Comments on H/D Isotope Effects on Polarizabilities of Small Molecules. Correlation with Virial Coefficient, Molar Volume, and Electronic Second Moment Isotope Effects

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Literature data on H/D isotope effects on polarizability are reviewed. An argument based on perturbation theory correlates the isotopic differences with electronic transition moments via vibrational averaging. The contribution of the second moment isotope effect is especially important. The approach is first illustrated with a calculation on H_2/D_2 and then employed to correlate differential refractive index data on about twenty other H/D isotopic pairs. A table of bond polarizability isotope effects is presented which permits the estimation of polarizability isotope effects for various kinds of H/D substituted compounds. Coupling these results with known isotope effects on vibrational amplitude permits calculation of vapor phase virial coefficient isotope effects, while combination with refractive index data on liquids yields reasonable values for the sum of the isotope effects on molar volume and electronic second moment. However the quantitative correlation of the polarizability isotope effect with isotope effects on vapor pressure or thermodynamic activity is less direct.

Key words: Polarizability, isotope effects, refractive index, electronic second moment isotope effects, bond polarizabilities, molar volume isotope effects.

Introduction

The effect of H/D substitution on refractive index and molecular polarizabilities was first studied in the 1930's. More recently Rabinovitch [1] made refractive index measurements on a wide series of deuterated organic molecules and also reviewed literature data on electronic polarizability isotope effects (PIE's). He gave qualitative arguments connecting PIE's with zero point energy (ZPE) differences. However the Rabinovitch approach neglected consideration of the IE's on the transition moments or related properties, and is therefore incomplete. The polarizability is a fundamental molecular property. There exist quantum mechanical methods to obtain polarizabilities and thence PIE's [2]. Even so it is useful to develop qualitative and semi-quantitative methods, especially difference methods, so that PIE's can be obtained for molecules where accurate wave functions are not available. Our discussion of such an approach will follow a brief review of polarizability, polarization and refractive index via second order perturbation theory.

An understanding of the origin of the PIE is important to the theory of condensed phase isotope effects (CPIE's) for the following reason. CPIE's like all isotope effects are normally rationalized in terms of the equations of motion on isotope independent inter- and intra-molecular potential surfaces. On the other hand we know from London dispersion theory [2] that intermolecular attractive forces scale with the polarizabilities of the interacting species, which (see above) are isotope dependent. While this approach does not necessarily imply isotope dependent intermolecular potentials, it has resulted in a good deal of confusion including conflicting claims about the physical origin of virial coefficient and certain condensed phase IE's [3–7]. Wolfsberg [8] has discussed the relationship between dispersion forces and IE's on condensed phase properties like the vapor pressure. His main interest in that discussion was the vibrational polarizability, which arises from contributions of excited vibrational states in the electronic ground state, but he did briefly refer to the contribution of electronic polarizability to the vapor pressure IE for molecular hydrogen. It is important to distinguish the contribution of excited

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vibrational states to the polarizability from those effects which arise from vibrational averaging of the polarizability over the ground electronic and vibrational states. It is this latter effect which principally concerns us in the present paper. We expect the bulk of the PIE to be rationalized in terms of isotope effects on vibrational averaging of the polarizability. The electronic polarizability can of course be expressed in terms of a sum of contributions from excited electronic states (*vide infra*). In the present paper our interest is in the electronic polarizability, and we essentially ignore excited state vibrational polarizability. A comprehensive review of vibrational and rotational corrections for electronic polarizabilities has recently been given by Bishop [9].

Although information concerning IE's on the polarizabilities of common molecules has been available for more than half a century, these data have not been treated quantitatively in the context of the theory of IE's. Such developments commonly employ a difference formalism to illustrate the effects of the isotopic difference directly. The object of the present paper is to formulate and then present such an analysis. We will proceed by reviewing the polarizability, its frequency dependence, and its relation to the refractive index. The PIE will be developed using a difference formalism and discussed in terms of ground state vibrational averaging. Upon completion of these introductory matters, the difference formalism will be exemplified for diatomic molecules and illustrated with a numerical calculation on the H_2/D_2 system. At that point the closure approximation will be introduced, principally because our goal is the development of an approximate formalism appropriate for the interpretation of experimental data, including data on systems where sophisticated quantum mechanical calculations are not yet available. Finally we will close with discussions of PIE's from refractive indices, and the correlation of PIE's with molar volume and virial coefficient IE's. Throughout *the emphasis will be on the development of an appropriate difference formalism to use in the interpretation of experimental data on the PIE and related effects.*

Polarizability and Refractive Index

Polarizability

The polarizability, $\boldsymbol{\alpha}$, of an atom or molecule is a tensor which describes the second order response of its energy to an impressed electric field. Second-order perturbation theory [2, 10] shows that the ground electronic state polarizability of an atom or molecule is

$$\boldsymbol{\alpha} = 2 \Sigma'_n ((\langle o | \boldsymbol{d} | n \rangle \langle n | \boldsymbol{d} | o \rangle)/(E_{no})) . \qquad (1)$$

