Rovibrational Averaging of Molecular Electronic Properties

Cynthia J. Jameson

Department of Chemistry, University of Illinois Chicago, Illinois 60680, USA

The measured value of a molecular electronic property is a rovibrational average for a given v, J state or a thermal average. These electronic properties may exhibit measurable isotope effects and are found to be v, J-state-dependent and temperature dependent. Rovibrational effects are intimately related to both the molecular potential surface and the electronic property surface. When both surfaces are available it becomes possible to correct the observed values of the property for rovibrational effects and thereby to elicit the value of the property at the equilibrium geometry of the molecule, for comparison with the ab initio theoretical value. Alternatively, temperature coefficients and isotope shifts may be calculated from both theoretical surfaces, for direct comparison with experiment. In some favourable cases it is possible to obtain an empirical estimate of the sensitivity of the property to a change in geometry from a measurement of a temperature coefficient or an isotope effect. A review of the theory and its applications to the nuclear magnetic shielding, spin-rotation constant, nuclear hyperfine constant, electric field gradient, spin-spin coupling, dipole moment, magnetizability, electric dipole polarizability and hyperpolarizabilities reveals some interesting general trends.

Z. B. Maksić (ed.), *Theoretical Models of Chemical Bonding*
© Springer-Verlag Berlin Heidelberg 1991

1 Introduction

Rovibrational averaging of a molecular electronic property manifests itself in various ways. Different values of the electronic property for each J or v level may be measured where individual J- or v-labeled states are observed, with different values for different isotopomers. Where thermal averages over all populated v, J states are observed, a temperature dependence of the electronic property in the limit of the isolated molecule or different thermal average values of the electronic property for different isotopomers may be observed. The property may be zero except upon isotopic substitution, as in the dipole moment of CH_3D. In NMR spectroscopy where ultrahigh resolution (mHz) is becoming more accessible, temperature dependent and mass-dependent effects have become ubiquitous [1]. Even in modest high resolution the effects of rovibrational averaging are observed. See for example Fig. 1 in which the individual peaks for the ^{19}F in the various isotopomers $^{m'}SeF_6$ are observed with intensities directly proportional to the natural abundance of the Se isotopes [2].

Rovibrational averaging is intimately connected with ab initio calculations of electronic properties. As calculations become more sophisticated and/or as measurements become more precise, the gap between the ab initio calculated value of a pro-

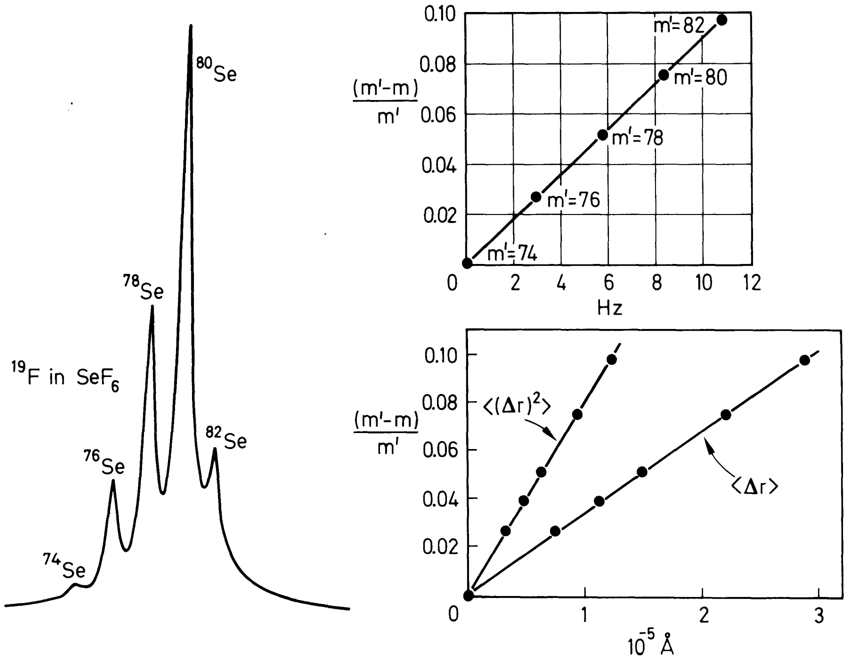


Fig. 1. ^{19}F NMR spectrum in liquid SeF_6 at 300 K at 188.3 MHz. The intensities of the peaks for the isotopomers are consistent with the natural abundance of Se isotopes. $^{77}SeF_6$ satellite peaks (not shown) are split by 1421 Hz. These isotope shifts between $^{m'}SeF_6$ and $^{m}SeF_6$ are plotted for m = 74, also the mean bond displacements and mean square amplitudes (at 300 K) of the Se—F bonds in SeF_6 molecule, are proportional to (m'—m)/m' (see text). Reproduced from Jameson et al. (1986) J. Chem. Phys. 85: 5480, 5484, with permission [2, 80]

perty and its experimental value becomes sufficiently small so that theoretical values calculated at the equilibrium geometry of a molecule cannot be compared directly with the measured value of the property even at 0 K. Rovibrational averaging is also intimately connected with determination of molecular geometry. The observed quantities in various methods of determining molecular structure are themselves particular rovibrational averages of various powers of atom-atom distances or averages of differences between various powers of atom position coordinates. Without the appropriate computations based on the averages which are directly observed, different techniques such as microwave spectroscopy, electron diffraction, and NMR spectroscopy lead to structures that are not consistent. Results from each technique have to be corrected by appropriate rovibrational averaging, back to the geometry corresponding to the minimum in the potential energy. Only the equilibrium geometry resulting from the various measurements can be directly compared.

The effective hamiltonian for a free molecule in a non-degenerate electronic state has been derived by Michelot [3, 4], which allows a study of the various interactions within the molecule and the direct and indirect effects induced by molecular vibration. In particular we could consider with this hamiltonian the terms characteristic of the interaction between a nuclear magnetic moment and an external magnetic field, the field induced at the nucleus by molecular motion, and the interaction of the magnetic moment induced by this molecular motion with an external magnetic field. The effective hamiltonian is obtained by a second order computation in degenerate perturbation theory and explicitly includes the parameters characteristic of spin-vibration and spin-rotation interactions together with those associated with vibrational and rotational Zeeman effects, and it can be written in a form of an effective hamiltonian for a given vibronic state.

Several levels of approximation are possible: (1) the Born-Oppenheimer approximation, (2) the adiabatic corrections, and (3) non-adiabatic corrections. At the level of the Born-Oppenheimer approximation, as the nuclei move about an equilibrium position corresponding to a minimum of the potential function, it is assumed that in this vicinity the electronic wavefunctions does not vary greatly with r. At level 1 the molecular potential of a given electronic state is invariant through isotopic substitution. Some electronic properties vanish at level 1 and at least level 2 approximation must be used. An example of this is the dipole moment of HD. To go beyond level 1, one may add a term $V_{ad}(r)$ to the potential energy, (see for example [4]) which depends upon nuclear mass and which accounts for the noninvariance upon isotopic substitution of the molecular potential of a given electronic state. Some properties are only partly accounted for at level 2 and level 3 must be used for a complete picture. Examples are the differences in the electron spin densities at the protons in aromatic radical ions such as $C_6H_6^-$ upon monodeuteration. Non-adiabatic corrections are introduced when the computation of the effective hamiltonian is extended to second order [3, 4]. The well-known relations between some electronic properties such as the spin-rotation tensor and the paramagnetic part of the shielding tensor [5], the molecular g tensor and the paramagnetic part of the magnetizability [6] only hold strictly for clamped nuclei. Nonadiabatic corrections make the relationships between these tensors only approximate for the vibrating molecule [3].

Many of the observed molecular electronic properties are coefficients of terms in the effective molecular hamiltonian. These coefficients may consist of the sum of a purely nuclear term and a term which depends upon electronic variables. This review comments on the latter only. Some rovibrational effects on properties are largely accounted for at level 1, i.e., within the context of the Born-Oppenheimer approximation, for example the isotope effects on NMR chemical shifts and coupling constants, the vibrational or rotational state dependence of *eqQ* and *C*. We shall concentrate our attention on these because they are the ones which are best understood from a theoretical point of view and also most clearly characterized from a quantitative experimental point of view. As a consequence of the Born-Oppenheimer approximation the concept of a mass-independent molecular electronic property surface can be used. This is analogous to the potential energy surface; the value of any property in a given electronic state can be expressed in terms of a Taylor series in the instantaneous displacement from equilibrium geometry.

$$\mathrm{P} = \mathrm{P_e} + \sum_{\mathrm{i}} \mathrm{P_i q_i} + \sum_{\mathrm{ij}} \frac{1}{2!} \mathrm{P_{ij} q_i q_j} + \sum_{\mathrm{ijk}} \frac{1}{3!} \mathrm{P_{ijk} q_i q_j q_k} + \cdots \tag{1}$$

The coordinates describing the nuclear displacements may be in dimensionless normal coordinates q_i, normal coordinates Q_i, curvilinear symmetry coordinates S_i or curvilinear internal coordinates $\mathbf{Я}_i$. The value of the property for nuclei fixed at the equilibrium geometry is denoted by P_e and the derivatives of the property surface P_i, P_{ij}, etc. are electronic properties which describe the sensitivity of P to small displacements of the nuclei away from equilibrium.

Molecular electronic property surfaces are emerging into their own rightful place in chemistry next to potential energy surfaces. They reflect basic features of the electronic distribution of the molecule, being sensitive to different portions of the distribution, depending on the nature of the property operator. Even those properties that are determined largely by the value of the wavefunction in the immediate vicinity of a nucleus are found to be sensitive to small changes in internuclear distances. One of the first formulations of coupled Hartree-Fock theory as applied to nuclear displacements, the influential paper by Geratt and Mills [7] considered dipole moment derivatives. Methods of computation of derivatives of a property surface have been reviewed for μ and α by Amos and also Helgaker [8]. The $\mu(\mathbf{Я})$ and $\alpha(\mathbf{Я})$ surfaces are of extreme importance in the calculations of transition probabilities, i.e., intensities in IR and Raman spectra. They are also relevant to the calculations of the purely vibrational components of the electric dipole polarizability α and the hyperpolarizabilities β and γ, the vibrational components of which have their origin in the perturbation of the nuclear motion by the electric field [9, 10], a deformation of the nuclear frame simultaneously with electronic deformation. In some cases these vibrational components of the hyperpolarizabilities can be of greater importance than the electronic hyperpolarizability itself [11].

The obvious method of determining property surfaces in ab initio calculations is by calculation of the property itself at the equilibrium geometry and at suitable values of curvilinear symmetry internal coordinates. The values of the property may be computed as expectation values of the corresponding perturbation operator or as the derivatives of the perturbed energy or as the derivatives of some other property. For example, the molecular electric dipole polarizability components can be computed from the molecular wavefunctions in finite static electric fields as the second derivatives of the energy with respect to the components of the electric field, or as the first derivatives of the electric dipole moment components with respect to the static electric field components. Alternatively, it is sometimes convenient to evaluate the first few derivatives at the equilibrium geometry using analytic gradient techniques [12]. Unfortunately, some properties require highly correlated wavefunctions, which makes the evaluation of derivatives difficult. The expansion in (1) is not appropriate when dealing with properties of molecules with very large amplitude internal motions such as to render meaningless the notion of an equilibrium geometry [13].

Examples of property surfaces are shown in Fig. 2, 3, 4 and 5. Fig. 2 shows the ab initio surfaces for the nuclear spin-spin coupling J(CO) in the NMR spectroscopy of CO molecule, calculated by [14]. Figure 3 shows the experimental surfaces (solid curves) for μ(HF) from [15], μ(HCl), μ(HBr) and μ(HI) from [16], in comparison with ab initio values calculated at various internuclear separations by [17] at the MCSCF and other levels of computation. In Fig. 4 reproduced from [18] is the ^{1}H nuclear magnetic shielding surface for H_2^+ molecule calculated by Hegstrom [19] and the experimental potential energy surface. In Fig. 5 the empirical nuclear quadrupole coupling function for $^{127}I_2$ in the ground and B electronic states have been obtained from the rotational and vibrational dependence in up to about 80 vibrational states [20].

Theoretical connections have been made between many molecular electronic properties at the equilibrium geometry [5, 6, 21, 22]. This would mean that by appropriate rovibrational corrections the same ab initio surface can be used for evaluating more than one property. See, for example, [23].

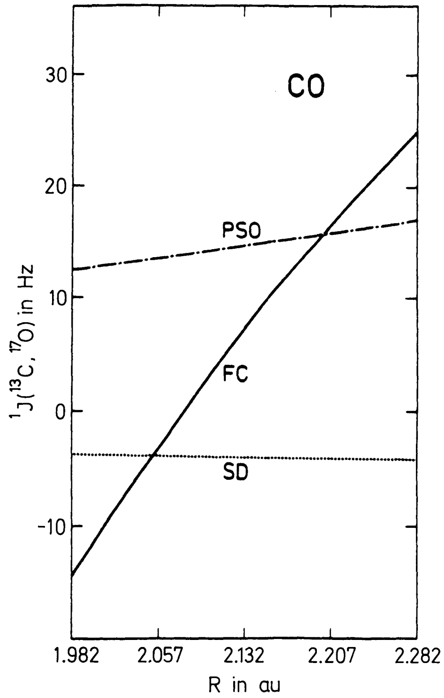


Fig. 2. Geometry dependence of the contributions to the nuclear spin-spin coupling constant of carbon monoxide, that is, the paramagnetic spin-orbit (PSO), the Fermi contact (FC), and the spin-dipolar terms (SD). The results are calculated in the second order polarization propagator approximation. Reproduced from Geertsen J, Oddershede J, Scuseria GE (1987) J. Chem. Phys. 87: 2138, with permission [14]

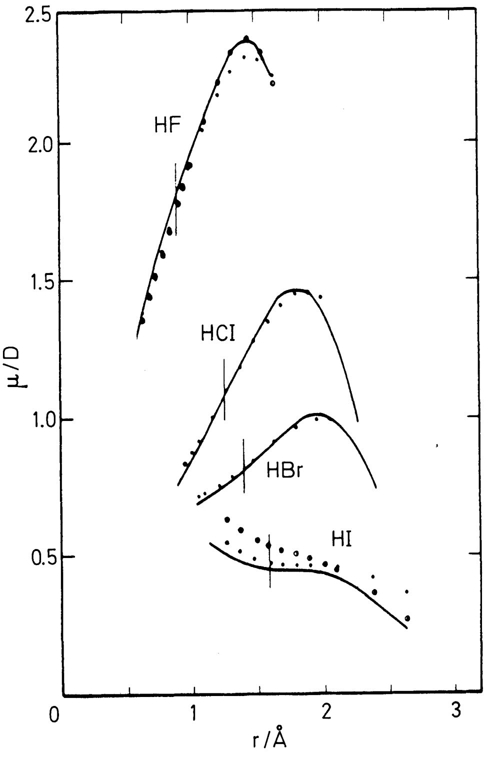


Fig. 3. Calculated and experimental dipole moment functions of the hydrogen halides. *Vertical bars* mark the equilibrium distances. *Solid curves* are from Sileo and Cool (HF) [15] and Ogilvie et al. (HCl, HBr, HI) [16], and the *calculated points* shown are for various ab initio calculations by Werner et al. [17]. Reproduced from Werner HJ, Reinsch EA, Rosmus P (1981) Chem. Phys. Lett. 78: 311, with permission [17]

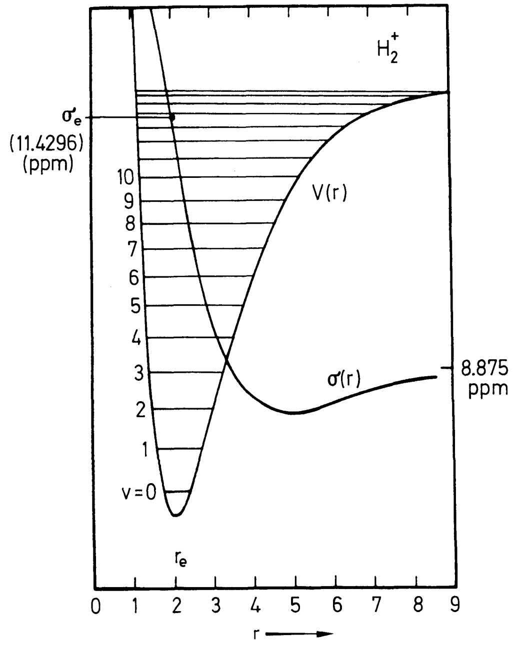


Fig. 4. The proton nuclear magnetic shielding surface and the potential energy surface for H_2^+, plotted from values given in [19]. Reproduced from Jameson CJ, Osten HJ (1986) Ann. Reports NMR Spectrosc. 17: 1, with permission [18]

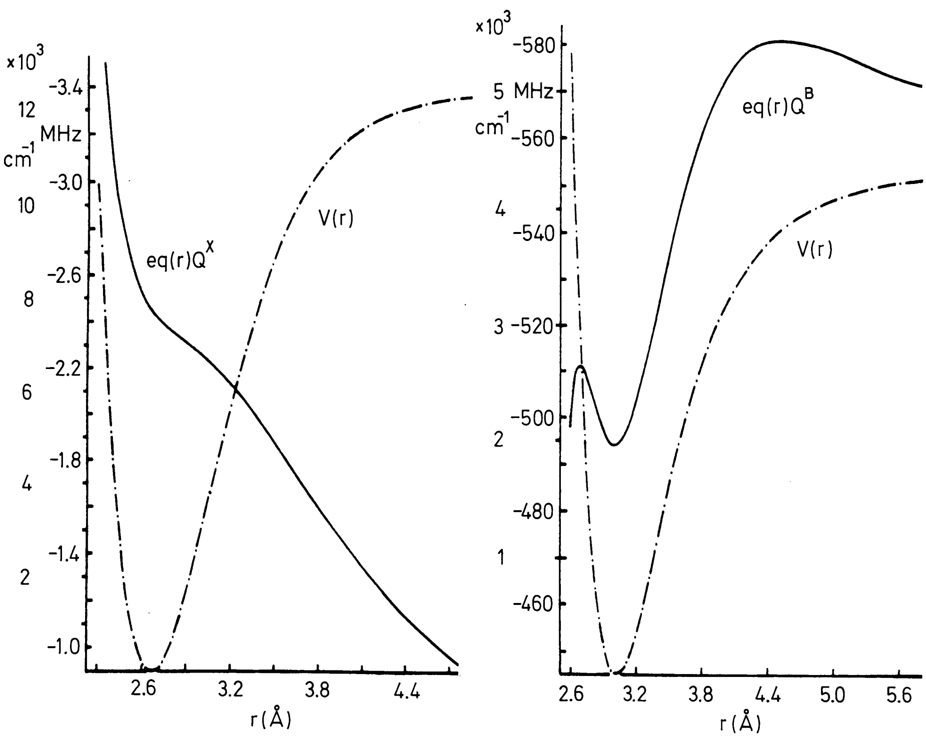


Fig. 5. Empirical nuclear quadrupole coupling function and potential energy curves for the X and B electronic states of $^{127}I_2$. Reproduced from Spirko V, Blabla J (1988) J. Mol. Spectrosc. 129: 59, with permission [20]

The properties discussed in this review can be expressed entirely in terms of nuclear position coordinates and thus the property surface can be expanded around the equilibrium geometry in terms of property derivatives with respect to nuclear coordinates of some type (Cartesian, normal, etc.). In those cases where the property has significant non-Born-Oppenheimer contributions, the concept of a property surface is still useful, provided that by means of perturbation theory, the first order vibronic function incorporates the change in electronic state that is due to small nuclear displacements q_i so that the electron cloud may be thought of as being modulated by the vibrational motion of the nuclei [24]. The concept of property surfaces has been extended by Buckingham et al. to include property surfaces expanded in terms of derivatives with respect to nuclear velocities or nuclear momentum. The latter have been used to describe VCD and other phenomena [24]. (See also [25–27].)

2 Theoretical Considerations

The expectation value of a property P in an arbitrary vibration-rotation state of a particular isotopic form of a molecule, $\langle P \rangle$, may be derived by Rayleigh-Schrodinger perturbation theory [28], by use of contact transformations [29], or by a method based on the Hellmann-Feynman theorem [30]. We require the expectation values of P in the state which is an eigenfunction of the molecular vibration-rotation hamiltonian operator

$$H = H_{(0)} + \lambda H_{(1)} + \lambda^2 H_{(2)} + \dots$$

in which $H_{(0)}$ is the hamiltonian for non-degenerate harmonic oscillators and a rigid rotor, having known solution $X^{(0)}$. λ is a smallness parameter, $H_{(1)}$ and $H_{(2)}$ are perturbations each of which includes terms due to anharmonicity and vibration-rotation interaction. The property P has a corresponding operator which can be expressed as in (1), in which the sums over the reduced dimensionless coordinates are unrestricted. To first order in λ, the expectation value can be evaluated as

$$\begin{aligned}\langle P\rangle_n &= \langle X_n^{(0)} + \lambda X_n^{(1)}|P|\,X_n^{(0)} + \lambda X_n^{(1)}\rangle \\ &= \langle X_n^{(0)}|P|X_n^{(0)}\rangle + 2\lambda\langle X_n^{(0)}|P|\,X_n^{(1)}\rangle\end{aligned} \tag{2}$$

or

$$\langle P\rangle = P_e + \sum_i \left[\frac{1}{2}P_{ii} - \sum_j \frac{1}{2}P_j\frac{\varphi_{iij}}{\omega_j}\right]\left\langle v_i + \frac{1}{2}\right\rangle + \text{rotational part} + \cdots \tag{3}$$

where ω_j and φ_{iij} are the quantities in

$$V = \frac{1}{2!}\sum_i \omega_i q_i^2 + \frac{1}{3!}\sum_{ijk}\varphi_{ijk}q_iq_jq_k + \cdots \tag{4}$$

Equation (3) was obtained by Toyama, Oka, and Morino [28]. The same result can be obtained by contact transformation, which see below.

The hamiltonian H itself is transformed by $T_1HT_1^{-1}$ into [29]

$$H'_{(0)} + \lambda H'_{(1)} + \lambda^2 H'_{(2)} + \dots \tag{5}$$

where

$$T_1 = e^{i\lambda S_1} \tag{6}$$

from which

$$H'_{(0)} = H_{(0)} \tag{7}$$

$$H'_{(1)} = H_{(1)} + i[S_1, H_{(0)}] \tag{8}$$

$$H'_{(2)} = H_{(2)} + \frac{i}{2}[S_1, (H_{(1)} + H'_{(1)})] \tag{9}$$

The function S_1 is chosen in such a way that all off-diagonal matrix elements of $H'_{(1)}$ vanish, i.e., such that the commutator of S_1 with $H_{(0)}$ is the negative of any term in $H_{(1)}$ which is non-diagonal. To obtain wavefunctions correct through second order, it is necessary to carry out a second contact transformation on H' to remove the off-diagonal elements of $H'_{(2)}$, i.e.,

$$H^\dagger = T_2 H' T_2^1 = H^\dagger_{(0)} + \lambda H^\dagger_{(1)} + \lambda^2 H^\dagger_{(2)} + \ldots \tag{10}$$

where

$$T_2 = e^{i\lambda^2 S_2} . \tag{11}$$

It then follows that

$$H^\dagger_{(0)} = H'_{(0)} \tag{12}$$

$$H^\dagger_1 = H'_{(1)} \tag{13}$$

$$H^\dagger_{(2)} = H'_{(2)} + [S_2, H'_{(0)}] \tag{14}$$

Since $H_{(0)}$ is diagonal in a harmonic oscillator basis set, and since $H'_{(0)} = H_{(0)}$, and $H'_{(1)}$ has been made diagonal in the same harmonic oscillator basis set, $H'_{(0)} + H'_{(1)}$ is diagonal in the harmonic oscillator basis set and the latter are therefore first order wavefunctions of H', i.e.,

$$\langle X^{(0)} | H'_{(0)} + H'_{(1)} | X^{(0)} \rangle = \langle X^{(0)} | T(H_{(0)} + H_{(1)}) T^{-1} | X^{(0)} \rangle \tag{15}$$

Therefore $T^{-1} X^{(0)}$ are first order wavefunctions of H. Similarly,

$$\begin{aligned}\langle X^{(0)} | H^\dagger_{(0)} + H^\dagger_{(1)} + H^\dagger_{(2)} | X^{(0)} \rangle = \langle X^{(0)} | &T_2 T_1 (H_{(0)} + H_{(1)} \\ &+ H_{(2)}) T_1^{-1} T_2^{-1} | X^{(0)} \rangle\end{aligned} \tag{16}$$

and therefore $T_1^{-1} T_2^{-1} X^{(0)}$ are second order wavefunctions of H. To use wavefunctions of second order in evaluating the expectation value of P, we shall need to evaluate the matrix elements

$$\langle X^{(0)} | T_2 T_1 P T_1^{-1} T_2^{-1} | X^{(0)} \rangle ,$$

which are, in fact, the harmonic oscillator matrix elements of the doubly contact-transformed P operator.

$$P = P_{(0)} + \lambda P_{(1)} + \lambda^2 P_{(2)} + \ldots \tag{17}$$

where

$$P_{(0)} = P_e + \sum_i P_i q_i \tag{18}$$

$$P_{(1)} = \sum_{ij} \frac{1}{2!} P_{ij} q_i q_j \tag{19}$$

$$P_{(2)} = \sum_{ijk} \frac{1}{3!} P_{ijk} q_i q_j q_k \tag{20}$$

The doubly contact transformed operator is then found [31]

$$T_2T_1PT_1^{-1}T_2^{-1} = P^\dagger = P^\dagger_{(0)} + P^\dagger_{(1)} + P^\dagger_{(2)} + \dots \tag{21}$$

where

$$P^\dagger_{(0)} = P_{(0)} \tag{22}$$

$$P^\dagger_{(1)} = P_{(1)} + \mathrm{i}[S_1, P_{(0)}] \tag{23}$$

$$P^\dagger_{(2)} = P_{(2)} + \mathrm{i}[S_1, P_{(1)}] + \frac{\mathrm{i}^2}{2}[S_1, [S_1, P_{(0)}]] + \mathrm{i}[S_2, P_{(0)}] \tag{24}$$

$$\begin{aligned} P^\dagger_{(3)} = {} & P_{(3)} + \mathrm{i}[S_1, P_{(2)}] + \mathrm{i}[S_2, P_{(1)}] - \frac{1}{2}[S_1, [S_1, P_{(1)}]] + \\ & + \mathrm{i}^2[S_2, [S_1, P_{(0)}]] - \frac{\mathrm{i}}{6}[S_1, [S_1, [S_1, P_{(0)}]]] \end{aligned} \tag{25}$$

From the commutators of S_1 and S_2 with the normal coordinate operators q_j, the commutators of S_1 and S_2 with $P_{(0)}$, $P_{(1)}$, and $P_{(2)}$ can be evaluated. The results are: [31]

$$P^\dagger_{(0)} = P_{(0)} = \mathrm{P_e} + \sum_{\mathrm{i}} \mathrm{P_i q_i} \tag{26}$$

$$P^\dagger_{(1)} = \sum_{\mathrm{ij}} \frac{1}{2!} \mathrm{P_{ij} q_i q_j} + \sum_{\mathrm{i \leqq j}} \sum_{\mathrm{k}} \{\mathrm{P_k S^k_{ij} q_i q_j} + \mathrm{P_k S^{ijk}}(1 + \delta_{\mathrm{ik}} + \delta_{\mathrm{jk}})\, \mathrm{P_i P_j}\} \tag{27}$$

The expression for $P^\dagger_{(2)}$ has been derived by Marcott, Golden and Overend [32]. The quantities $\mathrm{S^k_{ij}}$ and $\mathrm{S^{ijk}}$ involve the cubic force constants and harmonic frequencies. These and other quantities appearing in $P^\dagger_{(2)}$ are given by Amat et al. [29, 33]. The leading terms in the formula for the expectation value of a property of a diatomic molecule was derived by Buckingham [34], the general formula with terms up to 6th order by Herman and Short [35], Toyama, Oka, and Morino provided the leading terms in the formula for a polyatomic molecule [28]. The vibrational terms for a property of an asymmetry rotor was given to general nth order by Krohn, Ermler, and Kern, [36] to which rotational terms were added by Fowler et al. [30] (with an earlier version in [37]).

