can help in the proper evaluation of the standard errors for all parameters used. Whereas in computing the radial distribution curve all the experimental intensities are included with equal weights, even though some of them are less reliable because of certain reasons for which corrections often cannot easily be made, the intensities can be given appropriate weights in the least-squares treatment so that all the experimental data are amalgamated to yield a set of molecular data with specified errors.

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Approximate Isotopic Frequency Rule and Its Application to the Spectra of Complex Molecules

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An isotopic frequency rule is derived which is valid to a good approximation for individual modes of fully substituted hydrogen-containing groups in a complex molecule. It is given by $\lambda^i/\lambda = 1 - (\Sigma_j \Delta T_j / \rho T)$, where $\lambda = 4\pi^2\nu^2$, $\rho = m^i/m =$ ratio of the isotopic to the normal mass, $T =$ total kinetic energy associated with the vibration, and $\Sigma_j \Delta T_j =$ differential kinetic energy associated with the substituted atoms. When applied to H_2O and NH_3 this rule reproduces frequency ratios to better than 0.5%. The rule is used to predict the frequency ratios for the various modes of the CH_2 group, and with illustrations from the infrared spectra of high polymers it is shown how this rule can be of assistance in making assignments and in providing information on the separability of group vibrations.

INTRODUCTION

THE detailed analysis of the infrared and Raman spectra of a complex molecule (such as, for example, a high polymer) can provide significant information about the structure of the molecule and about the nature of its intramolecular and intermolecular forces. Such an analysis requires that a complete assignment be made of the observed bands in the spectrum to the predicted modes of vibration of the molecule. One of the techniques for identifying the origin of spectral bands, and thereby assisting in the assigning of these bands, is isotopic substitution. For example, when deuterium is substituted for hydrogen in a molecule, we can expect that the frequencies of those modes involving the motions of hydrogen atoms will be lowered. Thus, qualitatively, the shift of a band to lower frequencies upon such isotopic substitution serves to identify the band as originating to some extent in a hydrogen mode. In this article we are interested in investigating what can be said in greater detail about the normal mode from the quantitative magnitude of the frequency shift ratio.

From the theory of small vibrations it is possible to deduce an exact rule relating the frequencies of the normal and the substituted molecules, viz., the Teller-Redlich product rule.[1,2] The difficulty with using this rule in the analysis of complex molecules is that it relates the products of all frequencies belonging to the same symmetry species. Therefore, if a large molecule has low symmetry, as is usually the case, we only obtain a relationship between a large number of frequencies. Ideally, we would like a relation between only two frequencies, that of a given mode in the normal molecule and the frequency of the corresponding mode in the substituted molecule. Although such relations have been derived for small mass changes,[3] they are not very satisfactory when the mass alters by a factor of two, as when deuterium is substituted for hydrogen. Since the latter substitution is the most useful one in the study of complex molecules, we are concerned here with the derivation of a rule which, even if approximate, will be valid for such cases. Specifically, we wish to determine, for example, the frequency shift ratio for each of the modes of a CH_2 group when both hydrogen atoms are replaced by deuterium atoms.

THEORY

For a differential mass change in a molecule, the theory of small vibrations provides an exact expression for the differential frequency shift. It can be shown[4,5] that this is given by

$$d\lambda_k/\lambda_k = -\sum_j dT_j/T_k, \qquad (1)$$

[1] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), p. 231.
[2] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), p. 183.

[3] Work cited in footnote 2, p. 188.
[4] E. Teller, Hand- und Jahrb. Chem. Physik **9(II)**, 43 (1934).
[5] H. J. Bernstein, Can. J. Chem. **29**, 284 (1951).

where

$$\lambda = 4\pi^2\nu^2. \qquad (2)$$

In these equations, ν is the frequency, λ_k is the value of λ associated with the kth mode of the normal molecule, $T_k = \sum_l m_l \dot{q}_{kl}^2 = $ total kinetic energy associated with the kth vibration in the normal molecule, and $\sum_j dT_j = \sum_j dm_j \dot{q}_{kj}^2 = $ the differential kinetic energy in the kth mode associated with the substituted atoms j when a mass change dm_j is made. If we assume the substitution of all atoms of one kind in the group, viz., hydrogen in the present case, then Eq. (1) provides an exact expression for the derivative of λ_k with respect to m, the mass of the hydrogen atom:

$$d\lambda_k/dm = -\lambda_k\left(\sum_j \dot{q}_{kj}^2/T_k\right). \qquad (3)$$

If these exists an expression for λ_k as a function of m, then Eq. (3) can be used to obtain the finite change in λ, $\Delta\lambda_k$, associated with a finite change in mass, Δm.