The primed sum is over all excited electronic states (indexed by n) including the ionization continua (i.e. all n except $n=0$ which corresponds to the ground state). By proceeding in this way we are ignoring the contribution of excited vibrational states within the ground electronic state to the polarizability and its IE; this contribution was considered by Wolfsberg [8]. The denominator in (1) expresses the energy difference between the n'th upper state and the ground state. The bracket notation used for the transition moments is the standard one, $\langle o | \boldsymbol{d} | n \rangle = \int \Psi_0^* \boldsymbol{d} \, \Psi_n \delta\tau$, where $\delta\tau$ represents the differential unit of volume, $\boldsymbol{d}$ is the dipole moment operator, and the ground and excited state wave functions are purely electronic. When (1) is used to calculate the electronic polarizability of a molecule, a given nuclear configuration is assumed (usually the equilibrium configuration); this procedure is carried out within the framework of the Born-Oppenheimer approximation. When (1) is applied to liquids and vapors, where the molecules are freely tumbling, the measured polarizability is a spherical average,

$$\alpha = (2/3) \Sigma'_n (d_{on} d_{no}/(E_{no})) . \qquad (2)$$

In (2) the matrix element notation has been further simplified, $d_{no} = \langle n | \boldsymbol{d} | o \rangle$.

To calculate α with (2) it is necessary to evaluate all electronic excited state energies and wave functions, find the dipole weighted matrix elements for combination with the ground state, and evaluate the sums. Each term is proportional to the square of the appropriate transition moment and thus to the intensity of the spectral transition. The contribution of the n'th individual term to the polarizability is straightforwardly related to the oscillator strength for the $n \leftarrow 0$ transition, f_{no}. The sum of oscillator strengths is n_e, the number of electrons in the molecule. Polarizability and oscillator strength are related [10]:

$$\alpha = (h^2 e^2/(4 \pi^2 m)) \Sigma'_n (f_{no}/E_{no}^2) \qquad (3)$$

(m is the mass of the electron and e its charge).

The frequency dependence: If the impressed electric field is sinusoidally varying, it can change direction many times during the period of a single molecular rotation. In that event a molecule fixed permanent dipole only experiences the average field, which is

zero. On the other hand, the response of the induced moments is essentially instantaneous, and they do contribute to the high frequency polarization. Time dependent perturbation theory leads to the well-known result for the polarizability of a freely rotating molecule [10]

$$\alpha(v) = (2/(3\,h\,c))\,\Sigma'_n\,(v_{no}\,\boldsymbol{d}_{on}\,\boldsymbol{d}_{no}/(v_{no}^2 - v^2))\,. \quad (4)$$

Here v is the frequency (cm^{-1}) of incident radiation (which should be far removed from any absorption band), and v_{no} is the frequency corresponding to the energy difference between the excited and the ground states. For convenience frequencies are expressed in wave numbers, $h\,c\,v(\text{cm}^{-1}) = h\,v'(\text{Hz})$. Equation (4) reduces to the static field expression (2) as $v \to 0$. When using (4), we will assume that the frequency of the probe radiation is much higher than vibrational, rotational and other low frequencies, and that there is no physically significant contribution from such low energy states. At extremely high frequencies, $v^2 \gg v_{no}^2$ and the polarizability tends to zero in precise analogy to the null contribution which permanent dipoles make to the polarization at optical frequencies.

The refractive index: The polarizability and the refractive index, n_r, are related by the Lorenz-Lorentz formula (ε_0 is the permittivity of the vacuum and N is the number density),

$$\frac{n_r^2 - 1}{n_r^2 + 2} = \frac{N\,\alpha(v)}{3\,\varepsilon_0} = \frac{2\,N}{9\,h\,c\,\varepsilon_0}\,\Sigma'_n\,\frac{v_{no}\,\boldsymbol{d}_{on}\,\boldsymbol{d}_{no}}{(v_{no}^2 - v^2)}\,. \quad (5)$$

Clearly (5), with proper extrapolation to zero frequency, can be used to deduce static polarizabilities from refractive index measurements.

Isotope Effects on Polarizability and Refractive Index

The electronic polarizability (in this paper usually referred to a simply the polarizability), is often written in a form based on second order perturbation theory as in the previous section. An alternative derivation involves adding the interaction with the electric field to the electronic Hamiltonian operator of the molecule and then carrying out a variational calculation. From the dependence of the energy on the impressed electric field one then calculates the polarizability. This is the method used by Ishiguro, Arai, Mizushima, and Kotani [11] to calculate the static polarizability of molecular hydrogen and of its isotopic iso-

mers. These authors carried out variational calculations for a range of values of the internuclear separation and obtained the polarizability as a power series in $R = (r - r_0)$, where R corresponds to the displacement from the equilibrium internuclear separation, r_0. Thus

$$\alpha = \sum_{i=0}^{i_{max}} A_i \langle R^i \rangle\,. \quad (6a)$$

Here, A_0 is the polarizability when $R = 0$. To obtain the true polarizability of a molecule, (6a) must be averaged over the vibrational wave function, replacing R^i with $\langle \Delta R^i \rangle$, the expectation value of R^i in the appropriate vibrational state (say the zero-point state). Therefore

$$\langle \alpha \rangle = \sum_{i=0}^{i_{max}} A_i \langle R^i \rangle\,. \quad (6b)$$

A_0 is the leading term in (6b). Since (6a) applies to all isotopic variants of H_2, the isotope effect on $\langle \alpha \rangle$ depends on the isotope dependence of $\langle R^i \rangle$ induced by the mass dependence of the vibrational wave functions used in the averaging procedure. Ishiguro et al. found that only a few terms in the expansion were needed to obtain convergence ($i_{max} \approx 4$).