The expectation value of P for non-degenerate modes is then given by [30]

$$\begin{aligned} & \langle X^{(0)} |\, P^\dagger \,| \mathrm{X}^{(0)} \rangle = \\ & \langle P \rangle = \mathrm{P_0} + \sum_{\mathrm{s}} \mathrm{A_s} \left(\mathrm{v_s} + \frac{1}{2}\right) + \sum_{\mathrm{s \leqq s'}} \mathrm{B_{ss'}} \left(\mathrm{v_s} + \frac{1}{2}\right)\left(\mathrm{v_{s'}} + \frac{1}{2}\right) \end{aligned} \tag{28}$$

where

$$\mathrm{P_0} = \mathrm{P_e} + \sum_{\mathrm{s}} \frac{1}{64} \mathrm{P_{ssss}} - \sum_{\mathrm{s}} 7\mathrm{P_{sss}}\varphi_{\mathrm{sss}}/288\omega_{\mathrm{s}} + \sum_{\mathrm{s \neq s'}} 3\mathrm{P_{sss'}}\varphi_{\mathrm{sss'}}\omega_{\mathrm{s'}}/32(4\omega_{\mathrm{s}}^2 - \omega_{\mathrm{s'}}^2) \tag{29}$$

$$\mathrm{A_s} = \mathrm{P_{ss}}/2 - \sum_{\mathrm{s'}} \mathrm{P_{s'}}\varphi_{\mathrm{sss'}}/2\omega_{\mathrm{s'}} \tag{30}$$

$$\mathrm{B_{ss}} = \mathrm{P_{ssss}}/16 - \sum_{\mathrm{s'}} \mathrm{P_{sss'}}\varphi_{\mathrm{sss'}}(8\omega_{\mathrm{s}}^2 - 3\omega_{\mathrm{s'}}^2)/8\omega_{\mathrm{s'}}(4\omega_{\mathrm{s}}^2 - \omega_{\mathrm{s'}}^2) \tag{31}$$

$$\begin{aligned} \mathrm{B_{ss'}} = {} & \mathrm{P_{sss's'}}/4 - \sum_{\mathrm{s''}} (\mathrm{P_{sss''}}\varphi_{\mathrm{s's's''}} + \mathrm{P_{s's's''}}\varphi_{\mathrm{sss''}})/4\omega_{\mathrm{s''}} \\ & - \sum_{\mathrm{s''}} \mathrm{P_{ss's''}}\varphi_{\mathrm{ss's''}}\omega_{\mathrm{s''}}(\omega_{\mathrm{s''}}^2 - \omega_{\mathrm{s}}^2 - \omega_{\mathrm{s'}}^2)/\mathrm{D_{ss's''}} \end{aligned} \tag{32}$$

$$\begin{aligned} \mathrm{D_{ss's''}} \equiv {} & (\omega_{\mathrm{s}} + \omega_{\mathrm{s'}} + \omega_{\mathrm{s''}})(\omega_{\mathrm{s}} + \omega_{\mathrm{s'}} - \omega_{\mathrm{s''}}) \\ & \times (\omega_{\mathrm{s}} - \omega_{\mathrm{s'}} + \omega_{\mathrm{s''}})(-\omega_{\mathrm{s}} + \omega_{\mathrm{s'}} + \omega_{\mathrm{s''}}) \end{aligned} \tag{33}$$

In the first applications of these formulae the values of A_s, B_{ss}, and $B_{ss'}$ were calculated by Krohn et al. for the ^{17}O and D quadrupole coupling tensor and the dipole moment in H_2O, D_2O, and HDO [36]. Off-diagonal matrix elements, which correspond to transition integrals for P being the dipole moment operator, have also been derived by Overend [38–40] using contact transformations. The advantage of this type of approach for any electronic property is that the vibrational wavefunction need not be evaluated explicitly and only a knowledge of the derivatives of the property at the equilibrium geometry is necessary for calculations of vibrational state dependence, rotational state dependence, temperature and mass dependence of any electronic property.

Keeping only terms quadratic in the normal coordinates in the expansion (1) [28]

$$\langle P \rangle = P_e + \sum_s \left[\frac{P_{ss}}{2} - \sum_{s'}^{\text{tot. sym.}} P_{s'} \varphi_{sss'}/2\omega_{s'} \right] \left(v_s + \frac{1}{2} \right) + \text{rot. contrib.} \tag{34}$$

is directly obvious from

$$\langle q_{s'} \rangle = -\sum_s (\varphi_{sss'}/2\omega_{s'}) \left(v_s + \frac{d_s}{2} \right) \tag{35}$$

d_s is the degeneracy of the s^th^ mode. The rotational contribution to a single reduced non-vanishing only when s′ is totally symmetric, and

$$\langle q_s q_{s'} \rangle = \left(v_s + \frac{d_s}{2} \right) \delta_{ss'} \,. \tag{36}$$

normal coordinate $q_{s'}$, to be added to (35) is [28]

$$+ \frac{1}{4\pi c \omega_s} \left(\frac{1}{hc\omega_s} \right)^{1/2} \sum_\alpha \frac{a_{s'}^{\alpha\alpha}}{(I_{\alpha\alpha}^{(e)})^2} \langle J_\alpha^2 \rangle \tag{37}$$

where J_α^2 is the rotational angular momentum about the α inertial axis, and the coefficients $a_{s'}^{\alpha\alpha}$ are the derivatives of the α moment of inertia with respect to the s'^{th} normal coordinate. Simple forms of the rotational contribution have been obtained for $\sum_\alpha a_{s'}^{\alpha\alpha}/I_{\alpha\alpha}^{(e)}$ in highly symmetric molecules with only one totally symmetric mode [41]

$$\begin{aligned} \sum_\alpha \frac{a_{s'}^{\alpha\alpha}}{I_{\alpha\alpha}^{(e)}} &= \frac{6}{r_e(nm_X)^{1/2}} && \text{for } n = 6, 4, \text{ and } 3 \text{ in } AX_6(O_h), AX_4(T_d), \text{ and } AX_3(D_3) \\ &= \frac{4}{r_e(2m_X)^{1/2}} && \text{for } AX_2(D_{\infty h}) \\ &= \frac{4}{r_e\mu^{1/2}} && \text{for diatomic molecules.} \end{aligned} \tag{38}$$

The complete expressions for a symmetric top, involving degenerate vibrational modes, and for a spherical top are given by Fowler [30, 42]. The rotational contributions for asymmetric tops complete to second order in the contact transformation have also been derived by Fowler [43]:

$$\langle P\rangle_J - \langle P\rangle_0 = \frac{1}{\sqrt{3}}(B_e/\omega_1)^{3/2}\left[4P_1 + \sum_i P_{1ii}\right]J(J+1) \tag{39}$$

where P_1, P_{1ii} are the coefficients in the expansion (1).

The above expressions then allow the calculation of the rovibrational average of an electronic property P observed for any $|vJK\rangle$ state. For the thermal average property measured in NMR or electron diffraction, where the observed property is an average over the different populated rovibrational states, one needs only the thermal averages of $\langle J(J+1)\rangle$ and $\langle v + 1/2\rangle$. This is accurately obtained for small number of vibrational modes by summing up over the rovibrational states weighted by populations and degeneracies:

$$\langle P\rangle^T = \frac{\sum\limits_{v,J,K}(2J+1)\,g_{Ns}\langle P\rangle_{vJK}\exp(-E_{vJK}/kT)}{\sum\limits_{v,J,K}(2J+1)\,g_{Ns}\exp(-E_{vJK}/kT)} \tag{40}$$

including nuclear spin statistics. Nuclear spin statistics are important at low temperatures, as shown in Fig. 6 where the thermal average of nuclear shielding components of ortho and para H_2 and D_2 are compared with HD [44].

For diatomic molecules the potential energy and the molecular electronic property surfaces are conveniently expressed in terms of the dimensionless reduced coordinate

$$\xi = (R - R_e)/R_e \tag{41}$$

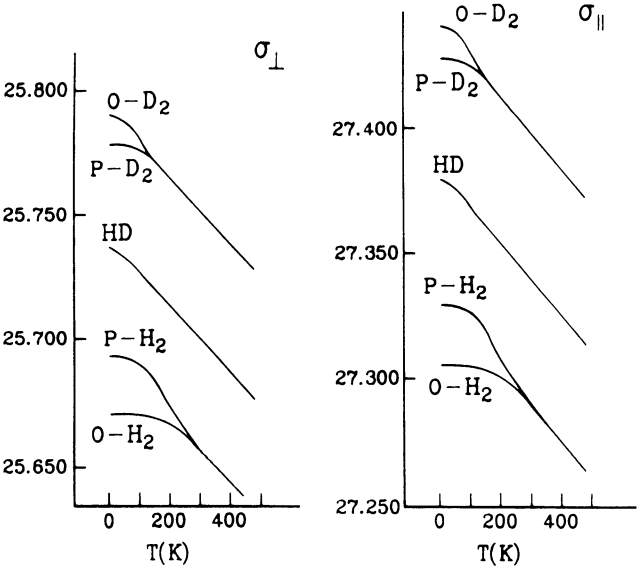


Fig. 6. Calculated nuclear magnetic shielding components for H or D in H_2, HD, and D_2 [44]. Reproduced from Ditchfield R (1981) Chem. Phys. 63: 185, with permission

as follows [34]:

$$V(R) = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + a_3\xi^3 + \ldots) \tag{42}$$

where

$$a_0 = \omega_e^2/4B_e \tag{43}$$

$$P = P_e + P'\xi + \frac{P''}{2!}\xi^2 + \frac{P'''}{3!}\xi^3 + \frac{P^{iv}}{4!}\zeta^4 + \ldots \tag{44}$$

The rovibrational averages $\langle\xi\rangle_{vJ}$, $\langle\xi^2\rangle_{vJ}$, ... can be obtained by second order perturbation theory:

$$\langle\xi\rangle_{vJ} = -3a_1\frac{B_e}{\omega_e}\left(v + \frac{1}{2}\right) \tag{45}$$

$$\langle\xi^2\rangle_{vJ} = 2\frac{B_e}{\omega_e}\left(v + \frac{1}{2}\right) \tag{46}$$

etc. Collecting terms, it is then possible to write,

$$\langle P\rangle = P_e + P_{rot}J(J + 1) + P_I\left(v + \frac{1}{2}\right) + P_{II}\left(v + \frac{1}{2}\right)^2 \tag{47}$$

where, keeping only terms up to $(B_e/\omega_e)^2$ [34],

$$P_{rot} = 4(B_e/\omega_e)^2\,P' \tag{48}$$

$$P_I = (B_e/\omega_e)\,[P'' - 3a_1P'] \tag{49}$$

and [35],

$$P_{II} = (B_e/\omega_e)^2\left\{\frac{P^{iv}}{4} - \frac{5}{2}a_1P''' - \left(\frac{15}{2}a_1^2 - 3a_2\right)P'' + \left(-\frac{45}{2}a_1^3 + 39a_1a_2 - 15a_3\right)P'\right\} \tag{50}$$

Note that P_{rot} and $P_{II} \propto \mu^{-1}$ and $P_I \propto \mu^{-1/2}$. Therefore differences in the rotational and vibrational dependence of molecular electronic properties of isotopomers of diatomic molecules will largely reflect this μ^{-1} and $\mu^{-1/2}$ dependence. In (50) are the terms P_{II} which come in at the second contact transformation in which it should be noted that P′ and P″ appear only with higher order terms in the potential energy (a_2 is a quartic force constant and a_3 is a quintic force constant).

The advantage of using an expansion such as (42) by Dunham is that the resulting $\langle P\rangle$ are expressible in the same a_i coefficients so that the relative order of magnitude of contributions to $\langle P \rangle$ are perceptible, as in (49)–(50). However, the numerical V(R) which is consistent with all the measured frequencies for the molecule may not be accurately described by (42). For more accurate average values $\langle \xi \rangle$ and $\langle \xi^2 \rangle$, one may need to perform a numerical integration using the numerical rotation-vibration wavefunctions which are the solutions of the Schrödinger equation with the numerical V(R). When a numerical integration over the numerical vibrational rotational wavefunctions (which reproduce the experimental spectroscopic energies of the ground state) of HD is used, the vibrational correction to the NMR spin spin coupling constant J(HD) at 0 K is found to differ by 0.09 Hz (out of a total rovibrational correction equal to 1.81 Hz) from that obtained using the Dunham expansion [45]. Such accuracy in the rovibrational averaging procedure is warranted when the property derivatives P′ and P″ have been calculated to sufficiently high accuracy by ab initio methods.

3 Observed Vibrational and Rotational State Dependence of Electronic Properties

Outside of the dipole moment, the largest number of examples of vibrational dependence of an electronic property are probably those of the nuclear quadrupole coupling constants obtained from the Stark hyperfine structure in molecular beam electric resonance (MBER) spectroscopy, or from high resolution microwave. This property can also be obtained from pure nuclear quadrupole resonance spectroscopy or from NMR but these are of course thermal averages rather than state-labeled values. The nuclear quadrupole coupling constant *eqQ* is a measure of the electrical interaction between a nonspherical nucleus and a surrounding electronic environment which is likewise non-spherical. Since the trace of the electric field gradient tensor is identically zero, then for a nucleus in a linear molecule only one value needs to be specified, the component usually referred to as q_{zz} or simply q. The *eqQ* values of ^{35}Cl in HCl and DCl have been measured for several vibrational and rotational states and an analysis in the form of (47)–(50) leads to

$$\frac{1}{q_e}\left(\frac{dq}{d\xi}\right)_e = 1.46 \pm 0.06 \text{ and } \frac{1}{q_e}\left(\frac{d^2q}{d\xi^2}\right)_e = -3.3 \pm 0.4[46],$$

which are in good agreement with Huo's theoretical values 1.49 and —3.07 respectively. Measurement of the rotational dependence of the ^{79}Br *eqQ* by MBER allowed P_{rot} in (47) to be obtained, from which by (48), $\frac{1}{q_e}\left(\frac{dq}{d\xi}\right)_e = 1.556(3)$ [47]. An earlier attempt to analyze the earlier much less precise data from millimeter wave spectra of the hydrogen halides and their isotopic species by using these same equations led to P_e, P_{rot}, and P_{II} values for each isotopomer [48], from which first and second derivatives could have been obtained. Unfortunately the experimental errors in the derived values P_{rot} and P_I themselves were too large. In I_2 the nuclear quadrupole coupling constant in the ground state has been determined for a large number of rovibrational states especially in the range v = 26–86 [20]. These are shown in Fig. 7. Although the data

Table 1. The linear and quadratic terms in the vibrational contributions to the electric field gradient. The numbers shown are the coefficients of $\left(v + \frac{1}{2}\right)$ in (44)–(46)[a]

Nucleus	$\frac{1}{q_e}\left(\frac{dq}{d\xi}\right)_e \langle\xi\rangle$	$\frac{1}{2q_e}\left(\frac{d^2q}{d\xi^2}\right)_e \langle\xi^2\rangle$	Sum
Cl in HCl	0.03701	−0.01090	0.02611
Br in HBr	0.03572	−0.00802	0.0277
O in HO^-	0.08422	0.00329	0.08749
S in HS^-	0.06294	−0.00923	0.05371
Cl in FCl	0.00624	−0.00624	0.0

[a] Calculated by Lucken [56] using theoretical derivatives given by Cade [47]

were not fitted specifically to the form of (47), there is clearly a quadratic dependence on $\left(v + \frac{1}{2}\right)$.

The sign and magnitude of the vibrational dependence of the electric field gradient in diatomic molecules is determined mainly by the first derivative and thus by the *anharmonic* contribution. In Table 1 the vibrational contributions are compared in selected diatomic molecules, for which the first and second derivatives had been calculated by Cade [49]. The anharmonic term clearly dominates in all but FCl molecule.

The ^{19}F spin-rotation constant in F_2 has been measured by Ozier and Ramsey [50] as a function of rotational quantum number:

$$C/\text{kHz} = -156.85 \pm 0.10 + (0.0024 \pm 0.0010)\, J(J+1)\,. \tag{71}$$

From (48) we identify

$$0.0024 \pm 0.0010 = 4(B_e/\omega_e)\, C'$$

from which

$$C' = (dC/d\xi)_e = -650\ \text{kHz}\,.$$

The interesting part of the spin rotation constant is that due to the electrons. According to the theory of Reid and Chu [51] the spin rotation constant for a state v,J is the sum of three contributions

$$C_{vJ} = C_{vJ}^{nucl} + C_{vJ}^{T} + C_{vJ}^{el}\,. \tag{52}$$

The nuclear contribution results from the magnetic field generated at the nucleus of interest (whose g factor is g_N) by the motion of all the other nuclei N′. For a diatomic molecule only the perpendicular component is non-vanishing and it simplifies to

$$\frac{C_{vJ}^{nucl}}{\text{Hz}} = \frac{e\mu_n g_N}{2\pi c\mu} Z_{N'} \langle R^{-3}\rangle_{vJ} \tag{53}$$

μ_n being the nuclear magneton and μ the reduced mass. This contribution is directly proportional to the direct nuclear spin-nuclear spin interaction constant which also can be measured independently from the experiment. The second term arises from the Thomas precession caused by the acceleration of the nucleus in question in the internal electric field, which for H_2 molecule is [51]

$$\frac{C^T_{vJ}}{Hz} = \frac{\hbar}{4\pi m_p^2 c^2} \left\langle \frac{1}{R} \frac{dV(R)}{dR} \right\rangle_{vJ} \tag{54}$$

where V(R) is in (42). This term is zero at the equilibrium geometry and is a very small contribution for state v,J. The third term arises from the mixing of excited electronic states into the ground state by the molecular rotation and is therefore directly related to the paramagnetic part of the nuclear magnetic shielding, of which only the perpendicular component is non-vanishing for a linear molecule. For a diatomic molecule at its equilibrium geometry the relationship can be written as

$$C_e^{el} = \frac{3}{2\pi} \frac{\mu_n}{\mu_B} \frac{g_N \hbar}{2\mu R_e^2} \sigma_e^p . \tag{55}$$

The relationship holds strictly only at the equilibrium configuration. As an approximation, we can use the following relation between the rovibrationally averaged properties

$$\begin{aligned} C_J^{el} &= C_e^{el} + C^{el\prime}\langle\xi\rangle_J + \frac{1}{2} C^{el\prime\prime}\langle\xi^2\rangle_J + \dots \\ &\cong \frac{3}{2\pi} \frac{\mu_n}{\mu_B} \frac{g_N \hbar}{2\mu} \left[\sigma_e^p + \sigma^{p\prime}\langle\xi/R^2\rangle_J + \frac{1}{2} \sigma^{p\prime\prime}\langle\xi^2/R^2\rangle_J + \dots \right] \end{aligned} \tag{56}$$

From the MBMR hyperfine spectrum of H_2 the values $C_{J=1} = 113.904\ (30)$ kHz, $C_{J=3} = 111.10\ (25)$ kHz, and $C_{J=5} = 105.37\ (32)$ kHz were measured by Verberne and Ozier [52]. From these, after making the corrections using (53) and (54), the electronic parts alone are —92.271 (30), —90.41 (25), and —87.74 (32) kHz respectively for J = 1, 3, 5 states. These are then written in the expansion (56) and the average $\langle\zeta^n/R^2\rangle_{J,v=0}$ are obtained. It was found that either the set $\sigma^{p\prime} = +2.810 \times 10^{-6}$ and $\frac{1}{2}\sigma^{p\prime\prime} = +0.29 \times 10^{-6}$ or the set $\sigma^{p\prime} = +2.963 \times 10^{-6}$ and $\frac{1}{2}\sigma^{p\prime\prime} = 0$ fit the experimental values of C_J^{el} equally well [52], that is, the leading rovibrational correction term goes as $\langle\xi/R^2\rangle$ rather than $\langle\xi^2/R^2\rangle$. This is consistent with (48) in which the rotational state dependence of an electronic property of a diatomic molecule depends only on the first derivative; the first correction to (48) involves the 3rd derivative, as already indicated in (39). A later analysis by Raynes and Panteli of the rotational dependence of the spin rotation data combined with isotope effects on shielding data again provides only the first derivative [53]. Their further conclusion is that even for the H_2 molecule the theoretical proton magnetic shielding surfaces are not sufficiently accurate to reproduce the observed NMR isotope effects within the experimental errors.

The ^{199}Hg nuclear spin-electron spin interaction constants b in ^{199}HgH, ^{199}HgD, and ^{199}HgT have been determined as a function of vibrational and rotational state in the ground electronic state, from an analysis of the hyperfine splittings observed in the electronic spectra [54]. Fermi contact and dipolar terms contribute to this property:

$$b = g_e g_{Hg} \mu_B \mu_n \left\langle \frac{8\pi}{3} \langle \varrho_{spin} \rangle - \left\langle \frac{(3\cos^2\theta - 1)}{2r^3} \right\rangle \right\rangle_{vJ} \tag{57}$$

$\langle \varrho_{spin} \rangle$, the electron spin density at the Hg nucleus and $\langle (3\cos^2 - 1)/2r^3 \rangle$ are averages over the molecular electronic function. The electronic spectra show a considerable decrease in b with increasing vibrational quantum number and is most pronounced in HgH, followed by HgD, and HgT. There was also a decrease in b with increasing rotation, which too was greater in HgH than in HgD or HgT [54]. The same parameter b can be obtained from the hyperfine structure in the ESR spectra of HgH and HgD in an argon matrix at 4 K [55]. Examination of the H–D isotope effect leads to the conclusion that the average spin density on Hg is slightly smaller in HgH than in HgD. The vibrational and rotational dependence of b and the isotope effects all are consistent with the $(\partial | \varrho_{spin} | / \partial R)_e$ being negative.

When the dependence on v of an electronic property of a diatomic molecule is measured, P_I and P_{II} in (47) can be determined and from P_I the quantity

$$(P'' - 3a_1 P')$$

can be obtained. In principle this can be combined with P′ obtained from the rotational state dependence so both P′ and P″ can be determined. The analysis is much more involved than this for polyatomic molecules.

