

Isotope Effects on Molecular Properties

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I. Introduction

The properties of a molecule are dependent on the masses of its nuclei. Some properties, such as the molecular weight, the position of the center of mass, the rotational constants and moments of inertia, and the vibrational frequencies, obviously vary with nuclear mass; others, depending on the electronic structure, such as the electric dipole moment, the polarizability, and the nuclear magnetic shielding, are found to change slightly from one isotopic species to another. Hyperfine interactions, such as nuclear quadrupole coupling constants, and nuclear spin-spin coupling constants, may be very different in different isotopic species because of large changes in the nuclear quadrupole moment and the nuclear magnetic moment, but there are also small changes in the "reduced" coupling constants proportional to the observed coupling constant divided by the appropriate nuclear moment.

Some properties, such as the electric dipole moment of HD or of HC≡CD and the optical activity of CHDX_Y,¹ arise solely because of the isotopic substitution. In the case of HD the dipole is due to a breakdown of the Born-Oppenheimer approximation, and its value is very small, $\pm(5.85 \pm 0.17) \times 10^{-4}$ D (1 D = 10^{-18} esu = 3.33564×10^{-30} C m);² the sense of the moment is probably H⁺D⁻,³ but a definitive calculation has not yet been performed.⁴ The dipole moment of acetylene-*d*₁ is $\sim 10^{-2}$ D,⁵ and it may be considered to arise from the nonsymmetric zero-point motion of the nuclei. In CH₃D a moment of 0.56409×10^{-2} D was observed in a molecular-beam electric-resonance experiment.⁶ The effects of deuterium substitution on the dipole moments of seven molecules were studied by Muentzer and Laurie⁷ who found changes of the order of 10^{-2} D, although in fluoroform the effect is smaller ($\mu_{\text{CDF}_3} - \mu_{\text{CHF}_3}$) = 0.7×10^{-3} D.

A striking illustration of an isotope effect is to be found in Figure 1. It shows the ³¹P nmr spectrum of a partially deuterated sample of hypophosphorous acid containing H₂POOH, HDPOOH, and D₂POOH.⁸ The resonance in D₂POOH is at 0.3 ± 0.01 ppm to higher field than in HDPOOH, which itself is at 0.39 ± 0.01 ppm to higher field than in H₂POOH. Isotope shifts in nuclear magnetic resonance spectroscopy were reviewed in 1967.^{9a}

This article is concerned with the theoretical description of isotope effects on the properties of polyatomic molecules. This topic has been briefly reviewed by Wolfsberg.^{9b} The Born-Oppenheimer separation of electronic and nuclear motion¹⁰ is assumed, so the very small effects due to the break-

down of this approximation are not considered. In this connection it may be noted that Kaiser¹¹ has found that the breakdown leads to an enhancement of $(1 \pm 0.2) \times 10^{-3}$ D in the dipole moment and 15 kHz in the ³⁵Cl quadrupole coupling constant of HCl over that of DCl; according to the theoretical analysis of Bunker^{12a} 97% of this dipole enhancement comes from the nonadiabatic correction, that is, from the mixing of Born-Oppenheimer electronic states by the nuclear kinetic energy.

The chemical properties of reactants may also depend significantly on nuclear mass; reviews have been published on isotope effects on chemical equilibria (Bigeleisen, Lee, and Mandel^{12b}) and on rate constants (Bigeleisen,¹³ Bigeleisen and Wolfsberg,¹⁴ and Westheimer¹⁵). The so-called "kinetic isotope effects" arise from the dependence of the activation energy on nuclear mass, and they may be very important in the separation of isotopes but are not considered further in this article.

II. Diatomic Molecules

To expose the principles involved in the evaluation of isotope effects on molecular properties, the simple case of a diatomic molecule is examined first. The dependence of an electronic property, such as the dipole moment or nuclear magnetic shielding, on nuclear mass arises from the vibrational averaging effects.

Within the Born-Oppenheimer approximation the property ϵ may be considered to be a function of the internuclear distance r :

$$\epsilon(r) = \epsilon_e + \epsilon_e' \xi + \frac{1}{2} \epsilon_e'' \xi^2 + \dots \quad (1)$$

where the dimensionless variable ξ is the relative displacement from the equilibrium separation r_e

$$\xi = (r - r_e)/r_e \quad (2)$$

and ϵ_e is the value of the property in the equilibrium configuration; ϵ_e' and ϵ_e'' are the first and second derivatives of ϵ with respect to ξ at $r = r_e$. In the vibrational state v and rotational state J , the value of ϵ is the expectation value $\langle vJ | \epsilon(r) | vJ \rangle$.