In the present work we use the same approach as Ishiguro *et al.* to calculate the PIE except that we employ the second order perturbation development of the previous section. This approach offers some useful physical insight and also leads to a parametrization which is useful for application to complicated molecular systems where detailed and rigorous calculations are impossible or inconvenient. Rewriting (4)

$$3\,h\,c\,\alpha/2 = \Sigma'_n\,\frac{\boldsymbol{d}_{no}\,\boldsymbol{d}_{on}}{v_{no}(1 - (v^2/v_{no}^2))}\,, \quad (7a)$$

limiting attention to molecules with little or no electronic intensity in the visible region, and using light in the visible region, i.e. assuming $v \ll v_{no}$, one has on expanding the denominator

$$\begin{aligned}3\,h\,c\,\alpha/2 \\ = \Sigma'_n\,((\boldsymbol{d}_{no}\,\boldsymbol{d}_{on})/v_{no} + ((\boldsymbol{d}_{no}\,\boldsymbol{d}_{on})/v_{no}^3)\,v^2)\,. \quad (7b)\end{aligned}$$

Each of the n terms contributing to the isotope effect is linearly dependent on the square of the probe frequency. Equation (7b) is of fundamental interest because it connects the PIE with measurable spectroscopic quantities. To evaluate the PIE's, we proceed by expanding each term in (7) over the ground state internuclear distance, take the vibrational averages,

$\langle (d_{no} d_{on})/v_{no} \rangle$ and $\langle ((d_{no} d_{on})/v_{no}^3) \rangle$, say for H and D isotopomers, and calculate the isotopic differences. Such a calculation is described in detail in a later section.

The connection to refractive index measurements is made by recognizing that the right hand side of (7) must be properly averaged over the vibrational wavefunction (usually the wavefunction of the zero-point vibrational state), and then writing the first order isotopic difference equation, recognizing both that the isotope effect is small and that the difference between the polarizability at the equilibrium configuration and the vibrationally averaged polarizability is quite small. In the following, Δ refers to isotopic differences, light – heavy. Quantities like α and $\langle \alpha \rangle$ are not distinguished from each other and are written as α. Thus differentiating (5) we obtain

$$\frac{\Delta f(n_r)}{f(n_r)} + \frac{\Delta V}{V} = \frac{6 n_r^2}{(n_r^2-1)(n_r^2+2)} \frac{\Delta n_r}{n_r}$$
$$+ \frac{\Delta V}{V} = \frac{\Delta \alpha(v)}{\alpha(v)}. \tag{8}$$

$\Delta V/V$ is the molar volume isotope effect, $\Delta V/V = -\Delta N/N$, N is the number density of molecules, and $f(n_r) = ((n_r^2-1)/(n_r^2+2))$.

To enable the interpretation of data on molecules with incomplete information on transition moments or excitation energies, it is convenient to introduce an approximate average of v_{no}, designated as v^*, into (4) and then to apply closure [10]. It is unlikely that sufficient information will be available to permit an a priori calculation of v^*, which will therefore enter parametrically. The new result, replacing (7) is to second order in v,

$$3hc\,\alpha(v)/2 = \frac{(\langle 0| d^2 |0 \rangle - \langle 0| d |0 \rangle^2)}{v^*(1-v^2/v^{*2})}$$
$$= (D/v^*) + (D/v^{*3}) v^2, \tag{9}$$

where for convenience we have written $D = (\langle 0| d^2 |0 \rangle - \langle 0| d |0 \rangle^2) = ((d_{00}^2) - (d_{00})^2)$. The operator D is consistently taken with the origin at the center of nuclear charge of the molecule. Equation (9) is of the form, $\alpha = (\text{constant}) * (\alpha_0 + \delta\alpha)$, with α_0 the static polarizability. One finds to second order in v

$$\Delta\alpha/\alpha = \Delta(D/v^*)/(D/v^*) \tag{10}$$
$$+ v^2 [\Delta(D/v^{*3}) - \Delta(D/v^*)/v^{*2}]/(D/v^*),$$

which is of the form $\Delta\alpha/\alpha = A + B v^2$. It should be noted that for nonpolar molecules, $d_{00} = 0$, so

$(\Delta \langle (d_{00}^2) - (d_{00})^2 \rangle) = \Delta \langle d_{00}^2 \rangle$, a considerable simplification. Even molecules with large dipole moments always show $(d_{00}^2) \gg (d_{00})^2$. As an approximation, we henceforth write $D \approx d_{00}^2$.

We proceed by substituting (10) into (8). In doing so, we decouple the contribution of the transition moment D and the transition energy v^3 to obtain simplified expressions. We appreciate that such a decoupling must be approximate and that, in the end, the only justification for such a procedure is its utility. After some manipulation we obtain

$$\Delta f/f = (\Delta\alpha_0/\alpha_0 - \Delta V/V)$$
$$- 2(\Delta v^*/v^*)(v/v^*)^2. \tag{11}$$

Thus, a plot of $\Delta f/f$ vs. v^2 gives a straight line with an intercept of $(\Delta\alpha_0/\alpha_0 - \Delta V/V)$ where $\Delta\alpha_0/\alpha_0 = (\Delta(d_{00}^2)/d_{00}^2 - \Delta v^*/v^*)$, and a slope equal to $-(2/v^{*2})(\Delta v^*/v^*)$. Figures 1 and 2 show fits of refractive index data for C_6H_{12}/C_6D_{12} (293.15 K, liquid)[1], CH_4/CD_4 (298.15 K, gas) [12] and H_2O/D_2O (288.15 and 363.15 K, liquid, and vapor) [13]. The intercepts and slopes are consistent with the development presented above. These and other related data will be discussed in more detail in a later section. It is important that the reader appreciate that the approximations employed in obtaining (9), (10), and (11), are much more drastic than the ones which led to (5) and (6). If sufficient data are available, it is possible to evaluate the sums in (5) and (6) directly, thereby avoiding the closure approximation.