The vibrational dependences of the nuclear quadrupole coupling constants of symmetric tops in which the quadrupolar nucleus lies on the symmetry axis, have been observed in the gas phase. A summary of data prior to 1983 is provided by Lucken [56]. The magnitude of eqQ is larger or smaller for $v_s = 1$ than for the ground vibrational state, depending on the vibrational mode. This is not surprising. As we can see in (28), for the sth mode the change is proportional to

$$\frac{1}{2}\left(\frac{P_{ss}}{2} - \sum_{s'} P_{s'} \frac{\varphi_{sss'}}{2\omega_{s'}}\right).$$

Since the first and second derivatives of the electric field gradient with respect to the reduced normal coordinates are of various signs, as are $\varphi_{sss'}$, the above expression can be of either sign. In most cases the property is known only for the $v = 0$ and $v = 1$ states, so that the determination of P_I depends on the assumption that the plot of the property vs. $\left(v + \frac{1}{2}\right)$ is a straight line, which has been shown in some cases to be a poor approximation (e.g., see Fig. 7). At best only combinations of first and second order derivatives of the property with respect to normal coordinates, e.g., $\frac{1}{2}\,[P_{33} - P_1\varphi_{331}/\omega_1 - P_2\omega_{332}/\omega_2]$, can be obtained from the experimental

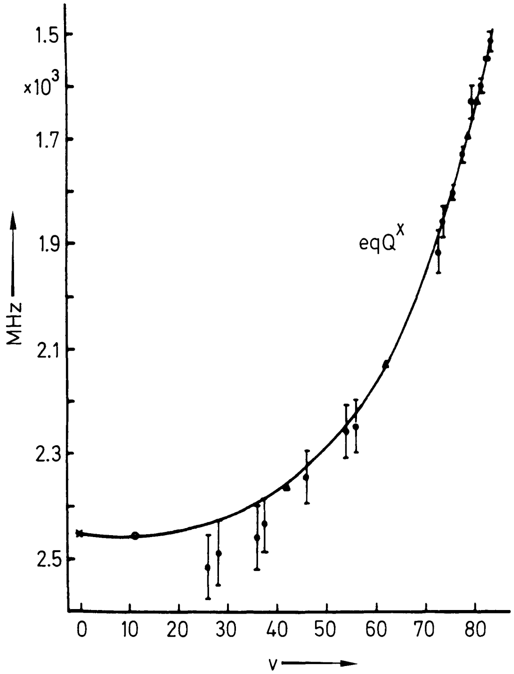


Fig. 7. Vibrational dependence of ^{127}I nuclear quadrupole coupling constant in I_2. Reproduced from Spirko V, Blabla J (1988) J. Mol. Spectrosc. 129: 59, with permission [20]

measurements of the vibrational dependence, even when linear plots of the property against $\left(v + \frac{1}{2}\right)$ are obtained. These are shown in Table 2 for AsF_3. Further drastic approximations (neglect of terms containing cubic force constants φ_{331}, φ_{332}, φ_{441}, and φ_{442} and neglect of off-diagonal L matrix elements in the normal coordinate analysis) lead to rough estimates of second derivatives with respect to bond extension and angle deformation [56]:

$$\frac{1}{q_e}\left(\frac{\partial^2 q}{\partial r^2}\right)_e \cong -3.5\text{Å}^{-2} \qquad \frac{1}{q_e}\frac{1}{r_e^2}\left(\frac{\partial^2 q}{\partial \alpha^2}\right)_e \cong -0.12\text{Å}^{-2}$$

for the electric field gradient at the ^{75}As nucleus in AsF_3.

Table 2. Empirical values of derivatives of $P = eqQ$ of ^{75}As in AsF_3

	s	ω_s/cm$^{-1\,a}$	$\left(\frac{P_{ss}}{2} - \sum_{s'}^{A_1} P_{s'}\frac{\varphi_{sss'}}{2\omega_s'}\right)\Big/$MHz^b
A_1	1	740.55	1.804(80)
A_1	2	336.50	0.988(6)
E	3	702.20	1.34(17)
E	4	262.30	0.23(15)

[a] Ref. [175]. [b] Obtained from eqQ ($v_s = 1$) — eqQ ($v = 0$)

4 Mass-independent Electronic Property Surfaces and Derivatives of Surfaces

While (28) gives the simplest form of the connection between the properties of the potential surface $\omega_{s'}$, $\varphi_{sss'}$, etc. and the rovibrationally averaged molecular electronic property, $\langle P \rangle$, they are not the relations of choice when discussing isotope effects, since the reduced dimensionless normal coordinates are mass-dependent. Furthermore, it is sometimes easier to understand the physical interpretation of a property derivative when it is expressed in terms of curvilinear internal displacement coordinates such as bond stretches and angle deformations. For these reasons, it becomes necessary to consider the transformation of the expansion (1) into these curvilinear internal coordinates $\mathfrak{R}_i$. For example, in the CH_4 molecule, $\mathfrak{R}_i$ ($i = 1$–4) denotes one of the four bond extensions Δr_1, Δr_2, Δr_3, and Δr_4 (which we will denote simply as r_1, r_2, r_3, r_4) and $\mathfrak{R}_i$ ($i = 5$–10) denotes one of the six interbond angle changes α_{12}, α_{13}, etc. $\mathfrak{R}_i$ have a nonlinear relationship to the dimensionless normal coordinates [57]

$$\boldsymbol{\mathfrak{R}} = \bar{\mathbf{L}}\mathbf{q} \qquad \text{or} \qquad \boldsymbol{\mathfrak{R}} = \mathbf{LQ} \tag{58}$$

which stand for the relationships

$$\mathfrak{R}_i = \sum_r \bar{L}_i^r q_r + \frac{1}{2} \sum_{r,s} \bar{L}_i^{rs} q_r q_s + \frac{1}{3!} \sum_{r,s,t} \bar{L}_i^{rst} q_r q_s q_t + \ldots \tag{59}$$

where the sums are unrestricted. Expressions for **L** elements are given by Hoy, Mills, and Strey [57] and $\bar{\mathbf{L}}$ elements are related to these since the reduced (dimensionless) normal coordinates q_s are related to the normal coordinates Q_s by

$$q_s = (\omega_s/\hbar)^{1/2} Q_s \, . \tag{60}$$

Additional $\bar{L}$ elements are given by Fowler and Raynes [58] and Louinila et al. [59]. For molecules possessing high symmetry, relationships between $\bar{L}$ elements lead to simplifications in (58). For $\mathfrak{R}_i = \Delta r_i$ in AX_n-type molecules of symmetry O_h, T_d, D_{3h}, $D_{\infty h}$ with only one totally symmetric mode of vibration of frequency ω_1, [41]

$$\bar{L}_i^1 = \left[\frac{\hbar}{2\pi c \omega_1 n m_X}\right]^{1/2}, \qquad i = 1 \text{ to } n \tag{61}$$

and $\bar{L}_i^s = 0$ for $s \neq 1$. For example, in CH_4-type molecules including up to quadratic terms in the normal coordinates,

$$\langle \Delta r_1 \rangle = \bar{L}_1^1 \langle q_1 \rangle + \frac{1}{2} \bar{L}_1^{2a2a} \langle q_2^2 \rangle + \frac{1}{2} \bar{L}_1^{3x3x} \langle q_3^2 \rangle + \frac{1}{2} \bar{L}_1^{4x4x} \langle q_4^2 \rangle + \ldots \tag{62}$$

$$\langle (\Delta r_1)^2 \rangle = (\bar{L}_1^1)^2 \langle q_1^2 \rangle + (\bar{L}_1^{3x})^2 \langle q_3^2 \rangle + (\bar{L}_1^{4x})^2 \langle q_4^2 \rangle + \ldots \tag{63}$$

In terms of these curvilinear internal coordinates, (1) can be rewritten

$$P = P_e + \sum_i \left(\frac{\partial P}{\partial \boldsymbol{\mathcal{R}}_i}\right) \boldsymbol{\mathcal{R}}_i + \frac{1}{2!}\sum_{ij}\left(\frac{\partial^2 P}{\partial \boldsymbol{\mathcal{R}}_i\,\partial \boldsymbol{\mathcal{R}}_j}\right)_e \boldsymbol{\mathcal{R}}_i\boldsymbol{\mathcal{R}}_j + \frac{1}{3!}\sum_{ijk}\left(\frac{\partial^3 P}{\partial \boldsymbol{\mathcal{R}}_i\,\partial \boldsymbol{\mathcal{R}}_j\,\partial \boldsymbol{\mathcal{R}}_k}\right)\boldsymbol{\mathcal{R}}_i\boldsymbol{\mathcal{R}}_j\boldsymbol{\mathcal{R}}_k + \dots \tag{64}$$

where the sums are unrestricted. Symmetry relations between the derivatives $(\partial P/\partial \boldsymbol{\mathcal{R}}_i)_e$, etc., also reduce the number of unique derivatives, depending on the property. The magnetizability, the electric dipole polarizability, and higher polarizability tensors of the molecule depend on the symmetry of the molecule as a whole in its equilibrium geometry. The number of unique non-vanishing components for various symmetry groups have been determined by Buckingham et al. [60] for molecular moments and polarizabilities in static fields. The numers of independent derivatives of the dipole moment, quadrupole moment, and dipole polarizability for various molecular types of given geometry and total charge have been tabulated by Fowler and Buckingham [21]. The symmetry properties of dipole moment, electric dipole polarizability and the first hyperpolarizability components have been given in detail for the various symmetry point groups by Cyvin, Rauch, and Decius [61]. Other properties are site-specific, such as the electric field gradient, the nuclear magnetic shielding, the spin rotation constant. These properties have the symmetry of the molecule if the site is at the center of the molecule; a different nuclear site leads to a lower symmetry. For example, in CH_4 the nuclear magnetic shielding and electric field gradient at the proton and the ^{13}C–^{1}H spin-spin coupling constant all have C_{3v} symmetry. Furthermore, because of this C_{3v} symmetry, the electric field gradient tensor at the proton has only one independent component. In CH_4 the ^{1}H–^{1}H spin-spin coupling is of C_{2v} symmetry. Buckingham et al. [62, 63] have tabulated the number of independent components of the spin-spin coupling tensor and also the nuclear shielding tensor [64–66] for some important point group symmetries. Furthermore, the number of non-vanishing unique first derivatives (and higher) of the property depends on this site symmetry. For example, in the pyramidal AB_3 molecule, the first derivatives of the electric field gradient at nucleus A with respect to the normal coordinates of the E vibrational modes are zero, but this does not apply to the electric field gradient derivatives at the B nuclei. There are similar site symmetry consequences for the property derivatives with respect to internal coordinates. For example, there is only one $(\partial\sigma^{C}/\partial r)_e$ for ^{13}C nuclear magnetic shielding in CH_4, but for ^{1}H shielding the derivatives $(\partial\sigma^{H_1}/\partial r_1)_e$ and $(\partial\sigma^{H_1}/\partial r_2)_e$ are different [41]. Thus, one may write as in [67]

$$\langle\sigma(^{13}C)\rangle = \sigma_e + \sigma_r(\langle r_1\rangle + \langle r_2\rangle + \langle r_3\rangle + \langle r_4\rangle) + \frac{1}{2}\sigma_{rr}(\langle r_1^2\rangle + \langle r_2^2\rangle + \langle r_3^2\rangle + \langle r_4^2\rangle) + \dots \tag{65}$$

where

$$\sigma_r \equiv (\partial\sigma^{C}/\partial r_1)_e = (\partial\sigma^{C}/\partial r_2)_e = (\partial\sigma^{C}/\partial r_3)_e = (\partial\sigma^{C}/\partial r_4)_e \tag{66}$$

whereas

$$\langle\sigma(^1\mathrm{H})\rangle = \sigma_e + \sigma_r\langle r_1\rangle + \sigma_s(\langle r_2\rangle + \langle r_3\rangle + \langle r_4\rangle) + \frac{1}{2}\sigma_{rr}\langle r_1^2\rangle + \frac{1}{2}\sigma_{ss}(\langle r_2^2\rangle + \langle r_3^2\rangle + \langle r_4^2\rangle) + \ldots \tag{67}$$

where, for the proton participating in C–H bond 1 of four C–H bonds in CH_4,

$$\sigma_r \equiv (\partial\sigma^{H_1}/\partial r_1)_e \,. \tag{68}$$

$$\sigma_s \equiv (\partial\sigma^{H_1}/\partial r_2)_e = (\partial\sigma^{H_1}/\partial r_3)_e = (\partial\sigma^{H_1}/\partial r_4)_e \,. \tag{69}$$

The relations between the mass-dependent property derivatives P_i in (1) and the mass-independent derivatives P_r in (64) can be written in terms of the **L** tensor elements (which contain the mass factors). See for example [58].

$$\begin{aligned} P_i &= \sum_r P_r L_r^i \\ P_{ij} &= \sum_r P_r L_r^{ij} + \sum_{rs} P_{rs} L_r^i L_s^j \\ P_{ijk} &= \sum_r P_r L_r^{ijk} + \sum_{rs} P_{rs}(L_r^i L_s^{jk} + L_r^j L_s^{ki} + L_r^k L_s^{ij}) + \sum_{rst} P_{rst} L_r^i L_s^j L_t^k \end{aligned} \tag{70}$$

In early treatments only the first order terms in the **L** tensor were included in the above equations [68]. Symmetry relations between the **L** tensor elements lead to simple relationships between the derivatives of the properties. For example, for the properties P which have the symmetry of T_d in the isotopomers $CH_{4-n}D_n$,

$$P_1 = -4P_r\bar{L}_1^1 \text{ (only one } A_1 \text{ mode) in } CH_4 \text{ and } CD_4 \tag{71}$$

or $$P_n = -P_r(\bar{L}_1^n + 3\bar{L}_2^n)\,, \quad n = 1, 2, 3 \subset A_1 \text{ in } CH_3D \text{ and } CD_3H \tag{72}$$

or $$P_n = -2P_r(\bar{L}_1^n + \bar{L}_3^n)\,, \quad n = 1\text{–}4 \subset A_1 \text{ in } CH_2D_2 \,. \tag{73}$$

In CH_4 and CD_4, the third derivatives are (leaving out the 3rd order terms in the **L** tensor) [69]:

$$P_{12a2a} = 8(P_{rr} + P_{rs})\,\bar{L}_1^1\bar{L}_1^{2a2a} + 9(P_{\alpha\alpha} + P_{\alpha\omega})\,\bar{L}_5^{2a}\bar{L}_5^{12a} + \ldots \tag{74}$$

and for u = 3x, 4x

$$P_{1uu} = 8(P_{rr} + P_{rs})\,\bar{L}_1^1\bar{L}_1^{uu} + 4(P_{\alpha\alpha} - P_{\alpha\omega})\,\bar{L}_6^u\bar{L}_6^{1u} + 16P_{r\alpha}\bar{L}_1^u\bar{L}_6^{1u} + \ldots \tag{75}$$

The analogs of (62) and (74) and (75) for the lower symmetry mixed-isotope species can be derived in a straightforward way for each molecular type and property site symmetry. For some explicit examples see Raynes [67]. The *first order* terms take on

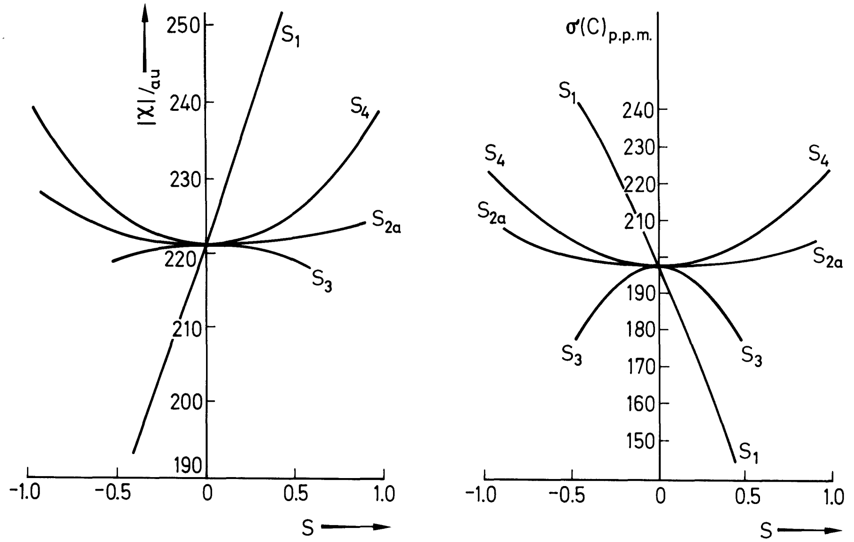


Fig. 8. Property surfaces of CH_4 molecule. The absolute value of the magnetizability and the ^{13}C nuclear magnetic shielding are plotted as functions of the symmetry coordinates defined in the text. S_1 and S_3 are in Angstroms and S_{2a} and S_{4z} are in radians. Reproduced from Lazzeretti P, Zanasi R, Sadlej AJ, Raynes WT (1987) Mol. Phys. 62: 605, with permission [70]

particularly simple forms in highly symmetric situations. For example in AX_n molecules (O_h, T_d and D_{3h} for n = 6, 4, 3) [41],

$$\langle P\rangle = P_e + (h/4\pi^2\omega_1 c n m_X)^{1/2}\,\langle q_1\rangle \cdot P' + \ldots \tag{76}$$

where
$$P' \equiv [(\partial P/\partial r_1)_e + (\partial P/\partial r_2)_e + \ldots + (\partial P/\partial r_n)_e] \tag{77}$$

where m_X is the mass of the X atom and $\langle q_1\rangle$ is given by (35) and (37) where ω_1 is the totally symmetric vibrational frequency.

In ab initio calculations of surfaces the sensible approach is of course to use not bond displacements but simultaneous displacements which reflect the symmetry of the molecule, i.e. symmetry internal displacement coordinates. The choice of symmetry coordinates is the same as for the potential energy surface. Figure 8 shows sections through the χ (magnetizability) surface and the σ^C (^{13}C nuclear magnetic shielding) surface calculated by Lazzeretti et al. [70] in the symmetry coordinates given below:

$$S_1 = \frac{1}{2}(r_1 + r_2 + r_3 + r_4) \tag{78}$$

where r_i describes the increase in the length of bond i relative to its equilibrium value.

$$S_{2a} = (12)^{-1/2}(2\alpha_{12} - \alpha_{13} - \alpha_{14} - \alpha_{23} - \alpha_{24} + 2\alpha_{34}) \tag{79}$$

and

$$S_{2b} = \frac{1}{2}(\alpha_{13} - \alpha_{14} - \alpha_{23} - \alpha_{34}) \tag{80}$$

where α_{ij} denotes the increase in the interbond angle between bonds i and j from its equilibrium value.

$$S_{3x} = \frac{1}{2}(r_1 - r_2 + r_3 - r_4)\,, \tag{81}$$

$$S_{3y} = \frac{1}{2}(r_1 - r_2 - r_3 + r_4)\,, \tag{82}$$

and

$$S_{3z} = \frac{1}{2}(r_1 + r_2 - r_3 - r_4)\,, \tag{83}$$

$$S_{4x} = 2^{-1/2}(\alpha_{24} - \alpha_{13})\,, \tag{84}$$

$$S_{4y} = 2^{-1/2}(\alpha_{23} - \alpha_{14}) \tag{85}$$

and

$$S_{4z} = 2^{-1/2}(\alpha_{34} - \alpha_{12})\,. \tag{86}$$

Similar surfaces in terms of the symmetry coordinates have been plotted for O and H nuclear shielding and magnetizability in H_2O [71], and for electric dipole polarizability and molecular quadrupole moment in CO_2 [26].

The largest contributions to the value of the property at the equilibrium geometry P_e, and to its derivative $(\partial P/\partial \mathfrak{R})_e$ may come from distinctly different regions within the molecule. For example the ^{19}F nuclear magnetic shielding in HF is dominated by the diamagnetic term which depends on r^{-1} of the electrons whereas $(\partial\sigma/\partial\mathfrak{R})_e$ is dominated by the paramagnetic term which depends on r^{-3} [18]. A mapping of the nuclear shielding density function shows the contributions to the shielding from various regions in the molecule, and a mapping of the distribution of $(d\sigma/d\mathfrak{R})_e$ shows which regions of the electronic distribution contribute to the change in shielding as the bond is extended [72]. A similar conclusion has been reached in the case of μ and $(\partial\mu/\partial\mathfrak{R})_e$ [73].

5 Temperature Dependence

5.1 Calculations

Calculation of the thermal average of a molecular property using (40) including nuclear spin statistics, is feasible for a molecule with only a few vibrational modes, e.g., H_2O [58]. In this example Fowler, Riley and Raynes used ab initio SCF property surfaces for the electric dipole moment, magnetizability, proton magnetic shielding and

^{17}O magnetic shielding to obtain the derivatives P_r, P_{rs}, etc. of the various properties [71]. An accurate empirical anharmonic force field was used to determine the quantities ω_s, $\varphi_{sss'}$, $a_s^{\alpha\alpha}$, and E_{vJK}. The thermal averages $\langle P \rangle_T$ were calculated using (28)–(33) and (40) [58]. Rovibrational states up to $J = 25$ and levels less than 5000 cm^{-1} above the zero-point levels were included for each of the 18 isotopomers (^1H, ^2H, ^3H, ^{16}O, ^{17}O, ^{18}O). The literal summing up of terms can be time-consuming when the density of rovibrational states is high. If nuclear spin statistics are ignored, if rotation is averaged classically, and if the harmonic oscillator density of states is used, then

$$\left\langle v_s + \frac{1}{2} \right\rangle^T = \frac{1}{2} \coth(hc\omega_s/2kT) \tag{87}$$

$$\langle J_\alpha^2 \rangle^T = I_{\alpha\alpha} kT \tag{88}$$

Equations (35)–(37) become

$$\langle q_s \rangle = -\frac{1}{2\omega_s} \sum_{s'} \varphi_{s's's} \frac{1}{2} \coth(hc\omega_{s'}/2kT) \tag{89}$$

$$\langle q_s q_{s'} \rangle = \frac{d_s}{2} \coth(hc\omega_s/2kT)\, \delta_{ss'} \tag{90}$$

and the rotational contribution to a single reduced normal coordinate q_s to be added to (89) is

$$\langle q_s \rangle_{cent} = + \frac{kT}{4\pi c\omega_s} \left(\frac{1}{hc\omega_s} \right)^{1/2} \sum_\alpha \frac{a_s^{\alpha\alpha}}{I_{\alpha\alpha}^{(e)}} \tag{91}$$

(See Toyama et al. [28], and Jameson [41, 68]). In this case, keeping only terms quadratic in the normal coordinates in the expansion (1) [28, 68]

$$\begin{aligned} \langle P \rangle^T = P_e + \sum_s \left[\frac{P_{ss}}{2} - \sum_{s'}^{\text{tot. sym.}} P_{s'} \varphi_{sss'}/2\omega_{s'} \right] \cdot \frac{1}{2} \coth(hc\omega_s/2kT) + \ldots \\ + \sum_{s'}^{\text{tot. sym.}} P_{s'} \frac{h}{2} \left(\frac{1}{hc\omega_s} \right)^{3/2} kT \sum_\alpha \frac{a_{s'}^{\alpha\alpha}}{I_{\alpha\alpha}^{(e)}} + \ldots \end{aligned} \tag{92}$$

With these approximations the form of the temperature dependence of an electronic property becomes more obvious than in (40). For $x \geqq 2.5$ the function coth x changes by less than 1 part in 100 when x changes by 1 part in 7. Thus, around room temperature ($T = 300$ K $= 208.5$ cm^{-1}) only those vibrational modes having frequencies such that $\omega_s/2kT \leqq 2.5$, i.e., $\omega_s < 1000$ cm^{-1} make substantial vibrational contributions to the temperature coefficient of any property. Inclusing only terms up to P'' and taking the coth approximation for the thermal average of $\langle v + \frac{1}{2} \rangle$, (as in (87)) for diatomic molecules:

$$\langle P \rangle^T = P_e + 4(B_e/\omega_e)^2 P' \frac{kT}{B_e} + \left(\frac{B_e}{\omega_e} \right) (P'' - 3a_1 P') \frac{1}{2} \coth(hc\omega_e/2kT) + \ldots \tag{93}$$

Table 3. Relative contributions to the P′ term of $(\langle P\rangle^{400K} - \langle P\rangle^{300K})$ for a diatomic molecule[a]

ω_e/cm^{-1}	% Rotation	% Anharmonic vibration
600	52	48
800	61	39
1000	70	30
1200	79	21
1400	86	14
1600	92	8

[a] Using $a_1 \cong -2$, which is a typical value

The above equation was derived by Buckingham [34].

The relative contributions of rotation, harmonic vibration, and anharmonic vibration to the temperature dependence of an electronic property of a diatomic molecule depend on ω_e and a_1, as well as the property derivatives. For 300 K to 400 K the relative contributions to the P′ term of the temperature dependence of $\langle P\rangle^T$ can be estimated, as shown in Table 3. For diatomic molecules (such as N_2 or CO) with fairly high vibrational frequencies the temperature dependence of a molecular electronic property can be dominated by rotation [68, 74].