The vibration-rotation wave functions of a diatomic molecule may conveniently be obtained through perturbation theory, the unperturbed system being the harmonic oscillator + rigid rotator. The full Hamiltonian is

$$\mathcal{H} = -hcB_e \frac{d^2}{d\xi^2} + a_0 \xi^2 [1 + a_1 \xi + a_2 \xi^2 + \dots] + (J_x^2 + J_y^2) hcB_e (1 + \xi)^{-2} \quad (3)$$

where the first and last terms are the vibrational and rotational kinetic energies (the z axis is the internuclear axis); the equilibrium rotational constant $B_e = h/8\pi^2 \mu c r_e^2$ wave numbers, $\mu = m_a m_b / (m_a + m_b)$ being the reduced mass (m_a and m_b are the masses of atoms a and b and may be taken

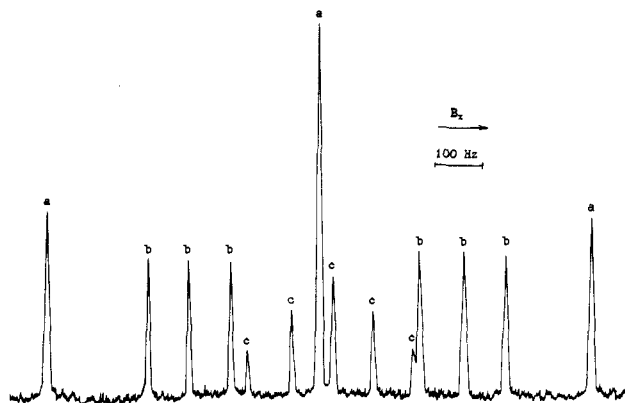


Figure 1. The ^{31}P nmr spectrum at 40.5 MHz of partially deuterated hypophosphorous acid. The lines marked "a" are the 1, 2, 1 triplet from H_2POOH , the doublet of 1, 1, 1 triplets (b) are from HDPOOH , and the 1, 2, 3, 2, 1 quintet (c) is from D_2POOH . There is an obvious increase in the ^{31}P -nuclear shielding on deuteration. The spectrum was recorded by Borisenko, Sergeyev, and Ustynuk.⁸

to include the electronic mass $Z_a m_e$, where Z_a is the atomic number of atom a; the harmonic force constant $2a_0 r_e^{-2}$ may be expressed in terms of the equilibrium vibrational and rotational constants through

$$a_0 = hc\omega_e^2/4B_e \quad (4)$$

For a molecule in a $^1\Sigma$ electronic state $J_z = 0$ and in the rotational state J , $J_x^2 + J_y^2 = J(J+1)$, and the rotational states are the well-known spherical harmonics $Y_{JM}(\theta, \varphi)$. The effective vibrational Hamiltonian may be written

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \quad (5)$$

where

$$\mathcal{H}_0 = -hcB_e \frac{d^2}{d\xi^2} + a_0 \xi^2 + J(J+1)hcB_e \quad (6)$$

and the perturbation is

$$\mathcal{H}' = a_0(a_1 \xi^3 + a_2 \xi^4 + \dots) - J(J+1)hcB_e(2\xi - 3\xi^2 + \dots) \quad (7)$$

This expansion for the potential energy in \mathcal{H} is known as a Dunham potential.¹⁶

Using perturbation theory it may easily be shown that¹⁷⁻¹⁹

$$\langle vJ|\epsilon(r)|vJ\rangle = \epsilon_e + \left(v + \frac{1}{2}\right) \frac{B_e}{\omega_e} (\epsilon_e'' - 3a_1 \epsilon_e') + 4(J^2 + J) \left(\frac{B_e}{\omega_e}\right)^2 \epsilon_e' + \dots \quad (8)$$

where the omitted terms include small terms in $(B_e/\omega_e)^2$, $(B_e/\omega_e)^3$, etc. Since B_e/ω_e is very small (it is 1.38×10^{-2} for H_2 , 3.54×10^{-3} for HCl , and 8.90×10^{-4} for CO), the expansion (8) converges rapidly. The cubic anharmonic constant a_1 is negative and is -1.607 for H_2 and D_2 , -2.341 for HCl and DCI , and -2.695 for CO . Normally ϵ_e , ϵ_e' , and ϵ_e'' are of comparable magnitude, so it is clear from (8) that there may be a change of the order of 1% in ϵ on vibrational excitation, and a much smaller change with J (unless J is very large). On isotopic substitution B_e/ω_e^2 is unchanged and B_e/ω_e changes to 1.20×10^{-2} in HD and 0.98×10^{-2} in D_2 , to 2.54×10^{-3} in DCI , and 8.69×10^{-4} in $^{12}\text{C}^{18}\text{O}$. Thus changes in ϵ of the order of 1% are expected on deuteration, and smaller changes on isotopic substitution of heavier nuclei.

