ \left. - \frac{16\sqrt{2}}{3}\mu_x(f_{d\alpha} - f_{\alpha\alpha'}) + (f_d - f_{dd}) \left(\mu_y + \frac{4}{3}\mu_x \right) \right] \\ + [(f_d - f_{dd})(f_{\alpha} - f_{\alpha\alpha'}) - 2(f_{d\alpha} - f_{\alpha\alpha'})^2] \\ \times \left[\left(\mu_y + \frac{4}{3}\mu_x \right) \left(2\mu_y + \frac{16}{3}\mu_x \right) - \frac{64}{9}\mu_x^2 \right] = 0, \end{aligned}$$

where the roots are $\lambda_3 = (2\pi c \nu_3)^2$ and $\lambda_4 = (2\pi c \nu_4)^2$.

Since we can only solve for four force constants simultaneously, some approximation must be made. Meister and Cleveland² chose to neglect f_{dd} , $f_{d\alpha}$, and $f_{\alpha\alpha'}$. However, as was stated earlier, that procedure often leads to imaginary results, because in the equations for $f_{d\alpha}$ we then substitute $(f_d + 3f_{dd})$ instead of $(f_d - f_{dd})$, thus introducing an error of $4f_{dd}$.

In the present investigation it was decided to neglect only $f_{\alpha\alpha'}$, but to substitute an approximate value of f_{dd} in the equations and thus to calculate f_d , f_{α} , $(f_{d\alpha} - f_{\alpha\alpha'})$, and $f_{\alpha\alpha}$.

Approximate values of f_{dd} can at present be obtained in two ways, viz., either by regarding the forces between nonbonded atoms as consisting purely of Van der Waals forces, and directly calculating them from the Van der Waals potential for the corresponding rare gas atoms, or otherwise by calculating f_{dd} using some approximate potential function that expresses one or more of the force constants in terms of the others. Such potential functions are, for instance, the OVFF or some modified forms of the Urey-Bradley potential.

The former procedure is not generally applicable. Expressions for the Van der Waals repulsive potential between helium and helium have been given by several workers,^{5,6} but in no case for distances smaller than about 2 Å. That immediately rules out its application to CH₄, for instance. Neither do such expressions take into account the partly ionic character of the hydrogen atoms. It is not, of course, applicable to molecular ions at all.

The only generally useful way seems to be to calculate f_{dd} from some approximate potential function, and then to substitute this value in the present equations. Use was made of the Urey-Bradley potential⁷ as modified by Simanouti.⁸ It must be kept in mind that the F used by Simanouti is equal to $\frac{3}{4}f_{dd}$ in the present investigation, assuming a perfectly tetrahedral structure. By this method, two values of f_{dd} are obtained. In no case, however, did both values result in real force constants on substitution in the present equations. One value could invariably be ruled out. The values calculated by this method are approximately the same as those computed using the OVFF approximation.⁹

No attempt was made to compare the values of f_d found in the present investigation with those calculated from Gordy's empirical rule,¹⁰ since this rule, in the case of tetrahedral hydrides, does not take into account the forces between nonbonded atoms.

3. RESULTS

The wave numbers used in the evaluation of the force constants are given in Table I. Except where

⁵ R. Buckingham, Proc. Roy. Soc. (London) A168, 264 (1938).

⁶ Hirschfelder, Ewell, and Roebuck, J. Chem. Phys. 6, 205 (1938).

⁷ H. C. Urey and C. A. Bradley, Phys. Rev. 38, 1989 (1931).

⁸ T. Simanouti, J. Chem. Phys. 17, 245 (1949).

⁹ D. Heath and J. Linnett, Trans. Faraday Soc. 44, 878 (1948).

¹⁰ W. Gordy, J. Chem. Phys. 14, 305 (1946).

otherwise stated, they were taken from Landolt-Börnstein's tables.¹¹

The force constants of the various molecules and ions are given in Table II. It is seen that in no case imaginary results were obtained. The force constants of GeH₄, calculated by Venkateswarlu and Sundaram,³ are also given in Table II to illustrate the difference between the two sets of results. It is quite clear that, in general, f_{dd} cannot be neglected.

In all cases two sets of values were obtained, of which only one set need be physically significant. However, it is hard to choose a preferred set, except in the case of the two isotopic pairs. Here we can expect approximately the same results for CH₄ and CD₄, and for NH₄⁺ and ND₄⁺, respectively. By referring to Table II, it can be seen that in both cases the set having the smaller value of $(f_{d\alpha} - f_{d\alpha}')$ should be preferred. Perhaps it is not unreasonable to regard the sets with smaller values of $(f_{d\alpha} - f_{d\alpha}')$ as being preferable in all cases.

TABLE I. Wave numbers¹¹ in cm⁻¹.