The relative contributions of various terms to thermal average shielding in a diatomic molecule can be seen in Tables 4 and 5. The sign and magnitude of the vibrational dependence is determined by $(P'' - 3a_1P')$. The values of a_1 being typically about -2, the vibrational dependence of many properties is contributed mainly by the first derivative and thus by the anharmonic contribution [68]. We note in Table 4 that the third and higher order terms in (44) have very little effect on the thermal average shielding. Terms up to the second derivative comprise 92–99% of the total calculated value. Although the rotational contribution to $\langle \Delta r\rangle^T$ is usually one order of magnitude smaller than the vibrational contribution, it plays an important role in the temperature dependence of an electronic property. As an example, the temperature dependence of nuclear magnetic shielding in some diatomic molecules calculated using (93) are shown in Table 5. The temperature dependence of the shielding depends nearly entire-

Table 4. The cumulative contributions, linear, quadratic and higher order rovibrational contributions to the thermal average shielding at 300 K, $\langle\sigma\rangle^{300} - \sigma_e$, in ppm [44]

Nucl.	Mol.	$(d\sigma/d\xi)_e\langle\xi\rangle$	$\left\{(d\sigma/d\xi)\langle\xi\rangle + \frac{1}{2}(d^2\sigma/d\xi^2)_e\langle\xi^2\rangle\right\}$	Up to 6th order
^{1}H	H_2	−0.5554	−0.3964 (97%)	−0.3814
^{1}H	HF	−0.7021	−0.3721 (95%)	−0.3911
^{19}F	HF	−7.42	−11.113 (99%)	−11.23
^{1}H	LiH	−0.1228	−0.1238 (99%)	−0.1228
^{7}Li	LiH	+0.1386	+0.0726 (92%)	+0.0786

Table 5. Temperature dependence of nuclear shielding, $\langle\sigma\rangle^{400} - \langle\sigma\rangle^{300}$, in ppm[a] [18]

Nucl.	Mol.	Rotational		Anharm. vib.	Harm. vib.	Total
^1H	H_2	−0.0282	(100%)	~0	~0	−0.0282
^1H	^7LiH	−0.0091	(79%)	−0.0008	−0.0016	−0.0115
^7Li	^6LiH	+0.0253	(96%)	+0.0023	−0.0013	+0.0263
^1H	HF	−0.0253	(100%)	~0	~0	−0.0253
^{19}F	HF	−0.2560	(100%)	~0	~0	−0.2560
^{13}C	$^{13}C^{16}O$	−0.1062	(98%)	−0.0016	−0.0002	−0.1081
^{17}O	$^{12}C^{17}O$	−0.1231	(98%)	−0.0020	−0.0003	−0.1254
^{15}N	$^{15}N_2$	−0.1405	(99%)	−0.0013	−0.0004	−0.1423

[a] Calculated using (93)

ly on rotation, with vibrational effects accounting for 0–2%. This is easily understood by consulting (93). The linear temperature dependence of the rotational contribution dominates the change of the average shielding with temperature, especially for these diatomic molecules which have strong bonds characterized by high vibrational frequencies. The (hcω/2kT) term is large, for which the coth function is very nearly a constant equal to 1.0. For F_2 and ClF molecules the rotational contribution still dominates although the anharmonic vibration contribution to the temperature dependence becomes significant [68].

5.2 Experimental Examples

The most extensive data on the temperature dependence of molecular electronic properties come from magnetic resonance. Measurements made in the gas phase in the zero-pressure limit in molecules which are incapable of undergoing rearrangement or conformational changes, can only be explained in terms of rovibrational averaging as described theoretically in the foregoing. Although the first attribution of a temperature-dependent vibrational averaging of a molecular electronic property was probably that by Petrakis and Sederholm [75], of the proton chemical shift variation with temperature in gas samples at 10 atm, it is now obvious that a large part of what was observed was due to intermolecular effects [76]. Buckingham called attention to the latter and also provided a general theoretical explanation for temperature dependence in diatomics which is that shown in (93) [34]. Extrapolation to the zero-pressure limit eliminates the intermolecular effects, leaving only the temperature dependence due to rovibrational averaging. The first such report was in ^{19}F nuclear magnetic shielding in F_2 and ClF [68], followed shortly by BF_3, CF_4, SiF_4, and SF_6 [77]. An example is shown in Fig. 9. Further examples have been reviewed [18, 76]. These results have been interpreted in terms of (92) which has a simple form for AX_n type molecules which have O_h, T_d or D_{3h} symmetry, as follows [41]:

$$\langle P\rangle^T = P_e + (\partial P/\partial r_1 + \partial P/\partial r_2 + \ldots \partial P/\partial r_n)_e$$
$$\times \left\{ (h/4\pi^2\omega_1 c n m_X)^{1/2} \sum_{s=1}^{3N-6} \frac{\varphi_{1ss}}{2\omega_1} \frac{1}{2} \coth\left(\frac{hc\omega_s}{2kT}\right) \right.$$
$$\left. + 3kT/4\pi^2 c^2 n m_X r_e \omega_1^2 + O(L_r^{ij}) \right\} + \ldots \qquad (94)$$

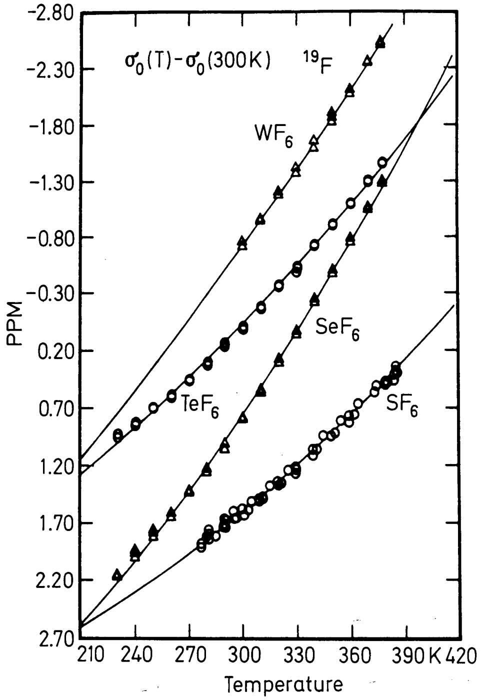


Fig. 9. Comparison of the observed temperature dependence [$\sigma_0(T) - \sigma_0(300\ K)$] of ^{19}F in octahedral fluorides with the calculated curves $(\partial\sigma/\partial r)_e\ [\langle \Delta r\rangle^T - \langle \Delta r\rangle^{300}]$, using $(\partial\sigma/\partial r)_e \approx -1930, -2690, -1770$, and -2500 ppm/Å for SF_6, SeF_6, TeF_6, and WF_6, respectively. (Except for TeF_6, the individual plots are arbitrarily offset for display.) $(\partial\sigma/\partial r)_e$ in these MF_6 cases are of the form $[(\partial\sigma^F/\partial r)_1)_e + (\partial\sigma^F/\partial r_t)_e + 4(\partial\sigma^F/\partial r_c)_e]$. Reproduced from Jameson CJ, Jameson AK (1986) J. Chem. Phys. 85:5484, with permission [80]

The terms of order $O(L_r^{ij})$ not explicitly shown above include terms in L_r^{ij}, L_j^{ijk}, ... which appear in (70) upon nonlinear transformation of the derivatives of the property with respect to normal coordinates into derivatives with respect to curvilinear internal coordinates. Alternatively the entire quantity in curly brackets in (94) may be calculated using another method, due to Bartell [78, 79], which gives equivalent results [80] when the same anharmonic force field is used. The terms denoted by + ... involve second and higher derivatives of the property surface. For the central nucleus (A) in these symmetrical AX_n molecules, $[(\partial P/\partial r_1)_e + (\partial P/\partial r_2)_e + \ldots + (\partial P/\partial r_n)_e]$ is $n(\partial\sigma^A/\partial r_1)$. On the other hand, for the peripheral nucleus F in CF_4 for example, it is $(\sigma_r + 3\sigma_s) \equiv [(\partial^{F_1}/\partial r_1)_e + 3(\partial\sigma^{F_1}/\partial r_2)_e]$, with $(\partial\sigma^{F_1}/\partial r_1)_e$ being the dominant contribution. For the F nucleus in the MF_6 molecules in Fig. 9 it is $(\sigma_r + \sigma_t + 4\sigma_c) \equiv [(\partial\sigma^{F_1}/\partial r_1)_e + (\partial\sigma^F/\partial r_t)_e + 4(\partial\sigma^F/\partial r_c)_e]$, where the contributions from the bonds *cis* and *trans* to the F nucleus of interest are expected to be smaller than $(\partial\sigma^{F_1}/\partial r_1)_e$. This linear combination of derivatives has been considered as an empirical parameter and the experimental data have been fitted by (94), neglecting second and higher derivatives. There is no guarantee that the neglected terms are much smaller than the terms involving the first derivative. Even though the absolute precision and accuracy of the experimental data are high (a few parts per billion) they do not warrant fitting to more than one empirical parameter. For this particular observable, the very large number of examples are typically of the form shown in Fig. 9, that is, the shapes of curves which best describe the experimental data points mimic the shapes of $\langle \Delta r\rangle^T$ vs. temperature for the molecule. Of course the functions $\langle (\Delta\alpha)^2\rangle^T$ also have similar shapes.

The temperature dependence of spin-spin coupling constants have been reported in two molecules, the B-F coupling in BF_3 [81] and the C-H coupling in CH_4 [82]. The latter has been interpreted using (94), keeping only the terms in the first derivatives. The empirical value of $(J_r + 3J_s) \equiv [(\partial J(CH_1)/\partial r_1)_e + 3(\partial J(CH_1)/\partial r_2)_e]$ was found to be 368(10) Hz $Å^{-1}$, that is, an increase of the coupling with increasing bond length [82]. This had been predicted to be a somewhat general trend (except where lone pairs are involved) from a study of isotope effects on coupling constants and from consideration of the change in electron density at the nuclei upon bond extension [83].

The other temperature-dependent electronic properties which have been widely reported are the nuclear spin hyperfine constants in ESR spectra of organic free radicals. Large temperature coefficients, characteristic of nuclear hyperfine constants at β position from the atom with the unpaired spin involve the averaging over torsional states of a highly torsional-angle-dependent electronic property. Oriented molecule studies in single crystals provide information on the second derivative of the hyperfine constant with respect to the torsional angle ϕ [84]:

$$a^H_\beta = B_0 + B_2 \cos^2 \phi \tag{95}$$

which could lead to temperature-dependent hyperfine constants a^H_β [85] under isotropic conditions in solution or in gas phase. A large number of examples have been reviewed [86]. This is similar to the 3-bond spin-spin coupling constants observed in NMR which are highly dependent on the dihedral angle. Averaging over the torsional angle in each conformation leads to a temperature dependent spin-spin coupling, but the largest temperature dependence comes from the temperature-dependent populations of the various conformers [87].

Table 6. Calculated and experimental results of rovibrational averaging of hyperfine constants in $\dot{C}H_3$ [90]

	calculated[a]	experimental[b]
$a^H(^{12}CH_3)$	−23.85	23.04 ± 0.01 [178, 148]
$\frac{\gamma^H}{\gamma^D}\, a^D(^{12}CD_3)$	−24.14	23.30 ± 0.07 [178]
ratio $\varkappa$	1 − 0.012	1 − 0.011 ± 0.003
$a^C(^{13}CH_3)$	52.23	38.34 ± 0.01 [178]
$a^C(^{13}CD_3)$	49.92	35.98 ± 0.01 [178]
ratio	1.0462	1.0656 ± 0.0004
$(da^H/dT)\ (^{12}CH_3)$	1.48	1.3 ± 0.2 [150], 1.5 ± 0.2 [149]
$\frac{\gamma^H}{\gamma^D}\,(da^D/dT)\ (^{12}CD_3)$	2.04	2.3 [149]
$(da^C/dT)\ (^{13}CH_3)$	11.6	13.5 [149]
$(da^C/dT)\ (^{13}CD_3)$	15.9	

[a] Rovibrational averaging calculations by [90] using ab initio theoretical property surface calculated by [89];

[b] Signs were not determined for a values

Of greater interest is the temperature dependence of simple systems such as the a^H in $\dot{C}H_3$, for example. Analyses of the temperature dependence of the ^1H and ^{13}C hyperfine constants indicate that the most important vibrational mode is the symmetric out-of-plane bend of the planar $\dot{C}H_3$ radical. The dependence of these properties on the out-of-plane angle θ has been calculated by various methods. The ab initio SCF-CI calculations with a small optimized basis set [88] yield

$$a^C(\theta) = 148.8 + 1395\theta^2 - 2560\theta^4 \tag{96}$$
$$a^H(\theta) = -54.27 + 250\theta^2 - 957\theta^4 \tag{97}$$

Vibrational averaging using harmonic oscillator functions in a normal coordinate approximated by the out-of-plane angle θ, and using the experimental $\omega = 580\ \mathrm{cm}^{-1}$ lead to calculated temperature coefficients of the right order of magnitude. An ab initio UHF calculation by Meyer for $\dot{C}H_3$, using a large basis set [89] yields spin densities which have been used by Schrader and Morokuma to calculate the temperature and mass dependence of a^C and a^H [90]. Results are shown in Table 6. The agreement between experiment and calculation is sufficiently good so that the phenomenon can be considered well understood.

6 Mass Dependence: Isotope Effects

Isotope effects on molecular electronic properties are a direct consequence of rovibrational averaging.

6.1 Calculations

6.1.1 Centrifugal Distortion

Complete to second order in the contact transformation, the rotational contribution to a rovibrationally averaged electronic property includes terms quadratic in the angular momentum and terms quartic in the angular momentum. These have been derived by Fowler for asymmetric tops [43]. There are contributions involving property derivatives P_s, $P_{ss'}$ and $P_{ss's'}$. For spherical tops (39) shows the term in P_1 and P_{1ss} where q_1 is the totally symmetric normal coordinate. The general leading term comes from the centrifugal distortion of a single reduced normal coordinate, (37) or its thermal average, (91). Note that this leading term does not depend on the anharmonic part of the potential. Thus, the centrifugal distortion contribution can be written simply in terms of the usual matrices which arise in a harmonic vibrational analysis such as [28]:

$$\langle \Delta r \rangle^T_{rot} = kT\tilde{U}F_S^{-1}\,G_S^{-1}\,UB\Omega X \tag{98}$$

where Ω denotes a diagonal matrix with the elements

$$\Omega^{(\alpha\alpha)}_{ii} = \frac{1}{I^{(e)}_{\beta\beta}} + \frac{1}{I^{(e)}_{\gamma\gamma}} \tag{99}$$

involving the equilibrium moments of inertia and X is a vector which has the Cartesian coordinates of the atoms at the equilibrium configuration as its elements. F_S^{-1} and G_S^{-1} are the inverse of the usual Wilson F and G matrices in symmetry coordinates. U is the transformation matrix from internal into symmetry coordinates and B is the transformation from Cartesian displacements into internal coordinates.

For highly symmetrical molecules the rotational effect on the mean bond length can be expressed in even simpler form, for example [28, 91]:
For a CO_2 type molecule

$$\langle \Delta r \rangle_{rot}^{T} = \frac{kT}{r_e(F_{11} + F_{12})} \tag{100}$$

For a AX_n type (planar, T_d or O_h):

$$\langle \Delta r \rangle_{rot}^{T} = \frac{3kT}{nr_eF_{11}} \tag{101}$$

where F_{11} and F_{12} are mass-independent quadratic force constants in internal coordinates. Since these equations involve only mass-independent terms, there will be *no rotational contribution* to the isotope effects on any molecular electronic property of these molecular types provided that isotopic substitution preserves the symmetry of the molecule, as in going from CH_4 to CD_4 (but not in CH_4 to CH_3D) [91].

6.1.2 Vibration in Diatomics

Of the quantities in (93), a_1 is mass-independent and the others depend on the reduced mass of the diatomic molecule as follows:

$$\begin{aligned} \omega_e^* &= (\mu/\mu^*)^{1/2}\,\omega_e \\ B_e^* &= (\mu/\mu^*)\,B_e \end{aligned} \tag{102}$$

Furthermore, the thermal average $\left\langle v + \frac{1}{2} \right\rangle^{T}$ is also mass-dependent since the populations of the vibrational energy levels over which this average is taken depend on the vibrational frequency ω_e. We note that B_e/ω_e^2 is mass-independent, so the rotational contribution to the thermal average shielding in the diatomic molecule is independent of mass.

Therefore the isotope shift, the isotope effect on the property which is the nuclear magnetic shielding σ, is given by [91]

$$\begin{aligned} \langle\sigma\rangle - \langle\sigma\rangle^* &= [(d^2\sigma/d\xi^2)_e - 3a_1(d\sigma/d\xi)_e]\,(B_e/\omega_e) \\ &\times \{\coth(hc\omega_e/2kT) - (\mu/\mu^*)^{1/2}\coth[hc(\mu/\mu^*)^{1/2}\,\omega_e/2kT]\} \end{aligned} \tag{103}$$

We have calculated the rovibrational corrections to shielding and the isotope shift using (93) and (103) for diatomic molecules, using shielding derivatives from the

Table 7. Anharmonic and harmonic vibrational contributions to the secondary isotope shift, in ppm[a]

Nucl.	Mol.	Anharm.	Harm.	Total	Expt.	Ref.
^{1}H	HD—H_2	−0.0723	+0.0090	−0.0632[b]	−0.036 ± 0.002	[179]
^{1}H	^{7}LiH—^{6}LiH	−0.0007	−0.0013	−0.0020		
^{7}Li	LiD—LiH	+0.0438	−0.0250	+0.0188		
^{1}H	DF—HF	−0.1719	+0.0796	−0.0923		
^{19}F	DF—HF	−1.7364	−0.7883	−2.5248	−2.5 ± 0.5	[180]
^{13}C	^{13}C^{18}O—^{13}C^{16}O	−0.0414	−0.0058	−0.0472[c]	−0.0476 ± 0.0016	[111]
^{17}O	^{13}C^{17}O—^{12}C^{17}O	−0.0438	−0.0063	−0.0501	−0.110 ± 0.001	[111]
^{15}N	^{15}N$_2$—^{15}N^{14}N	−0.0432	−0.0148	−0.0581	−0.0601 ± 0.002	[112]

[a] Ref. [18] using (103);

[b] For isotopomers of H_2 the classical treatment of rotation leads to significant error. A proper average taking into consideration the nuclear spin statistics gives better results: —0.045 [44];

[c] This may be compared with —0.06 ppm obtained from calculations including cubic terms

literature for H_2 [92], LiH [93], HF [94], CO [95] and N_2 [96]. Differences in shielding between pairs of isotopically related molecular species give the isotope shifts in Table 1. There is no rotational contribution to the isotope shift in diatomic molecules in the classical limit. The relative contributions of the anharmonic and harmonic vibrational effects vary so that neglect of the harmonic contribution in calculating the isotope shift can lead to error. Among these examples, the largest error would occur in the case of ^{19}F in the DF-HF system, in which the harmonic vibrational contribution is 31 % of the observed isotope shift.

In diatomic molecules the mean bond displacement and the mean square amplitudes can be written from (93) as

$$\langle \Delta r\rangle^{T} = \langle \Delta r\rangle^{T}_{rot} + \langle \Delta r\rangle^{T}_{vib} \tag{104}$$

$$\langle \Delta r\rangle^{T}_{rot} = \frac{4B_e r_e}{hc\omega_e^2} kT \tag{105}$$

$$\langle \Delta r\rangle^{T}_{vib} = -(3/2)\, a_1\, (B_e/\omega_e)\, r_e \coth (hc\omega_e/2kT) \tag{106}$$

$$\langle (\Delta r)^2\rangle^{T}_{vib} = (B_e/\omega_e)\, r_e^2 \coth(hc\omega_e/2kT) \tag{107}$$

From (106) we see that by making use of the implicit mass dependence of B_e and ω_e in (102) we can write [91]

$$\langle \Delta r\rangle - \langle \Delta r\rangle^* = -(3/2)\, a_1 r_e \{(B_e/\omega_e) \coth (hc\omega_e/2kT) - (\mu/\mu^*)^{1/2} (B_e/\omega_e) \coth[hc(\mu/\mu^*)^{1/2}\, \omega_e/2kT]\} \tag{108}$$

There are several approximations which can be invoked to simplify this expression further:

(i) if $\coth(hc\omega_e/2kT)$ is very close to 1.0 and $\coth[hc(\mu/\mu^*)^{1/2}\omega_e/2kT]$ is also very close to 1.0, i.e. for high vibrational frequencies, then $\langle \Delta r\rangle - \langle \Delta r\rangle^*$ reduces to

$$\langle \Delta r\rangle - \langle \Delta r\rangle^* \approx [1 - (\mu/\mu^*)^{1/2}]\, \langle \Delta r\rangle \tag{109}$$

Similarly

$$\langle(\Delta r)^2\rangle - \langle(\Delta r)^2\rangle^* \approx [1 - (\mu/\mu^*)^{1/2}]\,\langle(\Delta r^2)\rangle \tag{110}$$

(ii) $[1 - \mu/\mu^{*1/2}]$ can be further approximated by $(\mu^* - \mu)\ 2\mu^*$ except when isotopes of hydrogen are involved so that

$$\langle\Delta r\rangle - \langle\Delta r\rangle^* \approx \langle\Delta r\rangle\left(\frac{\mu^* - \mu}{2\mu^*}\right) = \langle\Delta r\rangle\,\frac{1}{2}\left(\frac{m' - m}{m'}\right)\left(\frac{m_A}{m_A + m}\right) \tag{111}$$

$$\langle(\Delta r)^2\rangle - \langle(\Delta r)^2\rangle^* \approx \langle(\Delta r)^2\rangle\left(\frac{\mu^* - \mu}{2\mu^*}\right) = \langle(\Delta r)^2\rangle\,\frac{1}{2}\left(\frac{m' - m}{m'}\right)\left(\frac{m_A}{m_A + m}\right) \tag{112}$$

where m_A is the mass of the observed nucleus A and the isotopes m′ and m of the other nucleus X in the diatomic molecule. Thus, for a reference diatomic molecule A^mX and its isotopomer $A^{m'}X$, neglecting higher order terms and using (111)–(112)

$$\underset{\text{in } A^mX}{\langle P\rangle} - \underset{\text{in } A^{m'}X}{\langle P\rangle^*} \cong \left\{\left(\frac{dP}{dr}\right)_e \langle\Delta r\rangle_{vib} + \frac{1}{2}\left(\frac{d^2P}{dr^2}\right)_e \langle\Delta r^2\rangle\right\} \times \frac{1}{2}\left(\frac{m' - m}{m'}\right)\left(\frac{m_A}{m_A + m}\right) \tag{113}$$

The vibrational correction for the reference molecule, $\langle P\rangle - P_e$, is given to second order by the quantity in curly brackets in (113).

6.1.3 Extension to Polyatomic Molecules

The mass dependence implicit in (28)–(33) are in the **L** tensor elements. The derivatives with respect to dimensionless normal coordinates P_i, P_{ij}, P_{ijk}, are related to the mass-independent derivatives by these **L** tensor elements as shown in (70) and the force constants in terms of dimensionless normal coordinates: ω_i^{-1}, φ_{ijk}, ... are likewise expressible in terms of mass-independent potential energy derivatives F_{ii}, F_{ijk}, ... and these **L** tensor elements. Thus, the calculations of isotope effects on any electronic property is straightforward when both the property surface and the potential energy surface are known. Equivalently, following (64), the isotope shift can be written in terms of mass-independent property derivatives and mass-dependent averages of curvilinear internal coordinates [18]:

$$\sigma - \sigma^* = \sum_i \left(\frac{\partial\sigma}{\partial\mathfrak{R}_i}\right)_e [\langle\mathfrak{R}_i\rangle^T - \langle\mathfrak{R}_i\rangle^{T*}] + \frac{1}{2}\sum_{ij}\left(\frac{\partial^2\sigma}{\partial\mathfrak{R}_i\,\partial\mathfrak{R}_j}\right)_e \times [\langle\mathfrak{R}_i\mathfrak{R}_j\rangle^T - \langle\mathfrak{R}_i\mathfrak{R}_j\rangle^{T*}] + \ldots \tag{114}$$

The isotope shift (at 0 K) of several properties of H_2O molecule have been calculated. The isotope shifts at 0 K of the electric dipole moment, electric quadrupole moment, the octapole moment and the diamagnetic part of the magnetizability were calculated by Ermler and Kern [97]. The effects of isotopic substitution on the electric dipole moment, the magnetizability and the nuclear magnetic shieldings [58] and the quadrupole moment, rotational g factor and spin rotation parameters [23] were also calculated by Fowler and Raynes. While it is not possible to do calculations at these levels for most systems of interest, it is essential to have at least a qualitative understanding of the extensive isotope shift data and to be able to combine these data with observed temperature coefficients for a partial knowledge of the nature of an electronic property surface. Since isotope shifts are usually easier to measure than temperature coefficients in the zero-pressure limit, it is worthwhile to find a simple model for the estimation of the isotope effects on an electronic property and a further simple model for the change in $\langle \Delta r \rangle$ and in $\langle (\Delta r)^2 \rangle$ upon a change in mass. The model has been described elsewhere [98] and we consider only a brief description here.