Formalism for Diatomic Molecules

Application to H_2/D_2

In this section the approach outlined in the previous section is illustrated by application to H_2/D_2, and relations useful for application to other diatomic molecules are developed. Two approaches are considered.

(a) The IE on Reciprocal Energy Weighted Transition Moments

First consider (7) and evaluate the individual squared and weighted transition moments $(d_{no}(R))^2$ of the different excited states of hydrogen. The principal states are listed in Table 1 [14]. Transitions to the Lyman B, $^1\Sigma_u^+$, and Werner C, $^1\Pi_u$, states from the X, $^1\Sigma_g^+$, ground state together account for about 58% of

Table 1. Some properties of the lower electronic states of H_2.

State, symbol		$10^{-3} \, \nu_{no}/cm^{-1}$	$(g_n)^a$	ω_n/cm^{-1}
Ground:	X, $^1\Sigma_g^+$	–	–	4395
Lyman:	B, $^1\Sigma_u^+$	91.7	0.28	1358
Werner:	C, $^1\Pi_u$	100.1	0.30	2444
	B', $^1\Sigma_u^+$	111.6	0.04	2039
	D, $^1\Pi_u$	113.9	0.04	2360
Continuum (ionizing)[b]		121.5[c]	0.01	2322[d]
(nonionizing)[b]		121.5[c]	0.08	
(Autoionization 15.4 − 16.7 eV)[b]				
Continuum (>16.7 eV)		150[c]	0.25	
SUM			1.00	
Reference		[14]	[38]	[14]

[a] $g_n = (f_{no}/\nu_{no}^2)/(\Sigma_n f_{no}/\nu_{no}^2)$.
[b] See [38].
[c] Weighted average, see [38].
[d] H_2^+.

the oscillator strength. Calculated matrix elements for the purely electronic contribution to these transitions have been reported to high accuracy as functions of the internuclear distance by Dressler and Wolniewicz [15]. Their values for $d_{no}(Q)$ $(1.0 < r/au < 2.5)$ were squared, then expanded in powers of the vibrational amplitude, $R = r - r_0$, r_0 the equilibrium internuclear distance,

$$(d_{no}(R))^2 = \sum_{i=0}^{i_{max}} A_n(i) R^i, \quad i_{max} \le 4. \quad (12)$$

Least squares values of $A_n(i)$ are reported in Table 2a. In order to test the dependence of the expansion on i_{max}, calculations are reported here for series expansions with i_{max} set equal to 2, 3, and 4. The parenthesized figures are the standard deviations in the least squares parameters of fit in the final significant figures. The expansions with $i_{max} = 4$ have the smallest errors of fit. Other errors (i.e. errors other than the statistical errors of fit) are not considered at this point. Reciprocal energy differences between ground and excited states were calculated from the Morse parameters for the different states [14]. The results were expanded according to (13) and are reported in Table 2b.

$$1/\nu_{no} = \sum_{i=0}^{i_{max}} B_n(i) R^i, \quad i_{max} \le 4. \quad (13)$$

Using (12) and (13), we write

$$(d_{no}(R))^2/\nu_{no} = \sum_{i=0}^{i_{max}} C_n(i) R^i, \quad i_{max} \le 4, \quad (14)$$

where $C_n(i) = \sum_{j=0}^{i} A_n(j) B_n(i-j)$ and $0 \le i \le i_{max}$. The $C_n(i)$'s are reported in Table 2c. The frequency dependent term in (7) is obtained similarly,

$$(d_{no}(R))^2/\nu_{no}^3 = \sum_{i=0}^{i_{max}} D_n(i) R^i, \quad i_{max} \le 4. \quad (15)$$

For numerical evaluation of the $D_n(i)$ parameters, we wrote

$$1/\nu_{no}^3 = \sum_{i=0}^{i_{max}} E_n(i) R^i, \quad i_{max} \le 4, \quad (16)$$

obtaining the $E_n(i)$ from the coefficients of (13) either by writing $E_n(i) = \sum_{k=0}^{i} B_n(i-k) \left(\sum_{j=0}^{k} B_n(j) B_n(k-j) \right)$, or by expanding the cube of the reciprocal energy difference directly. The $E_n(i)$'s calculated by the two methods were numerically equal and thus confirmed our numerical methods. In either case the $D_n(i)$ coefficients used in (16) are given by $D_n(i) = \sum_{j=0}^{i} A_n(j) E_n(i-j)$ for $0 < i < i_{max}$. They are reported in Table 2d.