Molecule	$\nu_1(a_1)$	$\nu_2(e)$	$\nu_3(t_2)$	$\nu_4(t_2)$
CH ₄	2914.2	1520	3020	1305
CD ₄	2084.7 ^a	1075	2259.3 ^b	995.86 ^c
SiH ₄	2180	970	2183	910
GeH ₄	1990	833	2110	933
NH ₄ ⁺	3040	1680	3145	1400
ND ₄ ⁺	2214	1215	2346	1065
PH ₄ ⁺	2304	1040	2370	930
AlH ₄ ^{-d}	1790	799	1741	769

^a G. MacWood and H. Urey, J. Chem. Phys. 4, 402 (1936).

^b H. Kaylor and A. Nielsen, J. Chem. Phys. 23, 2139 (1955).

^c A. Nielsen and H. Nielsen, Phys. Rev. 54, 118 (1938).

^d E. R. Lippincott, J. Chem. Phys. 17, 135 (1949).

The agreement between the preferred values for the two members of each isotopic pair can be regarded as a check on the accuracy of the method. It can be seen that this agreement is as good as can be expected, if allowance is made for the effect of anharmonicity.

GeH₄ and SiH₄ were the only molecules where it was possible to calculate f_{dd} by means of the Van der Waals potential. The value used was⁶

$$E = 4.39 \times 10^{-10} r^{-12} - 1.522 \times 10^{-12} r^{-6}$$

where E is in erg, r in Å, and $f_{dd} = \frac{4}{3}(d^2 E / dr^2)$.

For SiH₄,¹² $d = 1.4798$ Å was used, and for GeH₄, $d = 1.535$ Å, this being the average of the Ge-H bond distances for GeH₃Cl and GeH₃Br. The proper values of r (the H-H bond distance) can then easily be calculated.

These results are also given in Table II. It is seen that the two values of f_{dd} agree well in the case of

TABLE II. Force constants for the molecules in units of 10⁶ dynes cm⁻¹.

Molecule	f_{dd}	f_d	$(f_{d\alpha} - f_{d\alpha}')$	f_{α}	$f_{\alpha\alpha}$
CH ₄	0.100	4.745	0.813	0.725	0.134
			-0.212	0.461	0.001
CD ₄	0.120	4.797	1.156	1.028	0.285
			-0.134	0.464	0.003
SiH ₄ ^a	0.032	2.726	0.181	0.250	0.032
			-0.014	0.226	0.020
SiH ₄	0.042	2.696	0.255	0.278	0.046
			-0.090	0.235	0.025
GeH ₄ ^a	0.018	2.297	0.401	0.425	0.144
			-0.343	0.387	0.125
GeH ₄	0.322	1.386	0.471	1.025	0.444
			-0.444	0.979	0.421
NH ₄ ⁺	0.090	5.218	0.824	0.783	0.112
			-0.240	0.540	-0.009
ND ₄ ⁺	0.090	5.547	1.031	0.901	0.159
			0.039	0.512	-0.036
PH ₄ ⁺	0.660	1.172	0.124	1.539	0.662
			-0.095	1.514	0.650
AlH ₄ ⁻	0.076	1.675	0.243	0.246	0.060
			-0.141	0.197	0.035
GeH ₄ ^b	0.000	2.355	0.363	0.388	0.125
			-0.304	0.354	0.108

^a f_{dd} calculated from the Van der Waals potential.

^b Venkateswarlu and Sundaram's results (reference 3).

SiH₄, but not nearly so well in the case of GeH₄. This can be explained on the basis that the Van der Waals potential can only be applied to this problem when the electronic structure of the hydrogen atoms is nearly the same as that of helium atoms, i.e., in the case of an ideal covalent bond.

The value of f_{dd} obtained for NH₄⁺ was also used for ND₄⁺. Keeping in mind the relatively large uncertainty in the observed wave numbers for these ions, this procedure is certainly justified.

4. CONCLUSION

It seems clear that the earlier procedure of calculating the force constants of tetrahedral hydrides from infrared and Raman data by putting $f_{dd} = 0$ is inadequate. In that respect the present method is much more satisfactory. No claim is made that the force constants referring to nonbonded atoms are very accurate. Even so, these calculations can be expected to be more accurate than the earlier ones.

The values of the force constants calculated in this paper are the "effective" values. No corrections have been made for the effects of anharmonicity, since in the majority of instances that is as yet impossible. Consequently it was impossible to obtain the purely harmonic force constants.

5. ACKNOWLEDGMENTS

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¹¹ Landolt-Börnstein, *Atom- und Molekularphysik* (1951), 2 Teil.

¹² D. R. J. Boyd, J. Chem. Phys. 23, 922 (1955).