Consider a symmetrical molecule A^mX_n. For a property which is most sensitive to bond stretches rather than out-of-plane bends or bond angle deformations, the leading terms in (64) are

$$\langle P \rangle = P_e + \sum_i \left(\frac{\partial P}{\partial r_i}\right)_e \langle \Delta r_i \rangle^T + \frac{1}{2} \sum_{ij} \left(\frac{\partial^2 P}{\partial r_i^2}\right)_e \langle \Delta r_i^2 \rangle^T + \ldots \tag{115}$$

when $\left(\frac{\partial P}{\partial r_i}\right)_e$ are all equal, such as when P is the nuclear shielding of nucleus A, then the n terms can be combined,

$$\langle P \rangle = P_e + n\left[\left(\frac{\partial P}{\partial r_1}\right)_e \langle \Delta r_1 \rangle^T + \frac{1}{2} \left(\frac{\partial^2 P}{\partial r_1^2}\right)_e \langle \Delta r_1^2 \rangle^T\right] + \ldots \tag{116}$$

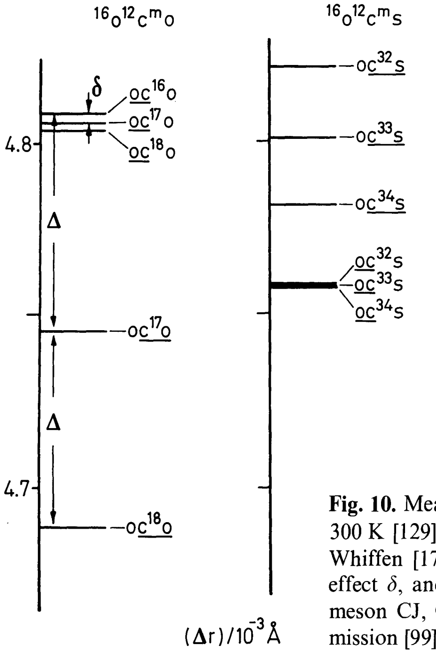


Fig. 10. Mean bond displacements in CO_2, and OCS calculated at 300 K [129] from the anharmonic force fields of Lacy [176] and Whiffen [177], illustrating the primary effect Δ, the secondary effect δ, and the additivity of the effects. Reproduced from Jameson CJ, Osten HJ (1984) J. Chem. Phys. 81: 4293, with permission [99]

Upon isotopic substitution of $^{m'}X$ for one ^{m}X in the $A^{m}X_n$ molecule, there will be a change in symmetry, the normal coordinate analysis will be altered so that all the mean bond displacements $\langle \Delta r_1\rangle$, $\langle \Delta r_2\rangle$, ... $\langle \Delta r_n\rangle$ will be changed. However, the primary change will be in $\langle \Delta r_1\rangle$ where $^{m'}X$ has replaced ^{m}X in the bond. There will be only very small secondary changes in the neighboring bonds [69, 99]. See for example Fig. 10. Thus, the difference between $\langle P\rangle$ in $A^{m}X_n$ and $\langle P\rangle$ in $A^{m}X_{n-1}{}^{m'}X$ will be determined primarily by

$$\left(\frac{\partial P}{\partial r_1}\right)_e [\langle \Delta r_1\rangle - \langle \Delta r_1\rangle^*] + \frac{1}{2}\left(\frac{\partial^2 P}{\partial r_1^2}\right)_e [\langle (\Delta r_1)^2\rangle - \langle (\Delta r_1)^2\rangle^*]\,. \tag{117}$$

Other important terms are

$$(n-1)\left(\frac{\partial^2 P}{\partial r_1\,\partial r_2}\right)_e [\langle \Delta r_1\,\Delta r_2\rangle - \langle \Delta r_1\,\Delta r_2\rangle^*]$$

and various others such as

$$\left(\frac{\partial^2 P}{\partial r_1\,\partial \alpha}\right)_e [\langle \Delta r_1\,\Delta \alpha\rangle - \langle \Delta r_1\,\Delta \alpha\rangle^*]\,.$$

We shall ignore these for the time being. With successive isotopic substitution at r_2, r_3, etc. the primary contributions to the isotope shift in $\langle P\rangle$ will be sequentially incremented by the terms in (117) except that Δr_2, Δr_3, etc. replace Δr_1. Thus, the isotope shift will be largely given by

$$\underset{\text{in } A^{m}X_n}{\langle P\rangle} - \underset{\text{in } A^{m}X_{n-s}{}^{m'}X_s}{\langle P\rangle^*} \cong s\left\{\begin{aligned} &\left(\frac{\partial P}{\partial r_1}\right)_e [\langle \Delta r_1\rangle - \langle \Delta r_1\rangle^*] \\ &+\frac{1}{2}\left(\frac{\partial^2 P}{\partial r_1^2}\right)_e [\langle (\Delta r_1)^2\rangle - \langle (\Delta r_1)^2\rangle^*]\end{aligned}\right\} \tag{118}$$

Furthermore, from (113) we can write the mass factors approximately in the form,

$$\underset{\text{in } A^{m}X_n}{\langle P\rangle} - \underset{\text{in } A^{m}X_{n-s}{}^{m'}X_s}{\langle P\rangle^*} \cong s\left(\frac{\langle P\rangle - P_e}{n}\right)\frac{1}{2}\left(\frac{m'-m}{m'}\right)\left(\frac{m_A}{m_A - m}\right) \tag{119}$$

Some properties are most sensitive to out-of-plane bends, for example a^C in planar $\dot{C}H_3$, in which case the deuteration isotope shift will be largely given by

$$\underset{\text{in } \dot{C}H_3}{\langle a^C\rangle} - \underset{\text{in } \dot{C}D_3}{\langle a^C\rangle^*} \cong 3\left\{\frac{1}{2}\left(\frac{\partial^2 a^C}{\partial \theta^2}\right)_e [\langle \theta^2\rangle - \langle \theta^2\rangle^*]\right\} \tag{120}$$

The above expressions indicate an additivity of the isotope effect upon systematic isotopic replacement of equivalent atoms. Indeed, the bulk of the observations on various properties show additivity, deviations from additivity where they are observed at all in NMR are small [100–103]. If we push the approximation further and consider *only* the $\left(\frac{\partial P}{\partial r}\right)_e$ term, and write very roughly for A^mX_n

$$\langle P\rangle - P_e \cong n\left(\frac{\partial P}{\partial r}\right)_e \langle\Delta r\rangle \tag{121}$$

then very roughly

$$\underset{\text{in } A^mX_n}{\langle P\rangle} \quad - \quad \underset{\text{in } A^mX_{n-s}{}^{m'}X_s}{\langle P\rangle^*} \cong s\left(\frac{\partial P}{\partial r}\right)_e \langle\Delta r\rangle \frac{1}{2}\left(\frac{m'-m}{m'}\right)\left(\frac{m_A}{m_A-m}\right) \tag{122}$$

It turns out that even for molecular types other than AX_n it is still possible to write for any single substitution of ${}^mX$ by ${}^{m'}X$, even when X is not an end atom, that

$$\langle\Delta r\rangle - \langle\Delta r\rangle^* \cong k\langle\Delta r\rangle\left(\frac{m'-m}{m'}\right) \tag{123}$$

$$\langle(\Delta r)^2\rangle - \langle(\Delta r)^2\rangle^* \cong k'\langle(\Delta r)^2\rangle\left(\frac{m'-m}{m'}\right) \tag{124}$$

This is illustrated in Fig. 1 in SeF_6 with masses $m = 74$ and $m' = 74$–82 for Se. The $\langle\Delta r\rangle$ and $\langle(\Delta r)^2\rangle$ calculated using a reasonably good anharmonic force field for the SeF_6 molecule show the direct dependence on $\left(\frac{m'-m}{m'}\right)$. The observed isotope shifts show the same dependence on this mass factor, indicating some support for (122). Equation (122) provides a simple way of estimating $\left(\frac{\partial P}{\partial r}\right)_e$ from the observed isotope effect on property $\langle P\rangle$ if we have some measure of $\langle\Delta r\rangle$ in A^mX_n molecule.

Estimation of $\langle\Delta r\rangle$

A method of estimating $\langle\Delta r\rangle$ has been proposed [98]. For diatomic molecules this is not a problem since there are usually enough known spectroscopic constants to calculate $\langle\Delta r\rangle$ without having to use estimates. We note that including only terms up to quadratic allows us to write

$$\langle\Delta r\rangle^T_{vib} = -(3/2)\,(a_1/r_e)\,\langle(\Delta r)^2\rangle^T \tag{125}$$

An especially useful form of an approximate potential for the diatomic molecule is the Morse function [104]:

$$V = D_e\{1 - \exp[-a(r - r_e)]\}^2 \tag{126}$$

For the Morse potential the ratio $\frac{1}{3}\,(d^3V/d\xi^3)_e/(d^2V/d\xi^2)_e = -ar_e$ can be identified with a_1, the same a_1 that we have previously defined so that, for diatomic molecules,

$$\langle \Delta r\rangle^{T}_{vib} = (3/2)\, a\langle \Delta r)^2\rangle^{T} \tag{127}$$

If the harmonic approximation is used for $\langle(\Delta r)^2\rangle$ it is possible to express $\langle \Delta r\rangle_{vib}$ as [98]

$$\langle \Delta r\rangle_{vib} \approx \left(\frac{3h}{8\pi}\right)(-F_3F_2^{-3/2})\,\mu^{-1/2} \tag{128}$$

where

$$F_3 \equiv (1/3)\,(\partial^3V/\partial r^3)_e \qquad F_2 \equiv (\partial^2V/\partial r^2)_e$$

and the temperature dependence has been suppressed. Herschbach and Laurie found that F_3 and F_2 are approximately exponential functions of internuclear distance, each described by a family of curves which are determined by the location of the bonded atoms in rows of the periodic table [105].

$$(-1)^nF_n = 10^{-(r_e-a_n)/b_n} \tag{129}$$

Thus we write

$$\langle \Delta r\rangle_{vib} \approx (3h/8\pi)\,\mu^{-1/2}\,10^{-D} \tag{130}$$

where

$$D \equiv (r_e - a_3)/b_3 - 3(r_e - a_2)/2b_2 \tag{131}$$

The constant in (130) is 19.35×10^{-3} if μ is in amu. The a_2, b_2, a_3 and b_3 are reproduced in Table 7 of [18]. A comparison of (130) with the $\langle \Delta r\rangle_{vib}$ calculated at 300 K using (107) and the known spectroscopic constants of a large set of diatomic molecules [106] shows good overall agreement for $\langle \Delta r\rangle_{vib}$ values from 3×10^{-3} Å to 25×10^{-3} Å [98]. What this means is that it is possible to estimate $\langle \Delta r\rangle$ for a diatomic molecule by knowing only the bond length. Similarly

$$\langle(\Delta r)^2\rangle \approx (h/4\pi)\,\mu^{-1/2}\,10^{+d} \tag{132}$$

where $d \equiv (r_e - a_2)/2b_2$.

To apply (122) to polyatomic molecules we need to be able to estimate $\langle \Delta r\rangle$ for a bond in a polyatomic molecule. For the majority of molecules, insufficient spectroscopic information is available to permit full dynamic calculations, so it is necessary to develop an approximation method in order to estimate the mean bond displacements for these molecules. It appears that stretching cubic constants for polyatomic molecules can be deduced from the bond length in the same way as for diatomic molecules. The Herschbach and Laurie parameters used for such estimation for diatomic molecules are found to describe F_3 for polyatomic molecules as well [98, 105].

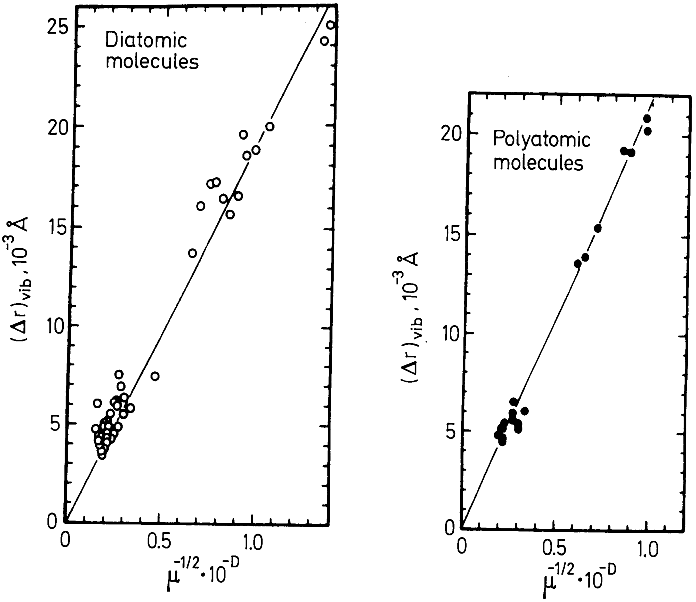


Fig. 11. Test of the approximation in (130) (straight line, slope = 19.35×10^{-3} is from (130)), against the calculated mean bond displacements for diatomic molecules. The same method is applied to polyatomic molecules; the straight line is a least-squares fit to the data (slope = 22×10^{-3}). D is defined in (131). Reproduced from Jameson CJ, Osten HJ (1948) J. Chem. Phys. 81: 4300, with permission [98]

Therefore we can use (130) to predict mean bond displacements in polyatomic molecules if the Morse anharmonic stretching accounts for most of the mean bond displacement [98].

In Fig. 11 the plots of $\mu^{-1/2}\ 10^{-D}$ vs. $\langle \Delta r \rangle_{vib}$ calculated for selected polyatomic molecules are compared with the results for some diatomic molecules [98]. A least-squares fit gives a slope of 22×10^{-3} rather than the 19.35×10^{-3} factor containing the fundamental constants in (130). The slope for the polyatomic molecules is somewhat larger because the other contributions due to bending and non-bonded interactions can be significant. Bartell has shown that, for molecules of the AX_n type, the Morse stretching contribution to $\langle \Delta r \rangle$ is only 64% in CH_4 [107], and only about 40% in SF_6 [108]. However, (130) with a modified factor of 22×10^{-3} for polyatomics gives a satisfactory estimate of $\langle \Delta r \rangle$ from r_e. Therefore we shall use

$$\langle \Delta r \rangle_{vib}/\text{Å} \approx 22 \times 10^{-3} \mu^{-1/2}\ 10^{-D} \tag{133}$$

where D is given by (131).

The rotational contribution to $\langle \Delta r \rangle$ is likewise easily estimated from r_e alone for an AX_n molecule [107]:

$$\langle \Delta r \rangle_{rot} = 2\bar{E}_{rot}/(nF_2 r_e) \tag{134}$$

where $\bar{E}_{rot}$ is the classical average, kT for linear molecules, and (3/2) kT for nonlinear ones, and F_2 is expressed according to (129). However, we do not even need $\langle \Delta r \rangle_{rot}$

for estimating most isotope shifts. For bent triatomic molecules it has been shown that rotation does not play a significant role in the isotope shifts of the central atom upon end atom substitution [109]. We have shown that for diatomic molecules there is no rotational contribution to the isotope shift; for symmetrical substitution in the highly symmetric molecular types (e.g., CH_4, BF_3, SF_6, CO_2) there is also no rotational contribution to the isotope shift. Even for unsymmetrical substitution in CH_4 isotopomers, the rotational contribution plays no role in the D-induced ^{13}C isotope shift. For the isotope shift of the end atom the rotational contribution is also not too important. For example, the dynamical factor relevant to the proton isotope shift in CH_4–CH_3D is -2.687×10^{-4} Å from rotation and 5.53×10^{-3} Å from vibration, only 5% contribution comes from rotation. For the proton isotope shift in $H_2{}^{16}O$–$H_2{}^{17}O$ the dynamical factor is -4.176×10^{-7} Å from rotation and 3.102×10^{-5} Å from vibration, only 1.4% rotational contribution [98].

On the basis of (122) and $\langle \Delta r \rangle$ estimated by (130) or (133), empirical estimates of $(\partial\sigma/\partial r)_e$ have been obtained from isotope shifts in various molecules [53, 98, 101, 109–112]. Some of these are compared with theory in Table 8. In these apparently favorable cases, there is reasonably good agreement between the empirical value of the derivative and the value obtained from theoretical (ab initio) calculations. In the inversion of the data to obtain an empirical first derivative, only the leading term involving the first derivative with respect to bond stretch was used and in many instances, only the estimation methods for Δr and $(\langle \Delta r \rangle - \langle \Delta r \rangle^*)$ as in (111) and (130) or (133) proposed by Jameson andOsten [98] were used instead of a full vibrational analysis. Some cancellation of second order terms may occur for this property as shown by Fowler and Raynes in the case of CH_4 [67, 69]. Fleischer et al. have noted that for a wide variety of small polyatomic molecules the nuclear shielding surface is remarkably close to a linear function of bond length at the equilibrium structure [113]. Ditchfield has found this to be the case also for the diatomic molecules H_2,

Table 8. Comparison of empirical estimates of $(\partial\sigma/\partial r)_e$ with theoretical values, ppm $Å^{-1}$

Nucleus	Molecule	$(\partial\sigma/\partial r)_e$ empirical	Ref.	$(\partial\sigma/\partial r)_e$ theor. (ab initio)	Ref.
^{1}H	H_2	−12.1, −11.5	[53, 98]	−20.7	[44]
	CH_4	−38	[110]	−25.42	[181]
^{11}B	BH_4^-	−26.7	[98]	−27.0	
^{13}C	CO	−456	[111]	−573.9, −535	[182, 183]
				−640, −413.7	[184, 95]
	CH_4	−35	[110]	−51.1, −52.62	[181, 70]
^{15}N	N_2	−910	[112]	−1090, −1132.5	[184, 182]
				−640	[96]
	NH_3	−124	[101]	−130.3, −129.2	[181, 185]
				−144	[113]
	NH_4^+	−65, −60	[98, 101]	−67.9	[181]
^{17}O	CO	−1150	[111]	−1166, −1077	[182, 183]
				−1240, −479	[184, 95]
	H_2O	−294	[109]	−270.9, −285	[58, 186]
		−296	[101]	−267.1, −275	[181, 185]
^{31}P	PH_3	−180	[117]	−150.8, −155, −148.4	[181, 113, 185]

LiH, and HF [44]. If the full shielding surface shown in Fig. 4 for H_2^+ is typical, the great sensitivity of nuclear magnetic shielding in molecules to bond stretching, and the nearly uniform negative sign of shielding derivatives with respect to bond stretch are easily understood.

6.2 General Trends in Secondary Isotope Effects

More observations of this mass dependence of electronic properties have been reported in NMR and ESR parameters than in other properties, thus many more of the general empirical observations have been made there than in other fields. The available high precision and resolution and the universality of the magnetic properties in all molecules make this possible. Isotope shifts of the order of a few parts per billion are now routinely observed in solution. NMR spectra showing isotope effects of the order of a few parts per million are shown in Fig. 12. These properties are site specific. The observations of a very large number of secondary isotope effects (i.e., the change in the observed property by isotopic substitution of an off-site (neighboring) atom) on nuclear magnetic shielding [114–116] have led to some interesting general trends.

The following trends were noted in the review of NMR isotope shifts by Batiz-Hernandez and Bernheim [114]:

1) The magnitude of the isotope shift is dependent on how remote the isotopic substitution is from the nucleus under observation.

2) The magnitude of the shift is largest where the fractional change in mass upon isotopic substitution is largest.

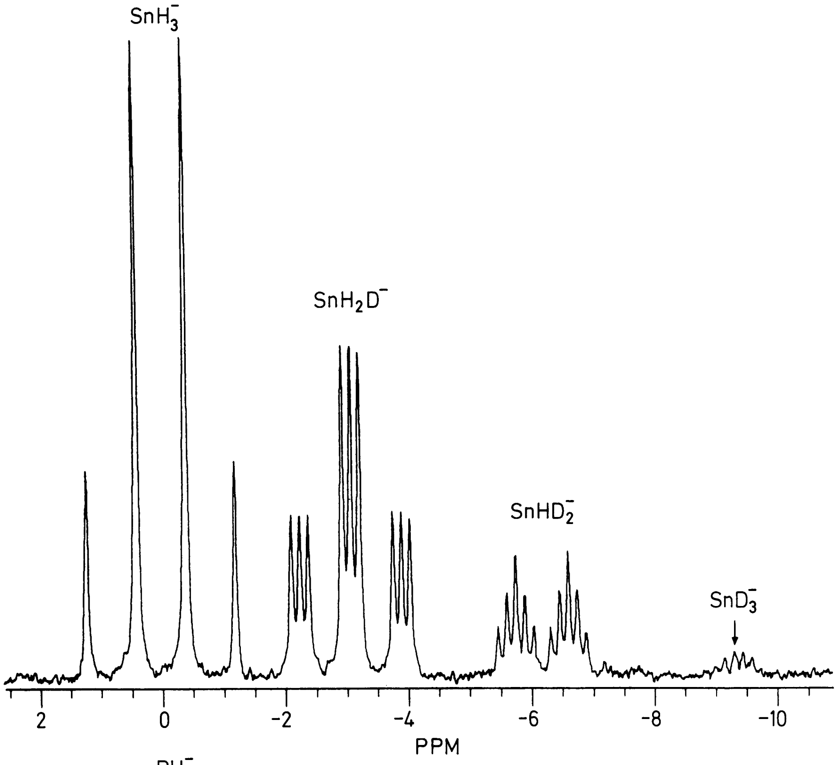
3) The magnitude of the shift is approximately proportional to the number of equivalent atoms in the molecule that have been replaced by isotopes.

4) Heavy isotopic substitution shifts the NMR signal of a nearby nucleus toward a higher magnetic field.

5) The magnitude of the shift is a function of the resonant nucleus, comparisons between nuclei reflecting the differences in their range of chemical shifts. The explanation of these observed trends have been given in [18, 91].

Secondary isotope effects on NMR spin-spin coupling constants have also been observed. These are fairly small so nearly all reports involve the large fractional mass change accompanying replacement of H with D. A review of the experimental data and interpretation in terms of the theory presented here was given by Jameson and Osten [83]. More recent experiments by Wasylishen et al. have revealed additional data such as isotope effects on J(NH) in NH_4^+ ion [100], J(PH) in PH_4^+ and PH_2^- [117] and J(SnH) in SnH_4 [102] and SnH_3^- [117]. The latter two isotope effects are large, −1.7 and 3.0 Hz respectively, and the signs are as predicted by the Jameson-Osten model.

Fig. 12. NMR spectra of ^{31}P in $PH_{2-n}D_n^-$ at 20 °C and of ^{119}Sn in $SnH_{3-n}D_n^-$ at −50 °C, both in liquid ▶ ammonia, showing the isotope effects on the average nuclear magnetic shielding. The shifts of the centers of the multiplets from the undeuterated species are additive. Reproduced from Wasylishen RE, Burford N (1987) Can. J. Chem. 65: 2707, with permission [117]


SnH$_3^-$
SnH$_2$D$^-$
SnHD$_2^-$
SnD$_3^-$
2
0
-2
-4
-6
-8
-10
PPM

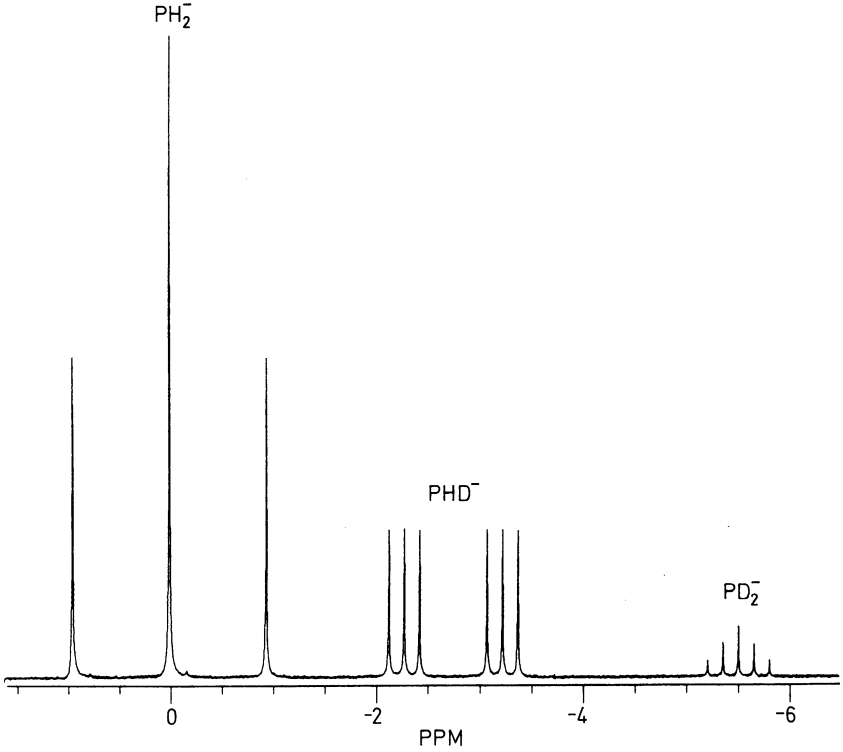

PH$_2^-$
PHD$^-$
PD$_2^-$
0
-2
-4
-6
PPM

Table 9. Secondary isotope effects in the gas phase quadrupole coupling constants of symmetric tops

Nucleus	Heavy-Light	Ref.	$\lvert eqQ \rvert_{Heavy} - \lvert eqQ \rvert_{Light}$	% Change
^{35}Cl	$^{13}CD_3Cl-CD_3Cl$	[187, 188]	−1.373 MHz	−1.8
^{75}As	AsD_3-AsH_3	[189]	+2.12	+1.3
^{121}Sb	SbD_3-SbH_3	[189]	+5.01	+1.1
^{35}Cl	$DCl-HCl$	[46]	−0.226	−0.33
^{79}Br	$^{13}CD_3Br-CD_3Br$	[190, 191]	−1.76	−0.31
^{79}Br	$DBr-HBr$	[47]	−1.673	−0.31
^{127}I	$DI-HI$	[192]	−4.912	−0.27
^{127}I	CD_3I-CH_3I	[193, 194]	−5.36	−0.27
^{79}Br	CD_3Br-CH_3Br	[191]	−1.42	−0.25
^{79}Br	$SiD_3Br-SiH_3Br$	[195]	−0.823	−0.25
^{35}Cl	CD_3Cl-CH_3Cl	[188]	−0.1802	−0.24
^{14}N	$DCN-HCN$	[196]	−0.0061	−0.13
^{14}N	CD_3CN-CH_3CN	[197]	+0.0049	+0.12
^{35}Cl	$DC{\equiv}CCl-HC{\equiv}CCl$	[198]	−0.01	−0.01
^{79}Br	$DC{\equiv}CBr-HC{\equiv}CBr$	[199]	−0.04	−0.006
^{127}I	$^{13}CH_3I-CH_3I$	[194]	−0.016	−0.0008

Other properties also show some of the same general trends. For example, in Table 9 the isotope shifts in nuclear quadrupole coupling constants upon deuteration at a neighboring site appear to be uniformly in the same direction, that is, the magnitude becomes smaller upon heavy atom substitution. The exceptions are the apex atoms As and Sb in the pyramidal hydrides. The general trend 1) is also noted in Table 9. The magnitude of the effect is dependent on the remoteness of the isotopic substitution from the nuclear site, comparing the DCl, HCl pair with $DC{\equiv}CCl$, $HC{\equiv}CCl$. Also, the $D_3{}^{13}CCl$–$D_3{}^{12}CCl$, difference is larger than the difference D_3CCl–H_3CCl in the chlorine nuclear quadrupole coupling constant. Trend 2) should be observed for all molecular electronic properties sensitive to bond stretching since the factor $(m'-m)/m'$ appears in both $\langle \Delta r \rangle$ and $\langle (\Delta r)^2 \rangle$.