To find the isotope effects on both the static and frequency dependent terms, we vibrationally averaged (14) and (15) over the ground state vibration using averaged R^i values for H_2 and D_2 calculated numerically just as did Ishiguro et al. [11] in their calculation of polarizability isotope effects. Vibrational averaging for H_2 and D_2 was carried out numerically from zero-point vibrational wave functions of the ground state Morse potential using the Numerov method [16]. Values for the averages of R^i are reported in Table 2e; where comparable, they are in essential agreement with those of Ishiguro et al.

Combination of Tables 2c and 2e, or 2d and 2e, yields the vibrationally averaged contributions of the Lyman and Werner bands to the static polarizability and their frequency dependence. These results are reported in Table 2f. The individual contributions to $\alpha(H_2)$ and to $(\alpha(H_2) - \alpha(D_2))$ were calculated for expansions using i_{max} values of 4, 3, and 2, respectively. Examination of the results shows little or no difference between the calculations for third and fourth order, but the IE calculated from the second order fit is significantly different from the one which includes third and fourth orders.

The summed contributions of the Lyman and Werner bands to the polarizability and its IE are reported in Table 2g. These bands contribute about 58% of the oscillator strength; so, crudely, one expects

Table 2. Contributions to PIE for H_2/D_2 in atomic units for distance (au_r) within a state, state-to-state energies (v) in cm^{-1}. Parenthesized entries denote standard errors in last significant figure(s). In Table 2a) and 2b) the last row labelled σ/unit designates the standard deviation of the least squares fit.

2a) The parameters of (12). $(d_{no}(Q))^2 = \Sigma_i A_n(i) R^i$.

i_{max}	4	4	3	3	2	2
n	B (Lyman)	C (Werner)	B (Lyman)	C (Werner)	B (Lyman)	C (Werner)
$A_n(0)/au_r^2$	0.9665 (7)	0.5529 (0)	0.9641 (25)	0.5530 (1)	1.0005 (149)	0.5564 (14)
$A_n(1)/au_r$	1.1196 (28)	0.3391 (2)	1.1404 (53)	0.3386 (2)	1.1419 (436)	0.3388 (38)
$A_n(2)$	0.3716 (54)	−0.0122 (3)	0.3950 (172)	−0.0127 (5)	0.0467 (458)	−0.0457 (43)
$A_n(3)/au_r^{-1}$	−0.1672 (146)	−0.0305 (8)	−0.2903 (136)	−0.0274 (4)		
$A_n(4)/au_r^{-2}$	−0.0774 (89)	0.0019 (5)				
σ/au_r^2	1.1 E-03	5.9 E-05	4.1 E-03	1.1 E-04	3.3 E-02	3.1 E-03

2b) The parameters of (13). $1/v_{no} = \Sigma_i B_n(i) R^i$.

i_{max}	4	4	3	3	2	2
n	B (Lyman)	C (Werner)	B (Lyman)	C (Werner)	B (Lyman)	C (Werner)
$10^5 B_n(0)/cm$	1.0185 (0)	0.9395 (0)	1.0184 (1)	0.9394 (0)	1.0184 (4)	0.9394 (2)
$10^5 B_n(1)/cm \cdot au_r^{-1}$	0.1593 (1)	0.2269 (0)	0.1593 (5)	0.2269 (1)	0.1436 (16)	0.2205 (7)
$10^5 B_n(2)/cm \cdot au_r^{-2}$	0.3175 (7)	0.0754 (1)	0.3359 (13)	0.0798 (3)	0.3359 (106)	0.0798 (44)
$10^5 B_n(3)/cm \cdot au_r^{-3}$	−0.3023 (14)	−0.1254 (2)	−0.3023 (89)	−0.1254 (21)		
$10^5 B_n(4)/cm \cdot au_r^{-4}$	0.2502 (94)	0.0602 (13)				
σ/cm	2.4 E-10	3.3 E-11	1.5 E-09	3.7 E-10	1.2 E-08	5.2 E-09

2c) Values $C_n(i)$ of (14) (calc. from Tables 2a and 2b). $(d_{no}(Q))^2/v_{no} = \Sigma_i C_n(i) R^i$.

i_{max}	4	4	3	3	2	2
n	B (Lyman)	C (Werner)	B (Lyman)	C (Werner)	B (Lyman)	C (Werner)
$10^5 C_n(0)/au_r^2 \cdot cm$	0.9844 (1)	0.5195 (0)	0.9818 (26)	0.5195 (1)	1.0188 (156)	0.5227 (15)
$10^5 C_n(1)/au_r \cdot cm$	1.2943 (30)	0.4441 (2)	1.3149 (63)	0.4436 (2)	1.3065 (485)	0.4409 (46)
$10^5 C_n(2)/cm$	0.8637 (68)	0.1072 (4)	0.9076 (211)	0.1090 (7)	0.5477 (704)	0.0762 (43)
$10^5 C_n(3)/au_r^{-1} \cdot cm$	−0.0478 (188)	−0.0752 (9)	−0.1412 (279)	−0.0710 (13)		
$10^5 C_n(4)/au_r^{-2} \cdot cm$	−0.0841 (232)	−0.0153 (14)				

2d) Values $D_n(i)$ of (15), $(d_{no}(Q))^2/v_{no}^3 = \Sigma_i D_n(i) R^i$.