No exact expression exists for $\lambda_k(m)$ which is generally true for all molecules. However, for the kinds of small molecules or groups which concern us (e.g., OH, CH_2, CH_3), it can be shown (see Appendix) that to a good approximation

$$\lambda_k = a_1 + (a_2/m), \qquad (4)$$

where a_1 and a_2 are constants. If we designate by a superscript i quantities relating to the isotopically substituted molecule, then Eq. (4) leads to

$$\Delta\lambda_k/\Delta m \equiv (\lambda_k{}^i - \lambda_k)/(m^i - m) = -(a_2/mm^i). \qquad (5)$$

Since it also follows from Eq. (4) that

$$d\lambda_k/dm = -(a_2/m^2), \qquad (6)$$

Eq. (5) can be written

$$\Delta\lambda_k/\Delta m = (\rho)^{-1}(d\lambda_k/dm), \qquad 7)$$

where

$$\rho = m^i/m. \qquad (8)$$

By substituting Eq. (3) into Eq. (7), we find that

$$(\lambda_k{}^i - \lambda_k)/\Delta m = -(\lambda_k/\rho)\cdot\left(\sum_j \dot{q}_{kj}^2/T_k\right). \qquad (9)$$

From this it follows that

$$\lambda_k{}^i/\lambda_k = 1 - \left(\sum_j \Delta T_j/\rho T_k\right), \qquad (10)$$

where $\sum_j \Delta T_j = \sum_j \Delta m \dot{q}_{kj}^2$. Equation (10) is the basic relation of the isotopic frequency rule.

RESULTS AND DISCUSSION

In order to test the validity of Eq. (10), we will consider its application to H_2O and NH_3. It becomes immediately apparent that in order to make use of this rule it is necessary to know the normal coordinates; only in this way can we know the relative amplitudes of motion of the atoms, and therefore the relative kinetic energies required in Eq. (10). Since such normal

TABLE I. Application of isotopic frequency rule to H_2O and NH_3.

	$(\nu/\nu^i)_{calc}$	$(\nu/\nu^i)_{obs}$	
		Fundamentals	Zero-order frequencies
H_2O, D_2O:			
$\nu_1(\nu_s)$[a]	1.384	1.369 (-1.1%)	1.387 ($+0.2\%$)
$\nu_2(\delta)$	1.365	1.348 (-1.2%)	1.363 (-0.2%)
$\nu_3(\nu_a)$	1.365	1.353 (-0.9%)	1.368 ($+0.2\%$)
NH_3, ND_3:			
$\nu_1(\nu_s)$	1.395	1.379 (-1.1%)	1.400 ($+0.4\%$)
$\nu_2(\delta_s)$	1.317	1.270 (-3.6%)	1.313 (-0.3%)
$\nu_3(\nu_a)$	1.359	1.350 (-0.7%)	1.357 (-0.1%)
$\nu_4(\delta_a)$	1.403	1.367 (-2.6%)	1.380 (-1.6%)

[a] ν=stretching, δ=bending, s=symmetric, a=antisymmetric.

coordinates are not known in complex molecules, it would seem that the frequency rule would be of little use. However, it frequently happens that the true normal coordinate is very well approximated by a suitably chosen symmetry coordinate. For the preceding type of small molecule, the condition of conservation of momentum then uniquely defines the amplitudes of motion, and therefore permits the application of Eq. (10). The departures from the predicted frequency ratios can then serve as a measure of the departure of the true mode in the complex molecule from that represented by the simple symmetry coordinate. For H_2O and NH_3, symmetry coordinates were chosen in which the atoms move along and perpendicular to the bonds in the molecule, viz., valence coordinates. [See Figs. 55(b) and 58 of footnote 1 for descriptions of these symmetry coordinates.] The results of applying Eq. (10) are shown in Table I, and are compared with the ratios for the observed fundamentals and the zero-order frequencies[6] (in the latter case the observed frequencies are corrected for anharmonicities). For example, for ν_1 of H_2O the relative amplitudes of motion of the H and O atoms (and therefore the $\dot{q}$) are in the ratio of 1 to $\frac{1}{8}$ cos $52.5°$, respectively. Therefore,

$$\lambda_k{}^i/\lambda_k = 1 - 2/[2(2 + \tfrac{1}{4}\cos^2 52.5)] = 0.5222,$$

and $\nu_1/\nu_1{}^i = 1.384$.

Several comments can be made on the results shown in Table I. First, as would be expected, the agreement is better for the zero-order frequencies than for the observed fundamentals. Second, in the cases of the ν_1, ν_2, and ν_3 modes of H_2O and the ν_1, ν_2, and ν_3 modes of NH_3 the chosen symmetry coordinate actually approximates closely the true normal coordinate, and it can be seen that the observed ratios are in quite good agreement with the calculated ones. For ν_4 of NH_3, the symmetry coordinate is, in fact, not a good approximation to the normal coordinate, and the observed ratio does deviate more significantly from the com-

[6] D. M. Dennison, Revs. Modern Phys. 12, 175 (1940).