The information obtainable from a measurement of the isotope dependence of ϵ could also be obtained through studies of vibrationally excited species; both yield $\epsilon_e'' - 3a_1 \epsilon_e'$, the former through a change in B_e/ω_e in (8) and the latter through a change in v . If the J dependence of ϵ could be determined it would be possible to obtain ϵ_e' , and hence ϵ_e'' , from $\epsilon_e' -$

$3a_1 \epsilon_e'$, but the required accuracy is extremely great. Accurate measurements of the properties of HCl and DCI have been reported by Kaiser¹¹ using a molecular-beam electric resonance apparatus; dipole moments, quadrupole coupling constants, and nuclear spin-rotation constants were determined. Dipole moments were measured in the $v = 0, 1, 2$ and $J = 1, 2$ states; no significant dipole difference was observed between $J = 1$ and 2, but the dipole moment function derivatives, μ_e , μ_e' , μ_e'' , μ_e''' , were determined by combining the dipole measurements with absolute infrared intensities.²⁰ The values obtained are¹¹

$$\begin{aligned} \mu_e &= 1.0933 \pm 0.0005 \text{ D} \\ \mu_e' &= 1.179 \pm 0.03 \text{ D} \\ \mu_e'' &= 0.26 \pm 0.18 \text{ D} \\ \mu_e''' &= 7.9 \pm 1.9 \text{ D} \\ \mu_e'''' &= -25 \pm 12 \text{ D} \end{aligned} \quad (9)$$

Using these values and eq 8, one obtains

$$\mu_{v,J} - \mu_{v,J-1} = 8J(B_e/\omega_e)^2 \mu_e' = 1.18J \times 10^{-4} \text{ D}$$

which, for $J = 2$, is smaller than the precision of Kaiser's relative measurements ($\pm 2.5 \times 10^{-4}$ D). However, the isotopic and vibrational dependence of μ was very accurately determined. In the case of ^{35}Cl nuclear quadrupole coupling, the variation of e^2qQ with J , v and on deuteration was measured, leading to accurate values for $(e^2qQ)_e$, $(e^2qQ)_e'$, and $(e^2qQ)_e''$.¹¹

At equilibrium at the absolute temperature T , the appropriate value of ϵ may be obtained from eq 8 by averaging v and $J^2 + J$ (eq. 10).¹⁹ Thus measurement of the isotope depen-

$$\begin{aligned} \bar{\epsilon} &= \epsilon_e + (B_e/\omega_e) (\epsilon_e'' - 3a_1 \epsilon_e') \times \\ &\left[\frac{1}{2} + \frac{\exp(-hc\omega_e/kT)}{1 - \exp(-hc\omega_e/kT)} \right] + \\ &4(B_e/\omega_e)(kT/hc\omega_e) \epsilon_e' + \dots \quad (10) \end{aligned}$$

dence of ϵ yields $\epsilon_e'' - 3a_1 \epsilon_e'$, and its temperature dependence gives ϵ_e' . These measurements have been suggested for determining the nuclear magnetic shielding function of the hydrogen molecule.¹⁹

III. Polyatomic Molecules

The electronic properties of a polyatomic molecule may, within the Born-Oppenheimer approximation, be expressed as a power series in the $3N - 6$ internal displacement coordinates R_i :³⁴

$$\epsilon(\mathbf{R}) = \epsilon_e + \sum_i (\partial\epsilon/\partial R_i)_e R_i + \frac{1}{2} \sum_{i,j} (\partial^2\epsilon/\partial R_i \partial R_j)_e R_i R_j + \dots \quad (11)$$

An internal coordinate is determined by the interatomic distances and angles and is unaffected by translation or rotation of the molecule as a whole; all R_i are zero in the equilibrium configuration. The constants ϵ_e , $(\partial\epsilon/\partial R_i)_e$, $(\partial^2\epsilon/\partial R_i \partial R_j)_e$, ..., characterize the ϵ surface and are independent of isotopic substitution. As for a diatomic, the molecular property for a particular stationary state is obtained by taking the appropriate expectation value of $\epsilon(\mathbf{R})$.

The potential energy of a polyatomic molecule is conveniently expanded as a power series in the $3N - 6$ normal coordinates Q_r , for there are then no quadratic cross terms and the kinetic energy takes the simple form

$$T = -\frac{\hbar^2}{2} \sum_r (\partial^2/\partial Q_r^2) \quad (12)$$

$$V = \frac{1}{2} \sum_r \lambda_r Q_r^2 + \frac{1}{6} \sum_{r,s,t} V_{rst} Q_r Q_s Q_t + \frac{1}{24} \sum_{r,s,t,u} V_{rstu} Q_r Q_s Q_t Q_u + \dots \quad (13)$$

The harmonic force constants $\lambda_r = 4\pi^2 c^2 \omega_r^2$, and V_{rst} and V_{rstu} are the cubic and quartic anharmonic force constants. It may also be convenient to use dimensionless normal coordinates q_r

$$q_r = (2\pi c \omega_r / \hbar)^{1/2} Q_r \quad (14)$$

when eq 13 becomes

$$V/hc = \frac{1}{2} \sum_r \omega_r q_r^2 + \frac{1}{6} \sum_{r,s,t} V_{rst} q_r q_s q_t + \frac{1}{24} \sum_{r,s,t,u} V_{rstu} q_r q_s q_t q_u + \dots \quad (15)$$

with ω_r , V_{rst} , and V_{rstu} in wave numbers.