i_{max}	4	4	3	3	2	2
n	B (Lyman)	C (Werner)	B (Lyman)	C (Werner)	B (Lyman)	C (Werner)
$10^{15} D(0)/au_r^2 \cdot cm^3$	1.0212 (1)	0.4585 (0)	1.0181 (3)	0.4585 (1)	1.0565 (166)	0.4614 (13)
$10^{15} D(1)/au_r \cdot cm^3$	1.6626 (37)	0.6134 (5)	1.6827 (9)	0.6131 (6)	1.6681 (575)	0.6088 (50)
$10^{15} D(2)/cm^3$	1.9761 (115)	0.3843 (21)	2.0720 (304)	0.3848 (33)	1.7071 (894)	0.3549 (112)
$10^{15} D(3)/au_r^{-1} \cdot cm^3$	0.5590 (306)	−0.0393 (65)	0.5397 (65)	−0.0364 (93)		
$10^{15} D(4)/au_r^{-2} \cdot cm^3$	0.3583 (714)	−0.0783 (966)				

2e) Morse oscillator vibrationally averaged bond moments and isotope effects for H_2/D_2 (atomic units).

	$\langle R^0 \rangle$	$\langle R \rangle/au_r$	$\langle R^2 \rangle/au_r^2$	$\langle R^3 \rangle/au_r^2$	$\langle R^4 \rangle/au_r^4$
H_2	1	0.0428	0.0308	0.00464	0.00304
$H_2 - D_2$	0	0.0127	0.00967	0.00238	0.00163

Table 2. (Continued)

2f) Products of matrix elements in Tables 2c and 2d with vibrationally averaged bond moments from Table 2e.
$10^5 C_n(i) \langle R^i \rangle/(\mathrm{au}_r^2 \cdot \mathrm{cm})$.

i_{max}	4	4	3	3	2	2
n	B (Lyman)	C (Werner)	B (Lyman)	C (Werner)	B (Lyman)	C (Werner)
$i=0$ H_2	0.9844 (1)	0.5195 (0)	0.9818 (26)	0.5195 (1)	1.0188 (156)	0.5227 (15)
H_2-D_2	–	–	–	–	–	–
$i=1$ H_2	0.0554 (1)	0.0190 (0)	0.0563 (3)	0.0190 (0)	0.0559 (21)	0.0189 (2)
H_2-D_2	0.0164 (0)	0.0056 (0)	0.0167 (1)	0.0056 (0)	0.0165 (6)	0.0056 (1)
$i=2$ H_2	0.0266 (2)	0.0033 (0)	0.0280 (6)	0.0034 (0)	0.0169 (22)	0.0024 (1)
H_2-D_2	0.0084 (1)	0.0010 (0)	0.0088 (2)	0.0011 (0)	0.0053 (7)	0.0007 (0)
$i=3$ H_2	−0.0002 (1)	−0.0004 (0)	−0.0007 (1)	−0.0003 (0)		
H_2-D_2	−0.0001 (0)	−0.0002 (0)	−0.0004 (0)	−0.0002 (0)		
$i=4$ H_2	−0.0003 (1)	−0.0000 (0)				
H_2-D_2	−0.0002 (0)	−0.0000 (0)				
Total H_2	1.0659 (6)	0.5414 (0)	1.0654 (39)	0.5416 (1)	1.0916 (212)	0.5440 (19)
H_2-D_2	0.0245 (2)	0.0064 (0)	0.0251 (4)	0.0065 (0)	0.0218 (13)	0.0063 (1)

$10^{15} D_n(i) \langle R^i \rangle/(\mathrm{au}_r^2 \cdot \mathrm{cm}^3)$.

	4	4	3	3	2	2
$i=0$ H_2	1.0212 (1)	0.4585 (0)	1.0181 (3)	0.4585 (1)	1.0565 (166)	0.4614 (13)
H_2-D_2	–	–	–	–	–	–
$i=1$ H_2	0.0711 (2)	0.0262 (0)	0.0720 (0)	0.0262 (0)	0.0713 (25)	0.0261 (2)
H_2-D_2	0.0211 (1)	0.0078 (0)	0.0214 (0)	0.0078 (0)	0.0211 (7)	0.0077 (1)
$i=2$ H_2	0.0609 (4)	0.0118 (1)	0.0638 (9)	0.0119 (1)	0.0526 (27)	0.0109 (3)
H_2-D_2	0.0191 (1)	0.0037 (0)	0.0200 (3)	0.0037 (0)	0.0165 (8)	0.0034 (1)
$i=3$ H_2	0.0026 (1)	−0.0002 (0)	0.0025 (0)	−0.0002 (0)		
H_2-D_2	0.0013 (1)	−0.0001 (0)	0.0013 (0)	−0.0001 (0)		
$i=4$ H_2	0.0011 (2)	−0.0002 (0)				
H_2-D_2	0.0006 (1)	−0.0001 (0)				
Total H_2	1.1569 (10)	0.4965 (1)	1.1564 (15)	0.4964 (2)	1.1804 (233)	0.4984 (18)
H_2-D_2	0.0421 (4)	0.0113 (0)	0.0427 (3)	0.0113 (0)	0.0377 (15)	0.0111 (2)

2g) Summed contribution to polarizability and polarizability isotope effects from Lyman and Werner bands.