TABLE II. Frequency shift ratios for CH_2 and CH_3 groups.

		$(\nu/\nu^i)_{calc}$
CH_2, CD_2:	$\nu_s{}^a$	1.379
	ν_a	1.349
	δ	1.349
	$\gamma_w{}^b$	1.323
	γ_t	1.414
	γ_r	1.379
CH_3, CD_3:	ν_s	1.398
	ν_a	1.349
	δ_s	1.300
	δ_a	1.403
	γ_r	1.292

a See footnote to Table I.

b γ_w=wagging, γ_t=twisting, γ_r=rocking.

puted one. However, if the true normal coordinate for ν_4 is used in the calculation, the computed value of ν/ν^i is in much better agreement with the observed value. Third, even though the ratios for the fundamental frequencies deviate somewhat more from the calculated values than do those for the zero-order frequencies, the relative values are in the same order as predicted. From the foregoing observations it can be concluded that the isotopic frequency rule given by Eq. (10) is valid to a good approximation for such small groups, and that it should provide a satisfactory basis for identifying individual modes.

Similar calculations for CH_2 and CH_3 groups are shown in Table II. These are again based on symmetry coordinates of the kind used for H_2O and NH_3. In the γ_w, γ_t, and γ_r (wagging, twisting, and rocking) modes of CH_2, motions perpendicular to the bonds have been assumed, the amplitudes being determined by the conservation of momentum condition. That is, the calculation is based on the assumption of isolated groups. In neither case can satisfactory tests of the validity of these ratios be made from the examination of small molecules, since the normal modes in such cases depart significantly from those assumed. Nevertheless, the magnitudes observed are in the order predicted. (For example, the ratio of zero-order CH_3 frequencies for CH_3Cl, CD_3Cl is[7]: ν_s—1.388, ν_a—1.350, δ_s—1.325, δ_a—1.391, γ_r—1.320.)

The application of the isotopic frequency rule to the spectra of complex molecules helps to establish its validity and range of application. We will consider the use of this rule in connection with the assignments of the $\nu_s(CH_2)$, $\nu_a(CH_2)$, $\delta(CH_2)$, $\gamma_w(CH_2)$, and $\gamma_r(CH_2)$ modes of some high polymers for which satisfactory data are available (the $\gamma_t(CH_2)$ mode is usually hard to identify). The results for these polymers are collected in Table III. For the detailed arguments on the assignments, reference is made to a recent review article.[8]

[7] W. T. King, I. M. Mills, and B. Crawford, J. Chem. Phys. 27, 455 (1957).

[8] S. Krimm, (to be published).

As we noted in the foregoing the calculated frequency ratios are for isolated CH_2 groups. When a CH_2 group is part of a larger molecule, it will generally be be true that atoms in the rest of the molecule also move during modes which we usually associate with only the CH_2 group. To the extent that other atoms partake in the vibrational motion, we may expect the observed frequency ratios to deviate from the calculated ones given in Table III. This deviation should provide a measure of the separability of the group frequency involved. From considerations of the motions of the atoms in the infrared active modes of the polyethylene chain, we expect the relative amplitudes of motion of the atoms in the CH_2 groups to approximate most closely those of an isolated CH_2 group. It is therefore gratifying to find that the ratios for the CH_2 modes in polyethylene most closely agree with the predicted values. (We expect some deviation because fundamental frequencies, rather than zero-order frequencies, are being used.) The larger ratio for γ_r as compared to ν_s may indicate that in the former mode there is less carbon motion than in the latter mode, or it may be a result of different anharmonicities for the two vibrations. In polyvinyl chloride, on the other hand, the ratios as well as their relative magnitudes differ significantly from the predicted values. This may be taken to indicate that what we call a CH_2 mode in this molecule actually significantly involves motions of the other atoms. That is, this is a poor instance of a separable group frequency. This situation is confirmed by other data on polyvinyl chloride: upon full deuteration of the molecule, the C—Cl stretching frequencies shift from a mean value of 623 cm^{-1} to one of 581 cm^{-1}. This 42-cm^{-1} drop in the chlorine stretching frequencies when the hydrogen atoms are replaced by deuterium is a clear indication that the vibrational modes of this molecule significantly involve motions of all of the atoms. It would appear also that the more nearly isolated the group vibration is from motions in the remainder of the molecule the more nearly equal will be the ratios for ν_a and δ, for example, even though the actual values deviate from the predicted ratios. Polystyrene seems to offer an illustration of this situation.