The internal displacement coordinates R_i are linearly related to the normal coordinates Q_r or q_r through the \mathbf{L} or $\bar{\mathbf{L}}$ matrix:

$$R_i = \sum_r L_{ir} Q_r \text{ or } \mathbf{R} = \mathbf{LQ} \quad (16)$$

$$R_i = \sum_r \bar{L}_{ir} q_r \text{ or } \mathbf{R} = \bar{\mathbf{L}}\mathbf{q} \quad (17)$$

The $3N - 6$ by $3N - 6$ matrix \mathbf{L} may be obtained by standard techniques.²¹ The internal coordinates R_i are the "approximate valence-force coordinates" of Pliva²² and are a first approximation to the "true curvilinear valence-force coordinates";^{22,23} for anharmonic oscillators the "true valence-force coordinates", unlike the R_i , do not transform linearly to the normal coordinates or to the $3N$ Cartesian displacement coordinates of the nuclei.

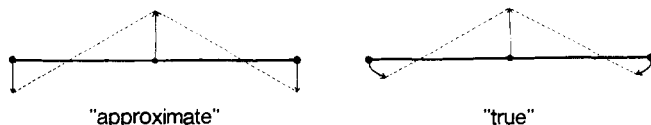


Figure 2. Valence-force coordinates for the bending mode of $^{12}\text{C}^{16}\text{O}_2$.

The harmonic constants ω_r in (15) are known from the vibrational spectrum of the molecule, but the cubic and quartic anharmonic constants have been deduced for only a few simple polyatomic molecules, particularly triatomics. The number of harmonic constants ω_r , namely $3N - 6$, rises linearly with the number of atoms N , but the number of cubic and quartic terms increases as N^3 and N^4 , respectively. A triatomic molecule of C_s symmetry, e.g., LiOH, has 3 harmonic constants, 10 cubic, and 15 quartic constants.

As for diatomics, the unperturbed eigenfunctions may be represented as a product of harmonic oscillator wave functions and a rigid-rotor wave function. For a symmetric rotor with rotational quantum numbers, J, K, M , the unperturbed eigenfunction is

$$\Psi_v^{(0)} \Psi_{JKM}^{(0)} = \prod_r H_{v_r}(q_r) \exp\left(-\frac{1}{2} q_r^2\right) \Psi_{JKM}^{(0)} \quad (18)$$

where $H_{v_r}(q_r)$ is a Hermite polynomial²¹ [thus $H_0(q_r) = 1$, $H_1(q_r) = 2q_r$, $H_2(q_r) = 4q_r^2 - 2$, and $H_{v_r+1}(q_r) = 2q_r H_{v_r}(q_r) - 2v_r H_{v_r-1}(q_r)$] and $\Psi_{JKM}^{(0)}$ the usual symmetric rotor eigenfunction.²⁴ For an asymmetric rotor the rotational wave function may be expressed as a sum of symmetric rotor functions having the same J value with tabulated coefficients for particular values of the asymmetry parameter $\tau = (2B - A - C)/(A - C)$, where $A \geq B \geq C$ are the usual rotational constants.²⁵ Vibration-rotation interaction through centrifugal distortion²⁵⁻²⁷ must be incorporated if terms analogous to that in $(J^2 + J)\epsilon_e'$ in eq 8 are to be included.

If $V - \frac{1}{2} hc \sum_r \omega_r q_r^2$ in eq 15 is treated as a perturbation to the harmonic oscillator, the vibrational wave function is

$$\Psi_v = \Psi_v^{(0)} + \sum_{v' \neq v} \frac{\langle v' | \frac{1}{6} hc \sum_{r,s,t} V_{rst} q_r q_s q_t | v \rangle}{W_v^{(0)} - W_{v'}^{(0)}} \Psi_{v'}^{(0)} + \dots \quad (19)$$

where $W_v^{(0)} = W_0^{(0)} + \sum_r (v_r + \frac{1}{2}) hc \omega_r$ is the unperturbed energy; the expectation value of $\epsilon(R)$ is

$$\langle \Psi_v | \epsilon(\mathbf{R}) | \Psi_v \rangle = \epsilon_e + \frac{1}{2} \sum_r \left(v_r + \frac{1}{2} \right) \left[(\partial^2 \epsilon / \partial q_r^2)_e - \sum_s \omega_s^{-1} v_{rrs} (\partial \epsilon / \partial q_s)_e \right] + \dots \quad (20)$$