Trend 3), universally observed in nuclear magnetic shielding, is clearly seen in the examples in Fig. 12 where the shift is in increments of —2.76, —5.52 ppm for one and two replacements of H by D in $PH_2{}^-$; similarly the increments are —3.1, —6.2, and —9.3 ppm for one, two, and three replacements of H by D in SnH_3^-. Additivity is also observed in the secondary isotope effects on NMR spin-spin coupling [83]. Some examples are J(PH) in $PH_{3-n}D_n$ [118] and $PH_{4-n}D_n^+$ [117], J(SnH) in $SnH_{4-n}D_n$ [102] and $SnH_{3-n}D_n^-$ [117]. Trend 3) has also been observed in proton hyperfine constants in naphthalene anion [119], that is, the effect of dideuteration can be deduced by adding up the effects observed in the monodeuterated anions, as shown in Fig. 13. The effect of α-deuterium substitution on the β proton hyperfine constants, and the effect of β deuterium substitution on α proton hyperfine constants are also additive for mono-, di-, tri-, and tetra-substituted isotopomers, although smaller than the α on α and the β on β effects shown in Fig. 13.

The *primary* isotope effects can not be determined easily in properties such as

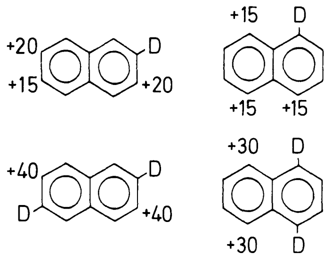


Fig. 13. Assignments of the experimental proton hyperfine splittings in the naphthalene-d anion radical and the corresponding splittings for the naphthalene-d_2 anion. Numbers are deviations of the splittings from the undeuterated naphthalene anion in milligauss, which are additive and are in agreement with the experimental data. Reproduced from Lawler RG, Bolton JR, Karplus M, Fraenkel GK (1967) J. Chem. Phys. 47: 2149, with permission [119]

nuclear magnetic shielding or nuclear quadrupole coupling constants because isotopic replacement of the nucleus in question involves not only a mass change but also a change in a nuclear parameter which is directly a part of the observed quantity, i.e., the nuclear magnetic dipole moment and electric quadrupole moment. Ratios of these quantities for nuclear isotopes are not very accurately known, with the exception of γ_H/γ_D which is 6.514 398 04 (120) [120]. Where γ_H/γ_D is involved, it is possible to make a determination of the primary isotope effect. Examples are discussed in Sect. 8.

The explanation of these general trends comes easily if we consider only the one term

$$\left(\frac{\partial P}{\partial r}\right)_e [\langle \Delta r \rangle - \langle \Delta r \rangle^*]$$

as in (122). Trends 1) to 3) can be attributed to dynamic factors. General trend 1) comes about because a secondary change in the average bond length at the site of the property upon isotopic substitution at a remote site is known to be negligibly small. At the same time, a site-specific property will clearly be most sensitive (large $(\partial P/\partial r)_e$) to changes in internal coordinates in its immediate vicinity; the change in a property upon infinitesimal bond extension at a remote site will be small in comparison, except when delocalized pi systems are involved. General trend 2) is clearly seen in the mass factors $[(m'-m)/m']$ $[m_A/(m_A + m)]$. General trend 3) is also clearly seen in (122) where the number s of isotopic substitutions explicitly appears as a factor when second and higher order terms are neglected. Deviations from additivity of isotope shifts are generally very small and have been found to be regular, in ratios 0:3:4:3:0 in $CH_{4-n}D_n$ types [99] or 0:1:1:0 in $PH_{3-n}D_n$ types [101], similar to deviations from additivity of zero-point energies [121]. The exceptions occur when intermolecular affects are involved [103].

The other general trends, such as 4) and 5) in nuclear shielding, are purely dependent on the nature of the electronic property surface at the equilibrium geometry of the molecule. Where the surface has a steep and nearly linear dependence on bond stretching at the equilibrium geometry, the single first derivative $(\partial P/\partial r)_e$ may dominate the observed mass dependence (and temperature dependence) of the property. On the other hand, some properties have an overwhelmingly large dependence on an out-of-plane bend in a planar molecule, in which instances (120) is used, i.e.,

$$\left(\frac{\partial^2 P}{\partial \theta^2}\right)_e [\langle \theta^2 \rangle - \langle \theta^2 \rangle^*]$$

will dominate the observed rovibrational effects. In either case the isotope shifts nearly directly provide information on the nature of $(\partial P/\partial r)_e$ or $(\partial^2 P/\partial\theta^2)_e$ even when a full rovibrational analysis is not feasible. Table 8 shows that in these favorable cases the empirical $(\partial\sigma/\partial r)_e$ obtained compares well with ab initio theoretical values where available. Other examples are given in [18].

Where both the isotope effect and the temperature dependence have been observed, it is sometimes possible to find a single empirical derivative which reproduces both effects within experimental error, using only the first term in (116) and (118). This has been found for $(\partial\sigma^F/\partial r)_e$ in SeF_6 and TeF_6 [80], $(\partial\sigma^V/\partial r)_e$ in $[V(CO)_6]^-$ and $(\partial\sigma^{Co}/\partial r)_e$ in $[Co(CN)_6]^{3-}$ [122]. In $\dot{C}H_3$ and $\dot{C}D_3$, using the observed temperature dependence of a^H, Moss obtains [123]

$$a_e^H = -24.46\,(29)\ \text{gauss}, \qquad (\partial^2 a^H/\partial\theta^2)_e = +152\,(24)\ \text{gauss rad}^{-2}$$

whereas, using the isotope effect he gets with (120), a very similar result

$$a_e^H = -24.19\,(13), \qquad (\partial^2 a^H/\partial\theta^2)_e = +111\,(13)\,.$$

Ab initio derivatives [89] with appropriate rovibrational averaging give the results shown in Table 6.

7 Higher Order Contributions

How important are the terms involving the second and higher derivatives? We have already seen in Tables 1, 4, and 5 the contributions of the terms in the second derivative of the electronic property to the rovibrational averages in diatomic molecules. In Table 4 we also see the combined contributions from 3rd to 6th derivatives. Calculations indicate that these contribute altogether only 1–5% of the rovibrational corrections to the proton shielding in H_2, HF, and LiH at 300 K, and 8% for ^{7}Li in LiH.

Let us now consider second derivative terms in polytomic molecules. A typical equation for a rovibrationally averaged property such as σ^C in CH_4 is (from (65) and (62)–(63)) [67]:

$$\begin{aligned}
\langle P\rangle = {} & P_e \\
\text{(a)}\quad & + 4P_r\bar{L}_1^1\langle q_1\rangle \\
\text{(b)}\quad & + 2P_r[\bar{L}_1^{2a2a}\langle q_2^2\rangle + \bar{L}_1^{3x3x}\langle q_3^2\rangle + \bar{L}_1^{4x4x}\langle q_4^2\rangle] \\
\text{(c)}\quad & + 2P_{rr}[(\bar{L}_1^1)^2\langle q_1^2\rangle + (\bar{L}_1^{3x})^2\langle q_3^2\rangle + (\bar{L}_1^{4x})^2\langle q_4^2\rangle] \\
\text{(d)}\quad & + 2P_{rs}[3(\bar{L}_1^1)^2\langle q_1^2\rangle - (\bar{L}_1^{3x})^2\langle q_3^2\rangle - (\bar{L}_1^{4x})^2\langle q_4^2\rangle] \\
\text{(e)}\quad & + \frac{9}{4}(P_{\alpha\alpha} + P_{\alpha\omega})(\bar{L}_5^{2a})^2\langle q_2^2\rangle + (P_{\alpha\alpha} - P_{\alpha\omega})[(\bar{L}_6^{3x})^2\langle q_3^2\rangle \\
& + (\bar{L}_6^{4x})^2\langle q_4^2\rangle] \\
\text{(f)}\quad & + 8P_{r\alpha}[\bar{L}_1^{3x}\bar{L}_6^{3x}\langle q_3^2\rangle + \bar{L}_1^{4x}\bar{L}_6^{4x}\langle q_4^2\rangle]
\end{aligned} \tag{135}$$

The individual contributions of terms (a) through (f) have been calculated for the CH_4 molecule, for the ^{13}C nuclear magnetic shielding in $^{13}CH_4$ and for the electric dipole polarizability and magnetizability in $^{12}CH_4$. Results are shown in Table 10. We see that the second order terms (b) through (f) cannot generally be neglected. In these examples the first derivative terms alone, (a) + (b), comprise 137% or 92% of the total calculated temperature dependence of σ^C or α and 120%, 69%, or 72% of the total mass dependence of σ^C, α, or χ and 122%, 69%, or 70% of the total zero-point correction to σ^C, α, or χ.

Early work in this field recognized that rotation plays an important role in the temperature dependence of an electronic property, even as the observed temperature and mass dependence of various properties are fitted to only the terms in the first derivatives [68–91]. A further approximation ignored the curvilinear corrections (terms of the type (b)) in (135) [41]. By the use of Bartell's method, curvilinear corrections (b) were also explicitly included [80, 124–131] but still only a fit to the terms in the first derivatives was used because there are far too many second derivatives to be determined empirically from experimental data. We now find (in Table 10) that

Table 10. Contributions of various terms in Eq. (135)[a]

P	Ref.	(a) P_r 1st order	(b) P_r 2nd order	(c) P_{rr}	(d) P_{rs}	(e) $P_{\alpha\alpha}$	(e) $P_{\alpha\omega}$	(f) $P_{r\alpha}$	Total
Zero-point corrections $\langle P\rangle^{0K} - P_e$									
$\frac{\sigma^C}{ppm}$	[69]	−2.781	−1.587	−1.696	−0.067	2.573	−0.057	0.024	−3.591
		(rot = 0)							
$\frac{\alpha}{au}$	[67]	0.366	0.209	0.131	0.003	0.125	0.001	0.004	0.839
		(rot = 0)							
$\frac{\chi}{10^{-29}JT^{-2}}$	[69]	−0.283	−0.162	0.021	0.001	−0.217	0.005	−0.003	−0.638
Temperature dependence $\langle P\rangle^{369K} - \langle P\rangle^{180K}$									
$\frac{\sigma^C}{ppb}$	[67]	−60.86	−11.14	−0.05	−0.03	15.61	3.87	0.11	−52.49
		(rot = −66.2)							
$\frac{\alpha}{10^4 au}$	[67]	79.90	14.34	0.04	0.01	7.42	0.29	0.15	102.10
		(rot = 86.8)							
Mass dependence $\langle P\rangle^{0K}_{CH_4} - \langle P\rangle^{0K}_{CH_4}$									
$\frac{\sigma^C}{ppm}$	[69]	0.763	0.406	0.453	−0.018	−0.686	0.059	0.001	0.978[b]
$\frac{\alpha}{au}$	[200]	−0.10	−0.053	−0.035	0.001	−0.033	−0.001	0.0	−0.221
$\frac{\chi}{10^{-29}JT^{-2}}$	[69]	0.077	0.041	−0.006	0.001	0.058	−0.006	0.0	0.165

[a] Rotational contribution ≈ 0 except where shown;

[b] Experimental value = 0.774

when only the terms in P_r are included, these terms account for 70–137% of the total rovibrational effects for a variety of electronic properties of CH_4. Calculations in H_2O also show that while the terms in P_r provide a large part of the contributions to the zero-point values, the temperature dependence, and the mass dependence of various molecular properties, the higher order terms can not be neglected. For example the isotope effect ($\langle P \rangle^{0K}_{OD2} - \langle P \rangle^{0K}_{OH_2}$) for σ^O is made up of -2.57, -0.01, -1.31, $+0.45$, -0.24 ppm from the terms in $(\partial\sigma/\partial r)_e$, $(\partial^2\sigma/\partial r^2)_e$, $(\partial\sigma/\partial\alpha)_e$, $(\partial^2\sigma/\partial\alpha^2)_e$, and 3rd and higher derivatives, respectively, giving a calculated total of -3.68 ppm [132].

It is fortunate that the P_r term constitutes such a large part of the observed rovibrational effects in some molecular electronic properties. Calculations to higher orders cannot be carried out in most molecules for which experimental data for electronic properties are available, whereas it is still necessary to make some sense out of the large body of information and look for some (albeit qualitative) predictive conclusions. However, the terms in the second derivatives are not insignificant. When the terms in the second derivatives are significant, a fitting of experimental data to one parameter leads to an empirical overestimation of P_r the first derivative of the property surface. On the other hand, fitting to more than one parameter is hazardous and could lead to unrealistic magnitudes specially when the contributions are not all the same sign. Examples of this pitfall are the fits to $(\partial\sigma^N/\partial r)_e$ and $(\partial\sigma^N/\partial\alpha)_e$ in NH_3 giving unphysical empirical estimates for these quantities [109], as is now obvious from ab initio calculations of these derivatives [133]. The empirical $(\partial\sigma^N/\partial r)_e$ values from the temperature dependence of the shielding of the two nitrogens in NNO are likewise flawed [129], being much too large compared to what one can obtain from the fit to the mass dependence [134].

These case studies of H_2O and CH_4 have included molecular electronic properties where the anharmonicity of the totally symmetric vibration gives an important contribution, since the properties happen to be very sensitive to bond extension and less so to angle deformations. Thus, the terms in the first derivatives of the property surfaces form the bulk of the rovibrational effects and the harmonic approximation is not at all applicable. In other molecular properties the terms in the first derivatives of the surface are not the most important ones. When the greatest sensitivity of the property is to non-totally symmetric displacements such as out-of-plane deformations, then the bulk of the observed rovibrational effects can be semi-quantitatively interpreted in terms of $\langle \theta^2 \rangle$ rather than $\langle \Delta r \rangle$ terms. In these cases the harmonic approximation is probably adequate unless some double- or multiple-minimum anharmonic potential describes the angle deformation.

8 Additional Examples

The best interpretation of experiment requires 1) experiments in the limit of zero pressure so as to exclude intermolecular effects, 2) measurements of rovibrational averages in several vibrational states and/or rotational states, 3) a good anharmonic potential energy surface with up to third derivatives with respect to normal coordinates and, 4) a sufficient number of theoretically calculated values of the electronic property at selected displacements from the equilibrium molecular structure such that derivatives P_r, P_α, $P_{r\alpha}$, etc. up to fourth derivatives of the electronic property with respect to curvilinear internal coordinates can be obtained by fitting. For some properties the measurements in specific rovibrational states are not feasible. Instead, averages given in (40) have been measured as a function of temperature and/or for different isotopomers. If simultaneously available, the temperature dependence and isotope shifts of the property can provide redundant or (less commonly) complementary information. When it is assumed that only one derivative overwhelmingly dominates both, then it becomes possible to interpret both observations with a single electronic factor such as $(\partial P/\partial r)_e$ [122] or $(\partial^2 P/\partial\theta^2)_e$ [90]. This forms the basis of the simultaneous interpretation of nuclear magnetic shielding temperature dependence in the zero-pressure limit and isotope shifts in the early work [41, 68, 91] which have been reviewed recently [18].

8.1 Primary Isotope Effects

The electron spin-nuclear spin hyperfine constant of an unpaired electron in a sigma bond provides a good example. In HgH molecule the electron spin density surface shifts the unpaired electron density from Hg to H as the bond lengthens, which is not unexpected since the unpaired spin is entirely on H in the limit of dissociation

$$(\mathrm{HgH})^{\bullet} \rightarrow \mathrm{Hg} + \dot{\mathrm{H}}$$

This shift corresponds to derivatives of the following signs:

$$\left(\frac{\partial \varrho_{\mathrm{Hg}}}{\partial r}\right)_e < 0 \quad \text{and} \quad \left(\frac{\partial \varrho_{\mathrm{H}}}{\partial r}\right)_e > 0\,.$$

If only the first derivative is included in the expansion in (1) then the effects of rovibrational averaging are as follows: ϱ_{Hg} and thus the nuclear hyperfine interaction constant a^{Hg} will decrease with increasing vibrational quantum number and decrease with increasing rotation. This is indeed observed in HgH, HgD, and HgT spectra, being most pronounced in HgH [54]. Since $\langle \Delta r\rangle_{\mathrm{HgH}} > \langle \Delta r\rangle_{\mathrm{HgD}}$ as discussed earlier then $[\langle a^{\mathrm{Hg}}\rangle_{\mathrm{HgD}}/\langle a^{\mathrm{Hg}}\rangle_{\mathrm{HgH}}] < 1$. This secondary isotope effect is indeed observed. ESR experiments reveal this ratio to be 0.992 and it was deduced that $\langle \varrho_{\mathrm{Hg}}\rangle_{\mathrm{HgD}} = 8.95$ au whereas $\langle \varrho_{\mathrm{Hg}}\rangle_{\mathrm{HgH}} = 8.88$ au [55]. Furthermore, we also expect $\langle \varrho_{\mathrm{H}}\rangle_{\mathrm{HgH}} > \langle \varrho_{\mathrm{H}}\rangle_{\mathrm{HgD}}$, a primary isotope effect. Since the observable a^{H} or a^{D} contains the factor γ_{H} or γ_{D}, the ratio $\varkappa$ is used:

$$\varkappa = \frac{\gamma_{\mathrm{D}}}{\gamma_{\mathrm{H}}} \cdot \frac{a^{\mathrm{H}}}{a^{\mathrm{D}}} = \frac{a^{\mathrm{H}}}{6.514\, a^{\mathrm{D}}} = \frac{\langle \varrho_{\mathrm{H}}\rangle_{\mathrm{HgH}}}{\langle \varrho_{\mathrm{D}}\rangle_{\mathrm{HgD}}}$$

$\varkappa$ in this case is predicted to be greater than 1. The ESR experiments showed $\varkappa = 1.019$ [55].

A related property is the nuclear spin-spin coupling J observed in NMR. The terms in the effective hamiltonian for a and J are shown below:

$$H_2 = 2\mu_B\hbar(\mu_0/4\pi) \sum_N \gamma_N \sum_k [3(\mathbf{S}_k \cdot \mathbf{r}_{kN})(\mathbf{I}_N \cdot \mathbf{r}_{kN}) r_{kN}^{-5} - (\mathbf{S}_k \cdot \mathbf{I}_N) r_{kN}^{-3}] \tag{136}$$

$$H_3 = (16\pi\mu_B\hbar/3)(\mu_0/4\pi) \sum_N \gamma_N \sum_k \delta(r_{kN}) \mathbf{S}_k \cdot \mathbf{I}_N \tag{137}$$

With these perturbation terms in the molecular hamiltonian $\mathbf{a}^N$ is the tensor which appears in the $\mathbf{S} \cdot \mathbf{a}^N \cdot \mathbf{I}_N$ terms in the first order correction to the energy for a non-singlet electronic state. $\mathbf{J}$ is the tensor in the $\mathbf{I}_N \cdot \mathbf{J}(NN') \cdot \mathbf{I}_{N'}$ terms in the second order correction to the energy. Only the trace of the tensor is observed in the gas or in solution. The reduced spin-spin coupling constant K is defined as

$$K(NN') = 4\pi^2 J(NN')/h\gamma_N\gamma_{N'} \tag{138}$$

We note that each half of the interaction in the second order perturbation theory expression for J is similar to that of the interaction for a. This has been used to advantage in creating models for interpretation of both properties [135–140, 83]. In the simplest case, the transfer of spin density from X to H upon bond extension in the above discussion of a^H and a^X translates to an increase in the reduced one-bond spin spin coupling constant K upon bond extension [83]. When only this first derivative is considered, this would mean that

$$\varkappa = \frac{\gamma_D}{\gamma_H}\frac{J(XH)}{J(XD)} > 1 .$$

The model depends on the dominance of the derivative of the Fermi contact mechanism, as has been shown theoretically in J(CO) [14] in Fig. 2. A review of the available data does show $\varkappa > 1$ where the above model is applicable. The model has been extended to one-bond couplings in which terms of opposite sign contribute in the Fermi-contact mechanism [83]. The presence of a lone pair on one of the coupled atoms has long been known to be associated with $K < 0$ for one-bond couplings. The sign of the derivative $(\partial K/\partial r)_e$ then depends on which term changes greatly upon bond extension. It was proposed by Jameson and Osten that in the usual situation (as for J(CH) in CH_4) $\varkappa > 1$, but in those other cases where a lone pair was involved, $\varkappa < 1$. Theoretical calculations on J(HF) lead to $\varkappa < 1$ as well, in agreement with these arguments [141]. Indeed, nearly all cases of $\varkappa < 1$ involve a lone pair on one of the coupled atoms, as in H_2Se, PH_3, $PhPH_2$, Ph_2PH [83]; and the more recently reported couplings in H_2O, PH_2^-, SnH_3^-, NH_3 also exhibit $\varkappa < 1$ [117, 142, 101]. In contrast, the lack of the lone pair in related molecules is accompanied by $\varkappa > 1$, in support of the Jameson-Osten model. These are shown in Table 11. NH_4^+ ion is an exception which has also exhibited exceptional ^1H secondary isotope shifts of the nuclear magnetic shielding constant, attributed to differential intermolecular (hydrogen bonding) effects [103].