The spectrum of polyvinylidene chloride provides an illustration of how the isotopic frequency rule can be used as an aid in making assignments. Assignments for the $\nu_s(CH_2)$, $\nu_a(CH_2)$, $\delta(CH_2)$, and $\gamma_w(CH_2)$ modes in polyvinylidene chloride can be made with little difficulty, both in the normal and in the deuterated molecules. There has been some question, however, about the $\gamma_r(CH_2)$ mode. One assignment would result in a frequency shift ratio of 1.240 on deuteration; an alternative assignment would give a ratio of 1.388. Upon examining the ratios for the other CH_2 modes, it is clear that the latter value is entirely reasonable, while the former is considerably out of line. Other arguments also favor the latter assignment, thus indicating that consistency with the results of the fre-

TABLE III. Application of isotopic frequency rule to some high polymers.

	ν_s (CH$_2$)	ν_a (CH$_2$)	δ(CH$_2$)	γ_w (CH$_2$)	γ_r (CH$_2$)
Predicted ratio	1.379	1.349	1.349	1.323	1.379
Observed ratio					
Polyethylene	1.372	1.342	1.341	...	1.384
Polyvinyl chloride	1.320	1.303	1.283	...	1.220
Polystyrene	1.358	1.330	1.334	...	...
Polyvinylidene chloride	1.378	1.340	1.340	1.322	1.388
Polyethylene terephthalate {C:	1.268	1.222	1.210	1.198(?)	1.271
{A:	1.365	1.356	1.352	1.302(?)	...

quency rule provides another criterion for judging whether or not an assignment is satisfactory. The results for polyethylene terephthalate are in agreement with observations made above, and indicate the possible difference between the vibrational modes of a group in the crystalline chain structure and in the amorphous chain structure.

In summary, we have been able to show that an isotopic frequency rule can be derived which is valid to a good approximation for single modes of groups within a complex molecule. Not only does the application of this rule provide information on the separability of group vibrations, but it also can be of assistence in making assignments.

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APPENDIX

The relation expressed by Eq. (4), while not generally true, is valid to a good approximation for some small molecules. For diatomic molecules this is obviously the case, since in this instance

$$\lambda = k/\mu = (k/m_1) + (k/m_2). \tag{A1}$$

For a nonlinear symmetric triatomic molecule, XY$_2$, the frequencies, on the assumption of a valence force field, are given by (see work cited in footnote 1, p. 168)

$$\lambda_3 = [1 + (2m_Y/m_X) \sin^2\alpha](k_1/m_Y) \tag{A2}$$

$$\lambda_1 + \lambda_2 = [1 + (2m_Y/m_X) \cos^2\alpha](k_1/m_Y)$$
$$+ (2/m_Y)[1 + (2m_Y/m_X)\sin^2\alpha](k_\delta/l^2) \tag{A3}$$

$$\lambda_1\lambda_2 = 2[1 + (2m_Y/m_X)](k_1/m_Y^2) \cdot (k_\delta/l^2). \tag{A4}$$

For the antisymmetric stretching frequency, given by Eq. (A2), it can be seen that a relation of the form of Eq. (4) is satisfied. From Eqs. (A3) and (A4) we find that

$$\lambda_1 = (A/m_X) + (B/m_Y) \pm [(B^2 - 4D) \cdot (1/m_Y^2)$$
$$+ (2AB - 4C) \cdot (1/m_Y^2) \cdot (m_Y/m_X) + (A^2/m_X^2)]^{\frac{1}{2}}, \tag{A5}$$

where A, B, C, and D are constants involving the force constants, k_1 and k_δ/l^2, and A^2, B^2, AB, C, and D are of the same order of magnitude. Since for example for CH$_2$ $m_X = 12m_Y$, and $(B^2 - 4D) \sim A^2$, the last term in the brackets of Eq. (A5) can be neglected; the error introduced is about 0.7%. Expanding the bracket, and dropping terms in $(m_Y/m_X)^2$ and higher powers (since they will be negligible compared to 1), we find that

$$\lambda_1 \cong \left[\frac{A}{m_X} \pm \frac{(B^2 - 4D)^{-\frac{1}{2}}(2AB - 4C)}{m_X}\right]$$
$$+ [B \pm (B^2 - 4D)^{\frac{1}{2}}] \cdot m_Y^{-1}. \tag{A6}$$

Since m_X is kept constant upon isotopic substitution, this can be written as

$$\lambda_1 \cong a_1 + (a_2/m) \tag{A7}$$

which is of the form of Eq. (4). An analogous relationship holds for λ_2, and can also be shown to be similarly valid for the frequencies of a pyramidal XY$_3$ molecule.