The derivatives $(\partial \epsilon / \partial q_r)_e$ and $(\partial^2 \epsilon / \partial q_r^2)_e$ and the anharmonic constants v_{rrs} in (20) are dependent on nuclear mass. The dependence can be eliminated by using the transformation (17):

$$\langle \Psi_v | \epsilon(\mathbf{R}) | \Psi_v \rangle = \epsilon_e + \frac{1}{2} \sum_r \left(v_r + \frac{1}{2} \right) \left[\sum_{ii'} (\partial^2 \epsilon / \partial R_i \partial R_{j'})_e \bar{L}_{ir} \bar{L}_{j'r} - \sum_s (hc \omega_s)^{-1} \sum_{i,i',k,l} (\partial^3 V / \partial R_j \partial R_k \partial R_l)_e (\partial \epsilon / \partial R_i)_e \times \bar{L}_{is} \bar{L}_{j'r} \bar{L}_{k'r} \bar{L}_{l's} \right] + \dots \quad (21)$$

In eq 21 the derivatives of $\epsilon(R)$ and the potential energy are independent of mass, but ω_s and $\bar{\mathbf{L}}$ are mass dependent and lead to an isotopic shift in the property ϵ . The first and second derivatives of ϵ can be separated through measurements on different isotopes since, unlike the position in diatomics (see eq 8), the two contributions in (20) or (21) depend differently on nuclear mass. If $(\partial \epsilon / \partial R_i)_e$ and $(\partial^2 \epsilon / \partial R_i \partial R_j)_e$ are to be determined through accurate measurements of isotopic shifts, it will be necessary to know the $\bar{\mathbf{L}}$ matrix elements and the cubic anharmonic constants. It appears that no polyatomic molecule has yet been studied from this point of view.

If ϵ_e and the first and second derivatives of ϵ and the harmonic and cubic anharmonic force constants were known, it would be possible to predict values for the property ϵ in new isotopic species.

In a diatomic molecule, the dimensionless normal coordinate is

$$q = \sqrt{\frac{\omega_e}{2B_e}} \xi$$

and the $\bar{\mathbf{L}}$ matrix has just one element:

$$\bar{L}_{11} = \sqrt{\frac{2B_e}{\omega_e}} R_e$$

Equations 20 and 21 reduce to (8) in this case.

The next section is concerned with an application of this theory to the linear symmetrical triatomic CO_2 .

IV. Application to the CO_2 Molecule

The linear symmetrical structure of the carbon dioxide molecule, together with the Fermi resonance involving the symmetrical stretch and the doubly excited bend, makes it an interesting molecule for studying vibrational force fields. Among those who have contributed to the elucidation of the problem are Dennison,²⁸ Nielsen,²⁹ Pliva,²² Pariseau, Suzuki, and Overend,³⁰ Kuchitsu and Morino,³¹ and Amat.³²

The potential energy of $^X\text{O}^Z\text{C}^Y\text{O}$ (where X, Y , and Z are the atomic mass numbers) may be written as a function of the dimensionless normal coordinates q_n , as well as of the "approximate valence force coordinates" R_i , as shown in eq 22 and 23, where R_1 and R_3 are displacement coordinates which are the changes in the CO bond lengths projected along the equilibrium internuclear axis, and R_2 is the change in OCO angle.²¹ The harmonic and anharmonic constants in

$$\frac{V}{hc} = \frac{1}{2} [\omega_1 q_1^2 + \omega_2 (q_{21}^2 + q_{22}^2) + \omega_3 q_3^2] + \frac{a_{111} q_1^3 + a_{333} q_3^3 + a_{122} q_1 (q_{21}^2 + q_{22}^2) + a_{133} q_1 q_3^2 + a_{322} q_3 (q_{21}^2 + q_{22}^2) + a_{113} q_1^2 q_3}{2} \quad (22)$$

$$2V = F_{11}(R_1^2 + R_3^2) + 2F_{13}R_1R_3 + F_{22}R_2^2 + K_{111}(R_1^3 + R_3^3) + K_{133}(R_1 + R_3)R_1R_3 + K_{122}(R_1 + R_3)R_2^2 \quad (23)$$

eq 22 and 23 are related through (17) as shown in eq 24 and 25. For $^{12}\text{C}^{16}\text{O}_2$, (20) reduces to eq 26. The contribution of

$$\begin{aligned} \omega_1 &= \frac{1}{hc} [F_{11}(\bar{L}_{11}^2 + \bar{L}_{31}^2) + 2F_{13}\bar{L}_{11}\bar{L}_{31}] \\ \omega_2 &= \frac{F_{22}}{hc} \bar{L}_{22}^2 \\ \omega_3 &= \frac{1}{hc} [F_{11}(\bar{L}_{13}^2 + \bar{L}_{33}^2) + 2F_{13}\bar{L}_{13}\bar{L}_{33}] \end{aligned} \quad (24)$$