A substantially different situation of rovibrational averaging attends the hyperfine constant of an unpaired electron largely in a pi orbital on an adjacent nucleus. Typical

Table 11. Comparison of primary isotope effect on spin spin couplings in related molecules

With lone pair	$\varkappa$	Ref.	No lone pair	$\varkappa$	Ref.
PH_2^-	0.98	[117]	PH_4^+	1.003	[117]
PH_3	0.93	[118]			
SnH_3^-	0.90	[142, 117]	SnH_4	1.001	[102]
			SnH_3^+	1.004	[102]
NH_3	0.992	[101]	NH_4^+	0.996	[101]
H_2O	0.996	[101]			

examples of this are $\dot{C}H_3$ and $[\dot{N}H_3]^+$ which are planar molecules. More complex examples are benzene anion or cation or other planar aromatic radicals. McConnell [143] has described the spin density on the proton in terms of a simple model,

$$\varrho_H \propto a^H = Q_{CH}\varrho^\pi \tag{139}$$

where $Q_{CH} < 0$; the spin density on H is due to a coupling between the sigma and pi electron system, with a spin polarization parameter Q_{CH} relating the spin density on H to the spin density on the adjacent carbon pi orbital. The coupling parameter is expected to decrease with increasing CH bond length and increase with out-of-plane bending. The first derivatives $(\partial\varrho_H/\partial q)_e$ where q is a normal coordinate are of either sign depending on whether the vibration assists spin polarization or not. If $(\partial\varrho_H/\partial r_{CH})_e < 0$ is the important term, then one expects to find

$$\varkappa = \frac{\langle\varrho_H\rangle}{\langle\varrho_D\rangle} < 1$$

and

$$\frac{d\langle\varrho_H\rangle}{dT} < 0 \quad \text{and} \quad \frac{d\langle a^H\rangle}{dT} < 0\,. \tag{140}$$

It has also been suggested that the observed temperature dependence is primarily due to out-of-plane vibrations, i.e., that the $(\partial^2\varrho_H/\partial\theta^2)_e\,\langle\theta^2\rangle^T$ term in (64) is responsible [144, 145], where θ is the out-of-plane angle and $(\partial^2\varrho_H/\partial\theta^2)_e < 0$. In the McConnell model these derivatives would correspond to

$$(\partial|\,Q_{CH}\,|/\partial r_{CH})_e < 0 \quad \text{and} \quad (\partial^2|\,Q_{CH}\,|/\partial\theta^2)_e < 0 \tag{141}$$

neglecting $(\partial\varrho^\pi/\partial r)_e$ and $(\partial^2\varrho^\pi/\partial\theta^2)_e$. Both the bond stretching and the out-of-plane bending lead to a primary isotope effect $\varkappa < 1$ and negative temperature coefficients $d\langle\varrho_H\rangle/dT < 0$. The $\varkappa < 1$ was first observed in $[\dot{N}H_3]^+$ and $[\dot{N}D_3]^+$ by Cole [146]; other examples are $\dot{C}H_3/\dot{C}D_3$ [147] and $CH_3\dot{C}H_2/CH_3\dot{C}D_2$ [147], in which $\varkappa$ was found to be respectively 0.986, 0.989, and 0.990. It is also found that $d\langle\varrho_H\rangle/dT < 0$ for $\dot{C}H_3$ [148–150], benzene anion [147], benzene cation [151], and $C_7H_7^-$ [152]. The relatively lower frequencies of out-of-plane bends compared to stretching frequencies and the relatively large temperature coefficients of *a* compared to other observables seem to indicate that (at least in the planar systems) the out-of-plane vibrational averaging makes significant contributions. The dominance of the out-of-plane bend over the other modes in the zero-point vibrational contributions to a^H has been demonstrated in calculations for $\dot{C}H_3$ [153] and $\dot{N}H_3^+$ [154]. Table 6 shows that the $\varkappa < 1$ and the temperature dependence in the typical case of $\dot{C}H_3$ and its isotopomers are reproduced reasonably well by calculations. It is encouraging that the calculations support the above semi-quantitative descriptions, lending credibility to their use in other cases where calculations as accurate as those in Table 6 are not available.

The sign of the temperature coefficient of a^H for protons attached to proximate $\dot{C}$ is by no means uniformly negative. An interesting correlation is that $d| a^H |dT < 0$ when the spin density is positive (usual) on both the proximate and adjacent carbons, whereas $d| a^H |/dT > 0$ are found for protons attached to sites of *negative* spin density although the adjacent carbons have large positive spin densities. This correlation is consistent with (141) and (139), and may be assisted by $(\partial \varrho^\pi/\partial r)_e$, $(\partial^2 \varrho^\pi/\partial \theta^2)_e > 0$.

β and γ C–H protons are known to exhibit large positive temperature coefficients. Early examples are $CH_3\dot{C}H_2$, in which it is also observed that $\varkappa = 1.011$ in the comparison $CH_3\dot{C}H_2/CD_3\dot{C}H_2$ and $\varkappa = 1.178$ in $CH_3\dot{C}H_2/CHD_2\dot{C}H_2$ [147]. In these cases Stone and Maki suggested that hindered internal rotations could lead to the large temperature coefficients of β proton hyperfine constants [85]. Single crystal studies reveal the torsional angle (ϕ) dependence [84]:

$$a^H_{CH_\beta} = a_0 + a_2 \cos^2 \phi \,. \tag{142}$$

Averaging over the torsional states alone, using a reasonable estimate of a torsional barrier accounts for most of the temperature dependence. Of course, complete agreement with experiment is not expected unless the calculations include all the vibrational modes. A review of temperature-dependent hyperfine constants in organic free radicals has been given by Sullivan and Menger [86].

8.2 Beyond the Born-Oppenheimer Approximation

The necessity of some nonadiabatic corrections have been suggested for isotope effects on various electronic properties, especially electric dipole moments. Some ab initio calculations of property surfaces which include nonadiabatic corrections are in Table A1 (see Appendix). In the interpretation of vibrational circular dichroism using theories based on the usual expansion of a property in terms of nuclear displacements, the calculations have to go beyond the Born-Oppenheimer approximation to include the distortion of the electronic wavefunction by nuclear displacements. Whereas the adiabatic approximation allows the vibronic wavefunctions to be written as $\phi_n^{(0)}(\mathbf{r}) \cdot \chi_v(\mathbf{R})$, the vibronic wavefunction which includes nonadiabatic corrections to first order is

$$\Psi_{nv}(\mathbf{r}, \mathbf{R}) \approx \phi_n^{(0)}(\mathbf{r}) \cdot \chi_v(\mathbf{R}) - \sum_{m \neq n} \sum_{v''} \sum_{s} \frac{\phi_m^{(0)} \chi_{v''} \langle \phi_m^{(0)} | (\partial H_0/\partial q_s)_{R_0} | \phi_n^{(0)} \rangle \langle \chi_{v''} | q_s | \chi_v \rangle}{E_m^{(0)} - E_n^{(0)} + \hbar\omega_{v''v}} \tag{143}$$

$\chi_v(R)$ are the second order wavefunctions of the rovibrational hamiltonian, $|T_1^{-1} T_2^{-1} X^{(0)}\rangle$ in (16). The appropriate average of a property $\langle P \rangle$ is then $\langle \Psi_{nv}| P |\Psi_{nv}\rangle$, which includes not only the averages over the zeroth order vibronic function (1st term in (143)) as explicitly given in (28)–(33) but also the contributions from the distortion of the electronic wavefunction by nuclear displacement. However, the alternate formalism by Buckingham, Fowler, and Galwas [24], in which a molecular electronic property surface (the magnetic dipole moment **m**) is expanded in terms of nuclear velocities, leads to a theory which provides the magnetic dipole vibrational transition integrals in terms of derivatives $(\partial \mathbf{m}/\partial \dot{\mathbf{R}}_N)$ which can be calculated within the clamped nucleus approximation [24].

A clear indication of non-Born-Oppenheimer behavior was noted in some free radicals. Hyperfine constants in orbitally degenerate or nearly degenerate electronic states show unusually large temperature coefficients and deuteration effects. Examples of these are $C_6H_6^-$ anion [155–157], $C_7H_7^-$ [158, 152], naphthalene anion [119]. The comparison of a^H with a^D as in $C_6H_6^-/C_6D_6^-$, show $\varkappa < 1$ as expected [157]. Furthermore, the proton hyperfine constants at the undeuterated positions in a partly deuterated species are altered, and the $\varkappa$ and the temperature coefficients for H positions made nonequivalent by deuteration are different from each other and are larger or smaller than in the parent anion [157]. It has been suggested [159] that these cases are subject to the effects of the Jahn-Teller theorem [160]. Vibronic interactions have to be taken into account because the observed effects on deuterium substitution are different and greater than would be expected in the context of the Born-Oppenheimer approximation. Symmetric substitution (as in benzene 1,3,5-d_3 and benzene-d_6 anions) do not lift the degeneracy.

8.3 Rovibrational Averaging Effects on the Determination of Molecular Geometry of Semi-rigid Molecules

Various definitions and interrelations of the geometric structures of polyatomic molecules have been reviewed by Kuchitsu and Oyanagi [161] and by Lide [162], and earlier by Herschbach and Laurie [163]. See also [163a] the desired geometry is of course the equilibrium geometry, that is, that which corresponds to the global minimum in the potential energy surface of the molecule as defined in the Born-Oppenheimer sense. This is never directly observed. Depending on the experiment, various rovibrationally averaged quantities related to geometry can be obtained, some of which are discussed here.

8.3.1 Diatomic Molecules

The averages which can be obtained from experiment are typically taken from spectroscopy in the form of the molecular rotational constant, or the direct nuclear spin-spin coupling, or a bond distance from electron diffraction. The rotational constant is inversely proportional to the moment of inertia so that the observed average is $\langle r^{-2}\rangle^{-1/2}$ for a given vibrational level. On the other hand, the direct nuclear spin spin coupling constant is proportional to components of the dipolar interaction tensor so that the observed average is $\langle r^{-3}\rangle^{-1/3}$ for a given vibrational level if observed in a molecular beam resonance spectrum, or a thermal average if observed in an NMR spectrum of oriented molecules. Thus, from spectroscopy one gets average nuclear *positions* in the principal inertial axes. On the other hand, from electron diffraction one gets thermal average internuclear *distances*, $\langle r \rangle$. Written in terms of the averages $\langle \xi \rangle$ and $\langle \xi^2 \rangle$ defined in (45)–(46) these are [163]:

$$\langle r^{-2} \rangle^{-1/2} = r_e \left\{ 1 + \langle \xi \rangle - \frac{3}{2} \langle \xi^2 \rangle + \ldots \right\} \tag{144}$$

$$\langle r^{-3} \rangle^{-1/3} = r_e \{ 1 + \langle \xi \rangle - 2 \langle \xi^2 \rangle + \ldots \} \tag{145}$$

$$\langle r \rangle = r_e \{ 1 + \langle \xi \rangle + \ldots \} \tag{146}$$

The structure obtained from rotational constants is called the "r_0" structure corresponding to the zero-point average, $\langle r^{-2} \rangle_{v=0}^{-1/2}$. On the other hand, $\langle r \rangle$ is essentially identical to one of the widely used types of distances derived from electron diffraction, the "r_g" structure, the center of gravity of the radial distribution function [164]

$$r_g = \frac{\int_0^\infty r P(r)\, dr}{\int_0^\infty P(r)\, dr} \tag{147}$$

which represents the average of instantaneous internuclear distance over all the vibrations of the molecule, is a function of the distribution of molecules over vibrational states.

8.3.2 Polyatomic Molecules

From rotational constants or effective moments of inertia I_0, one gets the r_0 structure which corresponds to the zero point average nuclear positions, as in diatomic molecules. On the other hand, these effective moments of inertia I_0 can be corrected to give a set of moments I^* from which a structure called the r_z structure can be calculated. It was shown by Morino et al. [165] and by Herschbach and Laurie [163] that the removal of the harmonic part of the vibrational dependence of the effective moments I_0 yields the moments (I^*) which correspond to a rigid molecule in which each atom is frozen at its average position. The differences in the r_z structure of various isotopomers of several triatomics have been calculated and these reveal additivity in multiple substitutions [161].

The simplest way of comparing the various types of averages in polyatomic molecules is by expressing the averages in terms of local cartesian displacements: Δz is an instantaneous displacement of r(A–X) projected on the equilibrium A–X axis taken as a local z axis, Δx and Δy denote the displacements perpendicular to the equilibrium internuclear axis z [165]. The thermal average internuclear *distance* from electron diffraction

$$r_g = \langle r \rangle = r_e + \langle \Delta r \rangle^T \cong r_e + \langle \Delta z \rangle^T + \frac{(\langle \Delta x^2 \rangle^T + \langle \Delta y^2 \rangle^T)}{2 r_e} + \delta r_{cent} \tag{148}$$

where δr_{cent} is the displacement due to centrifugal stretching, the rotational contribution already discussed in Sect. 6.1.1. The $\langle \Delta r \rangle^{T}$ in (148) for C–H in CH_4 is the same as in (62). Since anharmonic force fields are not accurately known for most molecules while harmonic force constants are more readily available, partial rovibrational corrections are usually attempted, leading to the "r_α" structure which is the distance between the average nuclear positions at thermal equilibrium

$$r_\alpha = r_g - \frac{(\langle \Delta x^2 \rangle^{T} + \langle \Delta y^2 \rangle^{T})}{2r_e} - \delta r_{\mathrm{cent}} \tag{149}$$

$$\cong r_e + \langle \Delta z \rangle^{T} \tag{150}$$

For C–H in CH_4, one obtains

$$r_\alpha = r_e + \bar{L}_1^1 \langle q_1 \rangle_{\mathrm{vib}} \tag{151}$$

when the harmonic corrections

$$\frac{\langle \Delta x^2 \rangle^{T} + \langle \Delta y^2 \rangle^{T}}{2r_e} \quad \text{or} \quad \frac{1}{2} \{ \bar{L}_1^{2a2a} \langle q_2^2 \rangle + \bar{L}_1^{3x3x} \langle q_3^2 \rangle + \bar{L}_1^{4x4x} \langle q_4^2 \rangle \}$$

are made on the electron diffraction distances. When extrapolated to 0 K r_α becomes practically identical with the r_z structure [161].

$$r_\alpha(0\,K) = r_e + \langle \Delta z \rangle^{0\,K} \cong r_z \tag{152}$$

Obviously, the harmonic corrections which need to be made on r_g values from electron diffraction or $\langle r^{-2} \rangle^{-1/2}$ values from rotational constants [165, 163] are different from the harmonic corrections which need to be made on $\langle r^{-3} \rangle^{-1/3}$ values from NMR dipolar coupling constants [166, 59], but all should lead to the same r_α structure. A knowledge of the anharmonic force field further converts [via (151) for CH_4, for example] the r_α structure to the desired equilibrium r_e structure. Actually, the harmonic corrections usually made to obtain the r_α structure are usually only approximate since the correct harmonic force field can only come out of a complete anharmonic vibrational analysis which reproduces all the observed frequencies for all isotopomers of the molecule.

8.4 Rovibrational Averaging in van der Waals Molecules

Rotational constants of van der Waals complexes can be obtained from their microwave spectra in molecular beam resonance spectroscopy. However, large amplitude anharmonic vibrations against the weak intermolecular bonds of these molecules usually mean that the average structural parameters of the various isotopes will differ significantly. In many cases, average nuclear quadrupole coupling constants and dipole moment components provide additional information. For the purposes of determining an average structure it is commonly assumed that the ^{35}Cl quadrupole coupling constant observed, in HCl–Ar for example, is unchanged from that in the isolated HCl molecule so that the observed coupling constant in HCl–Ar is merely a vibrationally averaged projection of $eq_{zz}Q$ of the diatomic along the inertial axis of HCl–Ar:

$$\langle eqQ \rangle \approx \langle eq_{zz}Q \rangle_{diat} \langle (3\cos^2\theta - 1)/2 \rangle \tag{153}$$

Since the diatomic molecule has been studied separately, the observed $\langle eqQ \rangle$ in the complex then provides the angle that HCl makes with the inertial axis of the complex, in the form of an average $\cos^{-1} \langle \cos^2\theta \rangle^{1/2}$. The equilibrium angle that corresponds to the nonvibrating complex at the minimum of its potential surface can be obtained only if the potential surface derivatives are known. In the examples of semi-rigid molecules discussed in the preceding sections, the values $\langle \Delta r \rangle$, $\langle (\Delta r)^2 \rangle^{1/2}$, $r_e \langle (\Delta\alpha)^2 \rangle^{1/2}$, etc. are very small, of the order of $10^{-3}\, r_e$ to $10^{-5}\, r_e$, so that the rovibrational corrections to obtain the equilibrium geometry are small. The same is no longer true in van der Waals complexes. The difference between the average and equilibrium geometry of these complexes is not usually small. In Ar–ClH the equilibrium polar angle θ is 0° while the average angles obtained via (153) from the ^{35}Cl quadrupole coupling constant are: $<$ArClD is 33.8° and $<$ArClH is 41.5° [167, 168].

It has been found that this assumption of no change in q_{zz} in the monomer upon complex formation is not appropriate. This has been demonstrated, for example, when the rotational constants and $\langle eqQ \rangle$ values for ^{14}N and D in 11 isotopomers of $(HCN)_2$ were determined from pulsed FT microwave spectroscopy [169]. If the dimer is treated as rigid linear monomers tilted away from the line of centers of mass, the average angles of tilt and the $\langle eq_{zz}Q(^{14}N) \rangle$ in (153) can be independently determined without making the assumption that the latter are the same as in the monomer. The difference between the derived $\langle eq_{zz}Q \rangle$ value in (153) and the $\langle eq_{zz}Q \rangle$ value for the isolated HCN monomer is found to be 4.9% and 2.3%, accounting for about 40% of the observed $[\langle eqQ \rangle_{complex} - \langle eq_{zz}Q \rangle_{monomer}]$ [(169].

The effects of isotopic substitution on the components of the dipole moment of a van der Waals complex along the inertial axes provide additional information. Here too it is not necessary to assume that $\langle \mu_z \rangle$ in the complex is the same as that for the isolated monomer. In cases where the quadrupole coupling constants as well as the dipole moment components of the complex are determined for a large number of isotopomers, the isotopic substitution trends in the quadrupole coupling and in the dipole moments are consistent [170].

A complete vibrational analysis of a van der Waals complex is made tractable by a separation of the large amplitude motions associated with the intermolecular or hydrogen bonds and the small amplitude motions associated with the semirigid monomers. The Born-Oppenheimer separation of slow coordinate ϱ from fast coordinates q_1 and q_2 can also be used for the separation of low and high frequency modes. The energy levels of the fast coordinates q_1 and q_2 can be solved at a frozen value for the slow coordinate ϱ. This is done for different values of ϱ to determine $E_v(\varrho)$. The latter is then used as the potential energy to solve for motion in ϱ. This has been applied to the $(HF)_2$ dimer. $(HF)_2$ is a hydrogen-bonded dimer with a planar asymmetric top structure which tunnels between two equivalent maxima on the potential surface. The slow coordinate ϱ is $(\theta_2 - \theta_1)$, a tunneling coordinate [171].

The empirical potential energy surface was determined by Barton and Howard [172] by inversion of the spectroscopic data from radiofrequency and microwave spectra of Dyke et al. [173]. Interpretation of high resolution infrared spectra of the dimer in the H-stretching region require corrections to the zero$^{\text{th}}$ order Born-Oppenheimer approximation, however [171]. The extra terms which appear in the Schrödinger equation for the slow coordinate have been derived in general [174]. In part these result from the change in the form of the high frequency normal coordinates with a change in the tunneling coordinate ϱ. The dynamic interaction of the tunneling momentum with the high frequency vibrations adds to the effective barrier when the high frequency stretching vibrations are excited [171]. Of course, for molecules with large amplitude internal motions, the notion of an equilibrium geometry is no longer appropriate. An alternative approach to the description of nuclear motion which has been found particularly useful in the study of van der Waals molecules is given by Sutcliffe and Tennyson [13].

9 Conclusions

We have shown that rovibrational corrections almost always need to be included in order to obtain from experiment the value of the electronic property at the structure corresponding to the potential energy minimum, and vice versa, rovibrational corrections have to be included in ab initio calculations of electronic properties before comparing with experiment. Where vibrational state dependence and rotational state dependence can be measured precisely (rarely) it is possible to obtain individually from experiment the derivatives of a property with respect to normal coordinates. The observed temperature dependence and isotope shifts of an electronic property contain information about the property derivatives but inversion of the data to find empirical property surface derivatives is not always possible. We have found some cases in which isotope shift data provide empirical derivatives which are in reasonably good agreement with the best available ab initio calculations.

When the property has a nearly linear dependence on bond stretching, or an overwhelmingly large $(\partial^2 P/\partial\theta^2)_e$ for example, then general trends appear in its temperature and mass dependence which make it possible to make qualitatively insightful predictions and correlations with other related properties of the same molecule. For quantitative interpretation of experiments however, it is virtually necessary to carry out a fully correlated ab initio calculation of the property surface in the immediate vicinity of the potential minimum as well as perform a complete rovibrational averaging on the potential surface (usually a semi-empirical one) in order that the terms in second or higher order can be included, since these are not always negligibly smaller than the leading terms.

10 References

1. Allerhand A, Dohrenwend M (1985) J. Am. Chem. Soc. 107: 6684
2. Jameson CJ, Jameson AK, Oppusunggu D (1986) J. Chem. Phys. 85: 5480
3. Michelot F (1982) Mol. Phys. 45: 971
4. Michelot F (1982) Mol. Phys. 45: 949

5. Flygare WH (1964) J. Chem. Phys. 41: 793
6. Eshbach JR, Strandberg WP (1952) Phys. Rev. 85: 24
7. Geratt J, Mills IM (1968) J. Chem. Phys. 49: 1719
8. Danishoh Jørgensen P, Simons J (eds) (1985) Geometrical derivatives of energy surfaces and molecular properties, Reidel, Dordrecht
9. Bishop DM (1987) J. Chem. Phys. 86: 5613
10. Bishop DM, Cheung LM, Buckingham AD (1980) Mol. Phys. 41: 1225
11. Adamowicz L, Bartlett RJ (1986) J. Chem. Phys. 84: 4988
12. Amos RD (1987) Adv. Chem. Phys. 67 (Part 1): 99
13. Sutcliffe BT, Tennyson J (1981) In: Avery J, Dahl JP, Hansen AE (eds) Understanding Molecular Properties, Reidel, Dordrecht
14. Geertsen J, Oddershede J, Scuseria GE (1987) J. Chem. Phys. 87: 2138
15. Sileo RN, Cool TA (1976) J. Chem. Phys. 65: 117
16. Ogilvie JF, Rodwell WR, Tipping RH (1980) J. Chem. Phys. 73: 5221
17. Werner HJ, Reinsch EA, Rosmus P (1981) Chem. Phys. Lett. 78: 311
18. Jameson CJ, Osten HJ (1986) Ann. Reports NMR Spectrosc. 17: 1
19. Hegstrom RA (1979) Phys. Rev. A 19: 17
20. Spirko V, Blabla J (1988) J. Mol. Spectrosc. 129: 59
21. Fowler PW, Buckingham AD (1985) Chem. Phys. 98: 167
22. Lazzeretti P, Zanasi R (1986) Phys. Rev. A 33: 3727
23. Fowler PW, Raynes WT (1982) Mol. Phys. 45: 667
24. Buckingham AD, Fowler PW, Galwas PA (1987) Chem. Phys. 112: 1
25. Lazzeretti P, Zanasi R, Stephens PJ (1986) J. Phys. Chem. 90: 6761
26. Morrison MA, Hay PJ (1979) J. Chem. Phys. 70: 4034
27. Nafie LA, Freedman TB (1983) J. Chem. Phys. 78: 7108; Nafie LA (1983) J. Chem. Phys. 79: 4950
28. Toyama M, Oka T, Morino Y (1964) J. Molec. Spectrosc. 13: 193
29. Amat G, Nielsen HH, Tarrago G (1971) Rotation-vibration of polyatomic molecules. Dekker, New York
30. Fowler PW (1981) Mol. Phys. 43: 591
31. Secroun C, Barbe A, Jouve P (1973) J. Mol. Spectrosc. 15: 1
32. Marcott C, Golden WG, Overend J (1978) Spectrochim. Acta A 34: 661
33. Amat G, Goldsmith M, Nielsen HH (1957) J. Chem. Phys. 27: 838
34. Buckingham AD (1962) J. Chem. Phys. 36: 3096
35. Herman RM, Short S (1968) J. Chem. Phys. 48: 1266
36. Krohn BJ, Ermler WC, Kern WC (1974) J. Chem. Phys. 60: 22
37. Riley G, Raynes WT, Fowler PW (1979) Mol. Phys. 38: 877
38. Overend J (1978) J. Chem. Phys. 64: 2878
39. Overend J (1982) In: Person WB, Zerbi G (eds) Vibrational intensities in infrared and Raman spectroscopy. Elsevier, Amsterdam, p 190, p 203
40. Person WB, Overend J (1977) J. Chem. Phys. 66: 1442
41. Jameson CJ (1977) J. Chem. Phys. 67: 2814
42. Fowler PW (1984) Mol. Phys. 51: 1423
43. Fowler PW (1982) Mol. Phys. 46: 913
44. Ditchfield R (1981) Chem. Phys. 63: 185
45. Oddershede J, Geertsen J, Scuseria GE (1988) J. Phys. Chem. 92: 3056
46. Kaiser EW (1970) J. Chem. Phys. 55: 1686
47. Johnson DW, Ramsey NF (1977) J. Chem. Phys. 67: 941
48. Tokuhiro T (1967) J. Chem. Phys. 47: 109
49. Cade PE (1967) J. Chem. Phys. 47: 2390
50. Ozier I, Ramsey NF (1966) Bull. Am. Phys. Soc. 11: 23
51. Reid RV, Chu AH (1974) Phys. Rev. A9: 609
52. Verberne J, Ozier I, Zandee L, Reuss J (1978) Mol. Phys. 35: 1649
53. Raynes WT, Panteli N (1983) Mol. Phys. 48: 439
54. Eakin DM, Davis SP (1970) J. Mol. Spectrosc. 35: 27
55. Knight LB, Weltner W (1971) J. Chem. Phys. 35: 2061
56. Lucken EAC (1983) Adv. Nucl. Quad. Reson. 5: 83