$\alpha = (2/3) \Sigma\, d_{no}\, d_{on}/E_{no}$; there are $2.1948 \times 10^5\ \mathrm{cm}^{-1}/\mathrm{au}_e$; we write $\alpha\,(\text{Lyman} + \text{Werner}) = \alpha_{BC} = \alpha_{BC,0} + \alpha_{BC,1}\, v^2$, v in cm^{-1} and $\Delta\alpha = \Delta\alpha_{BC,0} + \Delta\alpha_{BC,1} v^2$.

i_{max}	4	3	2	i_{max}	4	3	2
$\alpha_{BC,0}/$ $\mathrm{au}_r^3 \cdot \mathrm{molec}^{-1}$	2.3518 (10)	2.3514 (57)	2.3932 (285)	$\Delta\alpha_{BC,0}/$ $\mathrm{au}_r^3 \cdot \mathrm{molec}^{-1}$	0.0452 (1)	0.0462 (3)	0.0411 (15)
$10^{-10} \alpha_{BC,1}/$ $\mathrm{au}_r^3 \cdot \mathrm{molec}^{-1} \cdot \mathrm{cm}^{-2}$	2.4193 (15)	2.4184 (20)	2.4564 (345)	$10^{-10} \Delta\alpha_{BC,1}/$ $\mathrm{au}_r^3 \cdot \mathrm{molec}^{-1} \cdot \mathrm{cm}^{-2}$	0.0781 (1)	0.0790 (5)	0.0714 (15)

the calculated static polarizability to scale to $(2.35\ \mathrm{au}_r^3)/0.58 = 4.05\ \mathrm{au}_r^3$, which is about 20% below the accepted value, $5.18\ \mathrm{au}_r^3$ [17, 18]. Should the frequency dependence scale similarly, one finds $(2.42 \times 10^{-10}\ \mathrm{au}_r^3\ \mathrm{cm}^2)/0.58 = 4.2 \times 10^{-10}\ \mathrm{au}_r^3\ \mathrm{cm}^2$, about 10% below the observed value [12], $4.6 \times 10^{-10}\ \mathrm{au}_r^3\ \mathrm{cm}^2$. We deem this agreement satisfactory; after all, our intent is only to obtain isotopic ratios

conveniently. Exact polarizabilities can only be obtained by a more elaborate calculation.

Isotope effects calculated from the parameters in Table 2g are reported in Table 3 where they are compared with experiment and with the results calculated using the closure approximation as described below. The static IE calculated above (Calculation I) is larger than experiment by about 30%, while the coefficient

of the frequency dependent term is larger yet. If, as seems reasonable, the transitions to the continuum are not as isotope sensitive as those to bound states, $(\Delta\alpha/\alpha)_{calc}$ will move closer to $(\Delta\alpha/\alpha)_{obs}$ when these transitions are included in the calculation. This is shown parenthetically in Table 3 in the line referring to Calculation I.

It is clear that the present calculation reproduces the essential features of the PIE. The sign and magnitude of both the static and frequency dependent parts are in reasonable agreement with experiment, and that agreement is expected to improve for more nearly complete calculations. The analysis nicely demonstrates the vibrational origin of the PIE and introduces a formalism which should be useful in analysis of PIE's for more complicated molecules.

(b) Use of the Closure Approximation

The second approach employs closure to rewrite (7) and (8) in terms of the ground state second moment d_{00}^2 and its IE, and of v^* and its IE as in (11). We now proceed to make the calculation for molecular hydrogen. To evaluate $\Delta d_{00}^2/d_{00}^2$ we fit $d_{00}^2 = 2*(r_{00}^2 - 2x_1 x_2 - z_1 z_2)$ as calculated from the results of Kolos and Wolniewicz [19] (see their Table 5) to an expansion in powers of R,

$$\langle d_{00}^2 \rangle = \sum_{i=0}^{i_{max}} F_i R^i. \tag{17a}$$

We similarly expanded $\langle r_{00}^2 \rangle$ to examine the approximation $\Delta d_{00}^2/d_{00}^2 \approx \Delta r_{00}^2/r_{00}^2$ which could later prove convenient.

$$\langle r_{00}^2 \rangle = \sum_{i=0}^{i_{max}} G_i R^i. \tag{17b}$$

The F_i and G_i coefficients are reported in Table 4a. The averaging over R^i moments is carried out term by term, as before, using Table 2e. Results are reported in Table 4b, the IE is calculated from the sum (last column), $\Delta d_{00}^2/d_{00}^2 = 0.024/4.64 = 0.0052$; $\Delta\langle r_{00}^2 \rangle/\langle r_{00}^2 \rangle = 0.017/2.61 = 0.0065$. This value for $\Delta d_{00}^2/d_{00}^2$ is only 20% larger than the one, 0.0043, deduced from Larsen's dispersion measurements [11] assuming closure (see line 1 of Table 5). The agreement is as good as can be expected; the closure approximation is rough and ready. The estimate for $\Delta\langle r_{00}^2 \rangle/\langle r_{00}^2 \rangle$ based on Morse averaging is in reasonable agreement with

Table 3. Calculated and experimental polarizability isotope effects for the system H_2/D_2.
$\Delta\alpha/\alpha = (\Delta d_{00}^2/d_{00}^2 - \Delta v^*/v^*) - 2(\Delta v^*/v^*)(v^2/v^{*2}) = A_0 + A_1 v^2$.