$$\begin{aligned} a_{111} &= \frac{K_{111}}{2hc} (\bar{L}_{11}^3 + \bar{L}_{31}^3) + \frac{K_{133}}{2hc} (\bar{L}_{11}^2\bar{L}_{31} + \bar{L}_{11}\bar{L}_{31}^2) \\ a_{333} &= \frac{K_{111}}{2hc} (\bar{L}_{13}^3 + \bar{L}_{33}^3) + \frac{K_{133}}{2hc} (\bar{L}_{13}^2\bar{L}_{33} + \bar{L}_{13}\bar{L}_{33}^2) \\ a_{113} &= \frac{3K_{111}}{2hc} (\bar{L}_{11}^2\bar{L}_{13} + \bar{L}_{31}^2\bar{L}_{33}) + \frac{K_{133}}{2hc} (\bar{L}_{11}^2\bar{L}_{33} + \bar{L}_{31}^2\bar{L}_{13} + 2\bar{L}_{13}\bar{L}_{31}\bar{L}_{11} + 2\bar{L}_{33}\bar{L}_{31}\bar{L}_{11}) \\ a_{133} &= \frac{3K_{111}}{2hc} (\bar{L}_{11}\bar{L}_{13}^2 + \bar{L}_{31}\bar{L}_{33}^2) + \frac{K_{133}}{2hc} (\bar{L}_{11}\bar{L}_{33}^2 + \bar{L}_{31}\bar{L}_{13}^2 + 2\bar{L}_{13}\bar{L}_{33}\bar{L}_{11} + 2\bar{L}_{33}\bar{L}_{31}\bar{L}_{13}) \\ a_{122} &= \frac{K_{122}}{2hc} \bar{L}_{22}^2 (\bar{L}_{11} + \bar{L}_{31}) \\ a_{322} &= \frac{K_{122}}{2hc} \bar{L}_{22}^2 (\bar{L}_{13} + \bar{L}_{33}) \end{aligned} \quad (25)$$

the centrifugal stretching is not included in eq 26 because calculations have shown that terms involving the rotational quantum numbers J and K are negligible for small J and K ; these terms are proportional to $J(J+1) - K^2$.

$$\begin{aligned} \langle \Psi_v | \epsilon(\mathbf{R}) | \Psi_v \rangle &= \epsilon_e + \left(\bar{L}_{11} \frac{\partial \epsilon}{\partial R_1} + \bar{L}_{31} \frac{\partial \epsilon}{\partial R_3} \right) \times \\ &\quad \left[-\frac{3a_{111}}{\omega_1} \left(v_1 + \frac{1}{2} \right) - \frac{a_{122}}{\omega_1} (v_2 + 1) - \frac{a_{133}}{\omega_1} \left(v_3 + \frac{1}{2} \right) \right] + \left(\bar{L}_{13} \frac{\partial \epsilon}{\partial R_1} + \bar{L}_{33} \frac{\partial \epsilon}{\partial R_3} \right) \times \\ &\quad \left[-\frac{3a_{333}}{\omega_3} \left(v_3 + \frac{1}{2} \right) - \frac{a_{322}}{\omega_3} (v_2 + 1) - \frac{a_{311}}{\omega_3} \left(v_1 + \frac{1}{2} \right) \right] + \frac{1}{2} \left(\bar{L}_{11}^2 \frac{\partial^2 \epsilon}{\partial R_1^2} + \right. \\ &\quad \left. 2\bar{L}_{11}\bar{L}_{31} \frac{\partial^2 \epsilon}{\partial R_1 \partial R_3} + \bar{L}_{31}^2 \frac{\partial^2 \epsilon}{\partial R_3^2} \right) \left(v_1 + \frac{1}{2} \right) + \\ &\quad \frac{1}{2} \left(\bar{L}_{22}^2 \frac{\partial^2 \epsilon}{\partial R_2^2} \right) (v_2 + 1) + \frac{1}{2} \left(\bar{L}_{13}^2 \frac{\partial^2 \epsilon}{\partial R_1^2} + \right. \\ &\quad \left. 2\bar{L}_{13}\bar{L}_{33} \frac{\partial^2 \epsilon}{\partial R_1 \partial R_3} + \bar{L}_{33}^2 \frac{\partial^2 \epsilon}{\partial R_3^2} \right) \left(v_3 + \frac{1}{2} \right) \end{aligned} \quad (26)$$

Within the Born-Oppenheimer approximation, eq 26, with (24) and (25), enables us to consider isotope effects on $^{12}\text{C}^{16}\text{O}_2$ as the values of ϵ_e , $(\partial \epsilon / \partial R_i)_e$, and $(\partial^2 \epsilon / \partial R_i \partial R_j)_e$, as well as the potential energy constants F_{ij} and K_{ijk} , are invariant to isotopic substitution. For $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ the ω_i and a_{ijk} are known from spectra.^{22,28,30,31}

The equilibrium value of ϵ and its derivatives may be determined if $\langle \Psi_v | \epsilon(\mathbf{R}) | \Psi_v \rangle$ is known for sufficient isotopic species of CO_2 . Unfortunately, no property ϵ has yet been studied from this point of view. The molecular-beam resonance method may be able to provide appropriate experimental results on linear triatomics.

The theory is now applied to the prediction of the dipole moment of $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ in various vibrational states.