57. Hoy AR, Mills IM, Strey G (1972) Mol. Phys. 24: 1265
58. Fowler PW, Raynes WT (1981) Mol. Phys. 43: 65
59. Lounila J, Wasser R, Diehl P (1987) Mol. Phys. 62: 19
60. Buckingham AD (1967) Adv. Chem. Phys. 12: 107
61. Cyvin SJ, Rauch JE, Decius JC (1965) J. Chem. Phys. 43: 4083
62. Buckingham AD, Love I (1970) J. Magn. Reson. 2: 338
63. Buckingham AD, Pyykkö P, Robert JB, Wiesenfeld L (1982) Mol. Phys. 46: 177
64. Buckingham AD, Malm SM (1971) Mol. Phys. 22: 1127
65. Buckingham AD, Pople JA (1963) Trans. Faraday. Soc. 59: 2421
66. Raynes WT (1978) Nucl. Magn. Reson. 7: 1
67. Raynes WT (1988) Mol. Phys. 63: 719
68. Jameson CJ (1977) J. Chem. Phys. 66: 4977
69. Raynes WT, Fowler PW, Lazzeretti P, Zanasi R, Grayson M (1988) Mol. Phys. 64: 143
70. Lazzeretti P, Zanasi R, Sadlej AJ, Raynes WT (1987) Mol. Phys. 62: 605
71. Fowler PW, Riley G, Raynes WT (1981) Mol. Phys. 42: 1463
72. Jameson CJ, Buckingham AD (1980) J. Chem. Phys. 73: 5684
73. Hunt KLC (1989) J. Chem. Phys. 90: 4909
74. Jameson CJ, Jameson AK, Wille S, Burrell PM (1981) J. Chem. Phys. 74: 853
75. Petrakis L, Sederholm CH (1961) J. Chem. Phys. 35: 1174
76. Jameson CJ (1980) Bull. Magn. Reson. 3: 3
77. Jameson CJ, Jameson AK, Cohen SM (1977) J. Chem. Phys. 67: 2771
78. Bartell LS (1963) J. Chem. Phys. 38: 1827
79. Bartell LS (1979) J. Chem. Phys. 70: 4581
80. Jameson CJ, Jameson AK (1986) J. Chem. Phys. 85: 5484
81. Jameson AK, Moyer J, Jameson CJ (1978) J. Chem. Phys. 68: 2873
82. Bennett B, Raynes WT (1987) Mol. Phys. 61: 1423
83. Jameson CJ, Osten HJ (1986) J. Am. Chem. Soc. 108: 2497
84. Heller C, McConnell HM (1960) J. Chem. Phys. 32: 1535
85. Stone EW, Maki AH (1962) J. Chem. Phys. 37: 1326
86. Sullivan PD, Menger EM (1977) Adv. Magn. Reson. 9: 1
87. Gutowsky HS, Belford GG, McMahon PE (1962) J. Chem. Phys. 36: 3353
88. Chang SY, Davidson ER, Vincow G (1970) J. Chem. Phys. 52: 5596
89. Meyer W (1969) J. Chem. Phys. 51: 5149
90. Schrader DM, Morokuma K (1971) Mol. Phys. 21: 1033
91. Jameson CJ (1977) J. Chem. Phys. 66: 4983
92. Raynes WT, Davies AM, Cook DB (1971) Mol. Phys. 21: 123
93. Stevens RM, Lipscomb WN (1964) J. Chem. Phys. 40: 2238
94. Stevens RM, Lipscomb WN (1964) J. Chem. Phys. 41: 184
95. Stevens RM, Karplus M (1968) J. Chem. Phys. 49: 1094
96. Laws EA, Stevens RM, Lipscomb WN (1971) J. Chem. Phys. 54: 4269
97. Ermler WC, Kern CW (1971) J. Chem. Phys. 55: 4851
98. Jameson CJ, Osten HJ (1984) J. Chem. Phys. 81: 4300
99. Jameson CJ, Osten HJ (1984) J. Chem. Phys. 81: 4293
100. Wasylishen RE, Friedrich JO (1984) J. Chem. Phys. 80: 585
101. Wasylishen RE, Friedrich JO (1987) Can. J. Chem. 65: 2238
102. Leighton KL, Wasylishen RE (1987) Can. J. Chem. 65: 1469
103. Sanders JKM, Hunter BK, Jameson CJ, Romeo G (1988) Chem. Phys. Lett. 143: 471
104. Morse P (1929) Phys. Rev. 34: 57
105. Herschbach DR, Laurie VW (1961) J. Chem. Phys. 35: 458
106. Mills IM (1974) In: Dixon RN (ed) Theoretical chemistry. Royal Society of Chemistry, London, p 110
107. Bartell LS (1963) J. Chem. Phys. 38: 1827
108. Bartell LS, Doun SK, Goates SR (1979) J. Chem. Phys. 70: 4585
109. Osten HJ, Jameson CJ (1985) J. Chem. Phys. 82: 4595
110. Osten HJ, Jameson CJ (1984) J. Chem. Phys. 81: 4288
111. Wasylishen RE, Friedrich JO, Mooibroek S, Macdonald JB (1985) J. Chem. Phys. 83: 548
112. Friedrich JO, Wasylishen RE (1985) J. Chem. Phys. 83: 3707

113. Fleischer U, Schindler M, Kutzelnigg W (1987) J. Chem. Phys. 86: 6337
114. Batiz-Hernandez H, Bernheim RA (1967) Progr. NMR Spectrosc. 3: 63
115. Hansen PE (1983) Ann. Reports NMR Spectrosc. 15: 105
116. Hansen PE (1988) Prog. NMR Spectrosc. 20: 207
117. Wasylishen RE, Burford N (1987) Can. J. Chem. 65: 2707
118. Jameson AK, Jameson CJ (1978) J. Magn. Reson. 32: 455
119. Lawler RG, Bolton JR, Karplus M, Fraenkel GK (1967) J. Chem. Phys. 47: 2149
120. Smaller B, Yasaitis E, Anderson HL (1951) Phys. Rev. 81: 896
121. Bigeleisen J, Goldstein P (1963) Z. Naturforsch. A 21: 205
122. Jameson CJ, Rehder D, Hoch M (1987) J. Am. Chem. Soc. 109: 2589
123. Moss RE (1965) Mol. Phys. 10: 339
124. Jameson CJ (1980) Mol. Phys. 40: 999
125. Jameson CJ, Osten HJ (1985) Mol. Phys. 56: 1083
126. Jameson CJ, Osten HJ (1985) J. Chem. Phys. 83: 5425
127. Jameson CJ, Osten HJ (1985) Mol. Phys. 55: 383
128. Jameson CJ, Osten HJ (1984) J. Chem. Phys. 81: 4915
129. Jameson CJ, Osten HJ (1984) J. Chem. Phys. 81: 2556
130. Jameson CJ (1987) J. Am. Chem. Soc. 109: 2586
131. Jameson CJ, Rehder D, Hoch M (1988) Inorg. Chem. 27: 3490
132. Fowler PW, cited in Jameson CJ, Osten HJ (1986) Ann. Reports NMR Spectrosc. 17: 1
133. Schindler M (1987) J. Am. Chem. Soc. 109: 5950
134. Wasylishen RE, private communications
135. Karplus M (1960) J. Chem. Phys. 33: 1842
136. Karplus M, Fraenkel GK (1961) J. Chem. Phys. 35: 1312
137. Karplus M (1969) J. Chem. Phys. 50: 3133
138. Jameson CJ, Gutowsky HSG (1969) J. Chem. Phys. 51: 2790
139. Jameson CJ, Damasco MC (1970) Mol. Phys. 18: 491
140. Jameson CJ (1969) J. Am. Chem. Soc. 91: 6232
141. Murrell JN, Turpin MA, Ditchfield R (1970) Mol. Phys. 18: 271
142. Wasylishen RE, Burford N (1987) J. Chem. Soc. Chem. Commun. 1987: 1414
143. McConnell HM (1956) J. Chem. Phys. 24: 632, 764
144. Reddoch AH, Dodson CL, Paskovich DH (1970) J. Chem. Phys. 52: 2318
145. Schrader DM, Karplus M (1964) J. Chem. Phys. 40: 1593
146. Cole T (1961) J. Chem. Phys. 35: 1169
147. Fessenden RW, Schuler RH (1963) J. Chem. Phys. 39: 2147
148. Zlochower IA, Miller WR, Fraenkel GK (1965) J. Chem. Phys. 42: 3339
149. Garbutt GB, Gesser HD, Fujimoto M (1968) J. Chem. Phys. 48: 4605
150. Fischer H, Hefter H (1968) Z. Naturforsch. A 23: 1763
151. Cater MK, Vincow G (1967) J. Chem. Phys. 47: 292
152. Vincow G, Morrell ML, Volland MV, Dauben HJ, Hunter FR (1965) J. Am. Chem. Soc. 87: 3527
153. Sutcliffe BT, Gaze C (1978) Mol. Phys. 35: 525
154. Thuomas KA, Eriksson A, Lund A (1980) J. Magn. Reson. 37: 223
155. Fessenden RW, Ogawa S (1964) J. Am. Chem. Soc. 86: 3591
156. Lawler RG, Bolton JR, Fraenkel GK, Brown TH (1964) J. Am. Chem. Soc. 86: 520
157. Lawler RG, Fraenkel GK (1968) J. Chem. Phys. 49: 1126
158. Volland WV, Vincow G (1968) J. Chem. Phys. 48: 5589
159. Carrington A, Longuet-Higgins HC, Moss RE, Todd PF (1965) Mol. Phys. 9: 187
160. Longuet-Higgins HC, Öpik U, Pryce MHL, Sack A (1958) Proc. Roy. Soc. London A 244: 1
161. Kuchitsu K, Oyanagi K (1977) Faraday Discuss. Chemical Society London 62: 20
162. Lide DR (1975) In: Buckingham AD (ed) MTP International Review of Science. Physical Chemistry Series Two. Butterworts, London p 1 (Molecular Structure and Properties, vol 2)
163. Herschbach DR, Laurie VW (1962) J. Chem. Phys. 37: 1668
163a. Nemes L (1984) In: Durig JR (ed) Vibrational Spectra and Structure, Elsevier, Amsterdam 13: 161
164. Kuchitsu K (1967) Bull. Chem. Soc. Japan 40: 498
165. Morino Y, Kuchitsu K, Oka T (1962) J. Chem. Phys. 36: 1108

166. Sykora S, Vogt J, Bösiger H, Diehl P (1979) J. Magn. Reson. 36: 53
167. Novick SE, Davies P, Harris SJ, Klemperer W (1973) J. Chem. Phys. 59: 2273
168. Hutson JM, Howard BJ (1981) J. Chem. Phys. 74: 6520
169. Ruoff RS, Emilsson T, Chuang C, Klots TD, Gutowsky HS (1987) Chem. Phys. Lett. 138: 553
170. Nelson DD, Klemperer W, Fraser GT, Lovas FJ, Suenram RD (1987) J. Chem. Phys. 87: 6364
171. Mills IM (1984) J. Phys. Chem. 88: 532
172. Barton AE, Howard BJ (1982) Faraday Discuss. Chemical Society London 73: 45
173. Dyke TR, Howard BJ, Klemperer W (1972) J. Chem. Phys. 56: 2442
174. Born M, Huang K (1954) Dynamical theory of crystal lattices, Oxford University Press, London
175. Smith JG (1978) Mol. Phys. 35: 461
176. Lacy M (1982) Mol. Phys. 45: 253
177. Whiffen DH (1980) Mol. Phys. 39: 391
178. Fessenden RW (1967) J. Phys. Chem. 71: 74
179. Evans DF (1960) Chem. Ind. 1961
180. Hindermann DK, Cornwell CD (1968) J. Chem. Phys. 48: 4148
181. Chesnut DB (1986) Chem. Phys. 110: 415
182. Chesnut DB, Foley CK (1986) J. Chem. Phys. 84: 852
183. Weller T, Meiler W, Köhler HJ, Lischka H, Höller R (1983) Chem. Phys. Lett. 98: 541
184. Schindler M, Kutzelnigg W (1983) Mol. Phys. 48: 781
185. Chesnut DB, Foley CK (1986) J. Chem. Phys. 85: 2814
186. Schindler M, Kutzelnigg W (1982) J. Chem. Phys. 76: 1919
187. Imachi M, Tanaka T, Hirota E (1976) J. Mol. Spectrosc. 63: 265
188. Kukolich SG, Nelson AC (1972) J. Chem. Phys. 57: 869
189. Helminger P, Beeson EL, Gordy W (1971) Phys. Rev. A 3: 122
190. Morino Y, Hirose C (1967) J. Mol. Spectrosc. 24: 204
191. Williams JR, Kukolich SG (1979) J. Mol. Spectrosc. 74: 242
192. O'Reilly DE, Peterson EM, Kadaba P (1970) J. Chem. Phys. 52: 6444
193. Kuczkowski RL (1973) J. Mol. Spectrosc. 45: 261
194. Arimondo E, Glorieux P, Oka T (1978) Phys. Rev. A17: 1375
195. Dössel KF, Sutter DH (1979) Z. Naturforsch. A 34: 469
196. DeLucia FC, Gordy W (1969) Phys. Rev. 187: 58
197. Kukolich SG, Reuben DJ, Wang JHS, Williams JR (1973) J. Chem. Phys. 58: 3155
198. Jones H, Takami M, Sheridan J (1978) Z. Naturforsch. A33: 156
199. Jones H, Sheridan J, Stiefvater OL (1977) Z. Naturforsch. A32: 866
200. Raynes WT, Lazzeretti P, Zanasi R (1988) Mol. Phys. 64: 1061
201. Zeroka D (1973) J. Chem. Phys. 59: 3835
202. Ishiguro E, Koide S (1953) Phys. Rev. 94: 350
203. Snijders JG, Van der Meer W, Baerends EJ, DeLange CA (1983) J. Chem. Phys. 79: 2970
204. Huber H (1985) J. Mol. Struct. THEOCHEM 121: 207
205. Rosenberg BJ, Ermler WC, Shavitt I (1976) J. Chem. Phys. 65: 4072
206. Ermler WC (1970) M. S. Thesis, Ohio State University
207. Engström S, Wennerstrom H (1978) Mol. Phys. 36: 773
208. Bacskay GB, Gready JE (1988) J. Chem. Phys. 88: 2526
209. Docken KK, Hinze J (1972) J. Chem. Phys. 57: 4928, 4936
210. Huo WM (1965) J. Chem. Phys. 43: 624
211. Green S (1973) J. Chem. Phys. 58: 3117
212. Sundholm D, Pyykkö P, Laaksonen L, Sadlej AJ (1986) Chem. Phys. 101: 219
213. Cummins PL, Bacskay GB, Hush NS, Ahlrichs R (1987) J. Chem. Phys. 86: 6908
214. Kowalewski J, Roos B, Siegbahn P, Vestin R (1974) Chem. Phys. 3: 70
215. Schulman JM, Lee WS (1980) J. Chem. Phys. 73: 1350
216. Lazzeretti P, Zanasi R, Raynes WT (1989) Mol. Phys. 66: 831
217. Raynes WT, Lazzeretti P, Zanasi R, Fowler PW (1985) J. Chem. Soc. Chem. Commun. 1985: 1538
218. Raynes WT, Lazzeretti P, Zanasi R (1986) Chem. Phys. Lett. 132: 173
219. Kowalewski J, Roos B (1975) Chem. Phys. 11: 123
220. Keil F, Ahlrichs R (1979) J. Chem. Phys. 71: 2671
221. Lazzeretti P, Rossi E, Taddei F, Zanasi R (1982) J. Chem. Phys. 77: 408

222. Rychlewski J, Raynes WT (1980) Mol. Phys. 41: 843
223. Bishop DM, Cheung LM (1979) J. Phys. B 12: 3135
224. Hunt JL, Poll JD, Wolniewicz L (1984) Can. J. Phys. 62: 1719
225. Rychlewski J (1980) Mol. Phys. 41: 833
226. Sunil KK, Jordan KD (1988) Chem. Phys. Lett. 145: 377
227. Oddershede J, Svendsen EN (1982) Chem. Phys. 64: 359
228. Temkin A (1978) Phys. Rev. A17: 1232
229. Lazzeretti P, Rossi E, Zanasi R (1981) J. Phys. Chem. B14: L269
230. Rosmus P, Werner HJ (1985) In: Jørgensen P, Simons J (eds) Geometrical derivatives of energy surfaces and molecular properties. Reidel, Dordrecht, p 265
231. Wolniewicz L (1976) Can. J. Phys. 54: 672
232. Lazzeretti P, Zanasi R, Fowler PW (1988) J. Chem. Phys. 88: 272
233. Meyer W, Rosmus P (1975) J. Chem. Phys. 63: 2356
234. Werner HJ (1981) Mol. Phys. 44: 111
235. Werner HJ, Rosmus P (1980) J. Chem. Phys. 73: 2319
236. Rosmus P, Werner HJ, Grimm M (1982) Chem. Phys. Lett. 92: 250
237. Werner HJ, Meyer W (1981) J. Chem. Phys. 74: 5802
238. Langhoff S, Bauschlicher CW, Partridge H (1983) Chem. Phys. Lett. 102: 292
239. Werner HJ, Rosmus P, Reinsch EA (1983) J. Chem. Phys. 79: 905
240. Amos RD (1978) Mol. Phys. 35: 1765
241. Raynes WT, Stanney G (1974) J. Magn. Reson. 14: 378
242. Cummins PL, Bacskay GB, Hush NS (1987) J. Chem. Phys. 87: 416
243. Ishiguro E (1958) Phys. Rev. 111: 203
244. Raynes WT, Riley JP (1974) Mol. Phys. 27: 337
245. Chan SI, Ikenberry D, Das TP (1964) Phys. Rev. A 135: 960
246. Bishop DM, Lam B (1988) Chem. Phys. Lett. 143: 515
247. Elliott DS, Ward JF (1984) Mol. Phys. 51:45
248. Bishop DM (1981) Mol. Phys. 42: 1219
249. Hindermann DK, Williams LL (1969) J. Chem. Phys. 50: 2839
250. Wasylishen RE (1982) Can. J. Chem. 60: 2194
251. Fabricant B, Muenter JS (1977) J. Chem. Phys. 66: 5274
252. Schrötter HW, Klöckner HW (1979) In: Weber A (ed) Raman Spectroscopy of gases and liquids. Springer, Berlin Heidelberg New York, p 123
253. Spelling RI, Meredith RE, Smith FG (1972) J. Chem. Phys. 57: 5119
254. Chackerian C, Farrenq R, Guelachvili G, Rossetti C, Urban W (1984) Can. J. Phys. 62: 1579
255. Person WB, Zerbi G (eds) (1982) Vibrational intensities in infrared and Raman spectroscopy, Elsevier, Amsterdam, p 96

11 Appendix

A guide to the literature is given in Tables A1 to A3.2. No attempt at completeness has been made. References to ab initio calculations of various property derivatives are given in Table A1 and rovibrational calculations (at various levels) using theoretical derivatives are given in Table A2, and inversion of data to obtain empirical estimates of derivatives are given in Table A3.

Table A1. Ab initio theoretical calculations of property surfaces or their derivatives

σ:	Review [18] H_2^+ [19] H_2 [44, 181, 201, 202] LiH [44, 93] HF [113, 44, 94]
	HCl [181] CO [95, 182–184] N_2 [96, 182, 184] CN^- [182] LiF, P_2 [113]
	CH_4 [70, 181, 185] H_2O [71, 181, 185, 186] SiH_4, PH_3, NH_3 [113, 181, 185]
	PH_4^+, NH_4^+, BH_4^-, BH_3, AlH_3, AlH_4^-, H_2S [181]
	HCCH, H_2CC_2, CH_3CH_3, CH_3F, HCN [182] SiF_4, PF_3, NF_3 [113]
C:	LiH [93] HF [94] CO [95] N_2 [96] H_2O [23]
a:	$\dot{C}H_3$ [88]
q:	Review [56] at H in H_2, CH_4 [203]
	at H in H_2, LiH, CH_4, NH_3, H_2O, HF, NaH, SiH_4, PH_3, H_2S, HCl [204]
	H_2O [205, 206] HCl, HCN [207]
	at H in HF_2^- [208] OH^-, SH^-, HF, HCl, $HO^{\bullet}$, $HS^{\bullet}$ [49]
	LiH [209] CO, BF [210] ClF [211] NO^+, N_2 [212]
	at N and H in N_2, NO, NO^+, CN, CN^-, HCN, HNC, NH_3 [213]
J:	Review [83] HD [45, 214, 215] CH_4 [216–218] NH_3 [219] PH_3 [220]
	HF [141] CO, N_2 [14] PH_2^- [221]
χ:	H_2 [222] LiH [93] H_2O [71, 206] CH_4 [70] HF [94] CO [95] N_2 [96]
α:	H_2^+ [223] H_2 [224, 225] LiH [93] CH_4 [200] CO [226, 227]
$\alpha(\omega)$:	N_2, CO, HCl, CL_2 [227] N_2 [26, 228] CO_2 [26]
γ, B, C:	HCl, HBr [229]
μ:	Review [230] HD [231] LiH [232, 233] CH_4, NH_3 [232] CO [95, 226, 234]
	HF [94, 232, 233, 235] HCl [233, 235] HBr [235] HI [17] BF [236] LiF [237]
	OF [238] BeH, BH, CH, NH, OH, NaH, MgH, AlH, SiH, PH, SH [233]
	H_2O [71, 205, 206, 232] OH, OH^-, OH^+ [239]
	H_2^+ [26, 223] H_2 [224] LiH, CH_4, NH_3, HF [232] N_2 [26] H_2O [23, 232]
Ω:	HF [240] H_2O [206]
g_J or μ_J:	H_2 [222] HF [94] CO [95] N_2 [96] H_2O [23]

Table A2.1. Rovibrational averaging of properties in diatomic molecules using ab initio theoretical derivatives

Property	Using 1st and 2nd deriv. only	3rd and higher
σ	H_2, LiH, HF, CO, N_2 [18]	H_2 [44, 92] LiH, HF [44]
	HF [180] $N_2(v = 0)$ [96]	CO [241]
C	HF [94, 180] LiH [93] N_2 [96]	
q	CO, OH^-, HCl, LiCl, FCl [242]	
	N_2, NO^+, NO, CN, CN^- [213]	
J	HD [45, 214, 215, 243, 244] HF [141]	
	CO, N_2 [14]	
χ	H_2 [245] HF(v = 0) [94] N_2 [96]	CO [95]
α	LiH [93] HF [94]	
β, γ, B, C	H_2^+, H_2 [11, 246] HF(β) [11]	
μ	LiH, BeH, BH, CH, NH, OH, HF,	HF, HCl, HBr v = 0–8 [235]
	NaH, ... , HCl [233]	OH, OH^-, OH^+ v = 0–5 [239]
	HI(v = 0) [17]	BF, BF^+ v = 0–6 [236]
		OF v = 0–6 [238]
g_J or μ_J	H_2 [245] HF [94] N_2 [96]	

Table A2.2. Rovibrational averaging of properties in polyatomic molecules using ab initio theoretical derivatives

	1st and 2nd derivs. neglect 2nd order L tensor elements	1st deriv. only include 2nd order L tensor elements	1st and 2nd derivs. and 2nd order L elements	3rd and higher order
σ		H in CH_4 [103]	C in CH_4 [69]	H_2O [58]
C				H_2O [23]
a	$\dot{C}H_3$ [90] pi model $C_6H_6^-$ [157] naphthalene$^-$ [119]			
J		J(HH) in CH_4 [217] J(CH) in CH_4 [82]		^{2}J(HH) in NH_3 inversion mode [219]
χ			CH_4 [69]	H_2O [58]
α			CH_4 [200]	
β, γ	1st deriv. only $\gamma^v CH_nF_{4-n}$, SF_6 [247] β^v $CHCl_3$, CHF_3 [248]			
μ				H_2O [58, 97]
θ, g_J				H_2O [23, 97]

Table A3.1. Inversion of experimental data to obtain property derivatives of diatomic molecules

Property	1st deriv only	1st and 2nd derivs.	Complete surface
σ	H_2 [53] F_2 [249] ClF, F_2 [68] CN^- [98, 250] CO [74, 111] N_2 [74, 112]		
C	H_2 [52, 53] F_2 [249]		
q	Review [56] HBr [47] ClF [251]	HCl [46]	I_2 [20]
a	$\dot{C}H_3$ [123]		
α	Review [252]		
μ		HF [253] HCl [46]	HF [15] HCl, HBr, HI [16] CO [254]

Table A3.2. Inversion of experimental data to obtain property derivatives of polyatomic molecules[a]

Property	1st deriv. only estimate $\langle \Delta r \rangle$	1st deriv. only neglect 2nd order L tensor	1st deriv. incl. 2nd order L tensor
σ	O in H_2O, H_3O^+ [101] Sn in SnH_3^- [117] Sn in SnH_4, $SnH_{3-n}D_n^+$ [102] cen. nucl. in BH_4^- CO_2 CS_2 NH_4^+ NO_3^- PO_4^{3-} MnO_4^- MoO_4^- TcO_4^- $PtCl_6^{2-}$ $PtBr_6^{2-}$ [98] C in CO_2 [111] N in NO_2^- NO_3^- [18] P in PH_3, PH_2^- [117]	CF_4, BF_3, SiF_4 [41]	NF_3, PF_3, PCl_3, PBr_3 NH_3, PH_3, CO_2 [18] CO_2 [129] CH_4 [110] SF_6 [124] COF_2 [128] $CF_{4-n}H_n$ [125] H_2Se, H_2O [109] CF_3Cl ... $CFCl_3$ [127] MF_6 [80] $M(XY)_6$ [122, 131]
J	SnH_4 [102] SnH_3^- [117] PH_2^- [117]		J(CH) in CH_4 [82]

[a] See also [56] for approximate inversion of eqQ of ^{75}As in AsF_3. See [255] for reviews of inversion of intensities to obtain derivatives of electric dipole moments and of electric dipole polarizabilities in polyatomics