Eggers and Crawford³³ obtained dipole moment derivatives for $^{12}\text{C}^{16}\text{O}_2$ from absolute intensity measurements in the infrared spectrum. Most of their dipole derivatives are, however, not unequivocal.³³ We shall employ the following values:³³

$$\frac{\partial \mu}{\partial q_3} = (0.45 \pm 0.02) \text{ D}, \quad \frac{\partial^2 \mu}{\partial q_1 \partial q_3} = (0.050 \pm 0.003) \text{ D}; \quad \mu_e = 0$$

In order to be consistent, we shall employ the potential energy constants for $^{12}\text{C}^{16}\text{O}_2$ which Eggers and Crawford used (values in cm^{-1}):³³

$$\begin{aligned} \omega_1 &= 1351.2 & a_{111} &= -35 \pm 5 \\ \omega_2 &= 672.2 & a_{122} &= 71.3 \pm 0.4 \\ \omega_3 &= 2396.4 & a_{133} &= -250 \pm 7 \end{aligned}$$

Using the \bar{L} matrix of $^{12}\text{C}^{16}\text{O}_2$ (which we shall call \bar{L}')

$$\begin{aligned} \frac{\partial \mu}{\partial R_1} &= -\frac{\partial \mu}{\partial R_3} = \frac{1}{2\bar{L}'_{13}} \frac{\partial \mu}{\partial q_3} \\ \frac{\partial^2 \mu}{\partial R_1^2} &= -\frac{\partial^2 \mu}{\partial R_3^2} = \frac{1}{2\bar{L}'_{11}\bar{L}'_{13}} \frac{\partial^2 \mu}{\partial q_1 \partial q_3} \\ \frac{\partial^2 \mu}{\partial R_2^2} &= 0, \quad \frac{\partial^2 \mu}{\partial R_1 \partial R_3} = 0. \end{aligned}$$

With these relationships, eq 26 yields (27). The matrix \bar{L}' can

$$\begin{aligned} \langle \Psi_v | \mu(\mathbf{R}) | \Psi_v \rangle &= \frac{\partial \mu}{\partial q_3} \left\{ \frac{\bar{L}_{11} - \bar{L}_{31}}{2\bar{L}'_{13}} \left[-\frac{3a_{111}}{\omega_1} \left(v_1 + \frac{1}{2} \right) - \frac{a_{122}}{\omega_1} (v_2 + 1) - \frac{a_{133}}{\omega_1} \left(v_3 + \frac{1}{2} \right) \right] + \right. \\ &\quad \left. \frac{\bar{L}_{13} - \bar{L}_{33}}{2\bar{L}'_{13}} \left[-\frac{3a_{333}}{\omega_3} \left(v_3 + \frac{1}{2} \right) - \frac{a_{322}}{\omega_3} (v_2 + 1) - \frac{a_{311}}{\omega_3} \left(v_1 + \frac{1}{2} \right) \right] \right\} + \frac{\partial^2 \mu}{\partial q_1 \partial q_3} \times \\ &\quad \left\{ \frac{(\bar{L}_{11}^2 - \bar{L}_{31}^2) \left(v_1 + \frac{1}{2} \right) + (\bar{L}_{13}^2 - \bar{L}_{33}^2) \left(v_3 + \frac{1}{2} \right)}{4\bar{L}'_{11}\bar{L}'_{13}} \right\} \end{aligned} \quad (27)$$

be given analytically as shown in eq 28, where $m_{16}\text{O}$ and $m_{12}\text{C}$ are the atomic masses of ^{16}O and ^{12}C and r_e is the equilibrium distance between C and O.

Using the above values for ω_1 , ω_2 , and ω_3 , we obtain

$$\begin{aligned} \bar{L}'_{11} &= \bar{L}'_{31} = 0.2792 \times 10^{-9} \text{ cm} \\ \bar{L}'_{13} &= -\bar{L}'_{33} = 0.4015 \times 10^{-9} \text{ cm} \\ \bar{L}'_{22} &= 0.1309 \\ \bar{L}'_{12} &= \bar{L}'_{21} = \bar{L}'_{23} = \bar{L}'_{32} = 0 \end{aligned}$$

The L matrix elements for $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ are

$$\begin{aligned} L_{11} &= 0.1332 \times 10^{12} (\text{g})^{-1/2} \\ L_{31} &= 0.1370 \times 10^{12} (\text{g})^{-1/2} \\ L_{22} &= 0.4516 \times 10^{20} (\text{g})^{-1/2} \text{ cm}^{-1} \\ L_{13} &= 0.2647 \times 10^{12} (\text{g})^{-1/2} \\ L_{33} &= -0.2585 \times 10^{12} (\text{g})^{-1/2} \\ L_{12} &= L_{21} = L_{23} = L_{32} = 0 \end{aligned}$$

$$\bar{L}' = \begin{bmatrix} \sqrt{\frac{h(m_{16O})^{-1}}{8\pi^2\omega_1c}} & 0 & \sqrt{\frac{h[(m_{16O})^{-1} + 2(m_{12C})^{-1}]}{8\pi^2\omega_3c}} \\ 0 & \sqrt{\frac{h[(m_{16O})^{-1} + 2(m_{12C})^{-1}]}{2\pi^2r_e^2\omega_2c}} & 0 \\ \sqrt{\frac{h(m_{16O})^{-1}}{8\pi^2\omega_1c}} & 0 & -\sqrt{\frac{h[(m_{16O})^{-1} + 2(m_{12C})^{-1}]}{8\pi^2\omega_3c}} \end{bmatrix} \quad (28)$$

With $\omega_1 = 1331 \text{ cm}^{-1}$, $\omega_2 = 669 \text{ cm}^{-1}$, and $\omega_3 = 2388 \text{ cm}^{-1}$ the \bar{L} matrix elements are

$$\begin{aligned} \bar{L}_{11} &= 0.2732 \times 10^{-9} \text{ cm} & \bar{L}_{13} &= 0.4053 \times 10^{-9} \text{ cm} \\ \bar{L}_{31} &= 0.2810 \times 10^{-9} \text{ cm} & \bar{L}_{33} &= -0.3958 \times 10^{-9} \text{ cm} \\ \bar{L}_{22} &= 0.1306 & \bar{L}_{12} = \bar{L}_{21} = \bar{L}_{23} = \bar{L}_{32} &= 0 \end{aligned}$$

The anharmonicity constants for $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ are

$$\begin{aligned} a_{111} &= -34 \pm 4 \text{ cm}^{-1} & a_{133} &= -247 \pm 12 \text{ cm}^{-1} \\ a_{333} &= -4.2 \pm 0.2 \text{ cm}^{-1} & a_{122} &= 70.5 \pm 0.4 \text{ cm}^{-1} \\ a_{311} &= 3.1 \pm 0.4 \text{ cm}^{-1} & a_{322} &= 1.21 \pm 0.01 \text{ cm}^{-1} \end{aligned}$$

We can now calculate the dipole moment of $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ in various vibrational states. For the states

$$\begin{aligned} \text{(a)} \quad v_1 &= 0, & v_2 &= 0, & v_3 &= 0 \\ \text{(b)} \quad v_1 &= 0, & v_2 &= 0, & v_3 &= 1 \\ \text{(c)} \quad v_1 &= 0, & v_2 &= 1, & v_3 &= 0 \end{aligned}$$

the dipole moments in the direction of the axis of the molecule are

$$\begin{aligned} \text{(a)} \quad \langle 0,0,0 | \mu | 0,0,0 \rangle &= (7 \pm 2) \times 10^{-4} \frac{\partial \mu}{\partial q_3} + \\ & (37 \pm 2) \times 10^{-4} \frac{\partial^2 \mu}{\partial q_1 \partial q_3} = (5 \pm 1) \times 10^{-4} \text{ D} \\ \text{(b)} \quad \langle 0,0,1 | \mu | 0,0,1 \rangle &= (4.2 \pm 0.4) \times 10^{-3} \frac{\partial \mu}{\partial q_3} + \\ & (20.6 \pm 0.5) \times 10^{-3} \frac{\partial^2 \mu}{\partial q_1 \partial q_3} = (2.9 \pm 0.3) \times 10^{-3} \text{ D} \\ \text{(c)} \quad \langle 0,1,0 | \mu | 0,1,0 \rangle &= (7 \pm 2) \times 10^{-4} \frac{\partial \mu}{\partial q_3} + \\ & (37 \pm 2) \times 10^{-4} \frac{\partial^2 \mu}{\partial q_1 \partial q_3} = (5 \pm 1) \times 10^{-4} \text{ D} \end{aligned}$$

The dipole moment of $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ has not yet been measured. If its value in various vibrational states should be known, it would be possible to deduce the sign and magnitude of the derivatives of the dipole moment and compare the results with those obtained from infrared intensity measurements.

In case c, the dipole moment could be determined by measuring the *first-order* Stark effect arising when an electric field is applied.

V. Conclusion

In sections II and III it has been shown how vibrational averaging causes the electronic properties of diatomic and polyatomic molecules to vary with nuclear mass. Equations are given for calculating the expectation value of a property in various vibrational states. In order to predict values of a physical property for different isotopic species, the harmonic and cubic anharmonic force constants and the equilibrium value

and first and second derivatives of the property with respect to the internal coordinates must be known. As the number of force constants and property derivatives entering the equations increase rapidly with increasing number of atoms, more and more experimental data would be required for applications of the theory. Thus the treatment of isotope effects in the manner described is likely to be restricted to diatomics and small polyatomic molecules. The effects of deuterium substitution on the properties of larger molecules could be approximately described by the theory for diatomics, since the vibrations involving a proton can sometimes be considered to be localized in the bond containing it.

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VI. References and Notes

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