	$10^2 A_0$	$10^{12} A_1/cm^{-2}$
Experiment (Table 5)	1.4	1.45
Calculation I [a]	1.9 (1.1)	3.3 (1.9)
Closure, calc. IIa [b]	0.8$_4$	0.6$_4$
Closure, calc. IIb [c]	1.2	1.3

[a] State-to-state calculations scaled from Lyman and Werner bands. See Table 2 and text in the vicinity of (12)–(17). The parenthetical entries for Calculation I assume no IE for those states lying above the Lyman and Werner bands.
[b] Closure calculation. See text in the vicinity of (18)–(21) ($v^* = E^* - E_0 - ZPE/2$). This calculation averages the ground state potential energy.
[c] Closure calculation. See text following (21) ($v^* = E^* - E_0 - ZPE$). This calculation averages the total ground state vibrational energy, but such averaging is without theoretical rationale (even though this calculation agrees best with experiment).

Table 4. Ground state electronic and radial second moments and their isotope effects for H_2/D_2.

4a) The parameters of (17a) and (17b) [19]. $\langle d_{00}^2 \rangle = \Sigma_i F(i)\langle R^i \rangle$ and $\langle r_{00}^2 \rangle = \Sigma_i G(i)\langle R^i \rangle$. σ is the standard deviation of the least squares fit.

	$i = 0/au_r^2$	$i = 1/au_r$	$i = 2$	$i = 3/au_r^{-1}$	$i = 4/au_r^{-2}$	σ/au_r^2
$F(i)$	4.5562	1.9727	−0.0797	−0.1548	−0.0143	6.5 E-05
$G(i)$	2.5483	1.2838	0.1199	−0.0168	0.0137	1.7 E-05

4b) Vibrationally averaged values of (d_{00}^2) and $\Delta(d_{00}^2)$, and (r_{00}^2) and $\Delta(r_{00}^2)$ calculated from Tables 2e and 4a.

	$F(0)\cdot R^0/au_r^2$	$F(1)\cdot R/au_r^2$	$F(2)\cdot R^2/au_r^2$	$F(3)\cdot R^3/au_r^2$	$F(4)\cdot R^4/au_r^2$	SUM/au_r^2
H_2	4.5562	0.0844	−0.0025	−0.0007	−0.0000	4.6374
H_2-D_2	–	0.0251	−0.0008	−0.0004	−0.0000	0.0239

	$G(0)\cdot R^0/au_r^2$	$G(1)\cdot R/au_r^2$	$G(2)\cdot R^2/au_r^2$	$G(3)\cdot R^3/au_r^2$	$G(4)\cdot R^4/au_r^2$	SUM/au_r^2
H_2	2.5483	0.0549	0.0036	−0.0001	0.0000	2.6067
H_2-D_2	–	0.0161	0.0011	0.0000	0.0000	0.0172

Table 5. Isotope effects on refractive indices; parameters of fit to (11), $\Delta f(n_r/n_r) = A + m v^2$, $A = (A\alpha/\alpha)_s - \Delta V/V$, and $m = -(2/v^{*2})(\Delta v^*/v^*)$; static and dynamic contributions to polarizability isotope effects; static PIE's from bond polarizability isotope effects. σ (column 4) is the standard deviation of the least squares fit reported in columns 2 and 3.

$System^{ref}_{phase}$	$10^3 \cdot A$	$10^{12} \cdot (m/cm^2)$	$10^4 \cdot \sigma$	$10^3 \cdot (\Delta V/V)$ and ref.	$10^{-10} \cdot v^{*2}$ (cm^{-2})	$10^3 \cdot (\Delta\alpha/\alpha)_s$	$-10^3 \cdot \Delta v^*/v^*$	$10^3 \cdot \Delta d_{00}^2/d_{00}^2$	$10^3 \cdot (\Delta\alpha/\alpha)_0$ Table 6 [f]
$(H_2/D_2)_g$ [12]	13.7±0.1	1.45±0.08	1.4	–	1.30[a]	13.7±0.1	9.4±1.0	4.3±1.1	(13.7)
$(CH_4/CD_4)_g$ [12]	16.2±0.1	2.02±0.06	1.0	–	1.29	16.2±0.1	13.0±1.1	3.2±1.2	(16.2)
$(HCl/DCl)_g$ [12]	2.22±0.06	0.43±0.05	1.0	–	1.17	2.2±0.1	2.5±0.6	−0.3±0.7	
$(HBr/DBr)_g$ [12]	1.41±0.10	0.54±0.10	1.5	–	0.921	1.4±0.1	2.5±0.8	−1.1±0.9	
$(H_2S/D_2S)_g$ [12]	4.1±0.10	1.34±0.11	1.4	–	0.792	4.1±0.1	10.6±1.4	−6.5±1.5	
$(NH_3/ND_3)_g$ [22]	11.9±0.1	−8.2±3.8	8.9	–		11.9±1.4	c	c	(11.9)
$(H_2O/D_2O)_g$ [23]	9.6±0.1	2.48±0.4	0.4	–		9.6±0.1 6.8±0.4[e]			
$(H_2O/D_2O)_l$ [13]									
288.15 K	b	4.97±0.47	0.2	−4.4 [1]	1.275	7.45±0.07	29.9±0.9		
313.15	b	4.76±0.49	0.2	−2.9 [1]	1.275	7.35±0.07	29.8±0.9	−22.4±0.9	(7.2)
348.15	b	4.54±0.51	0.2	−2.1 [1]	1.272	7.09±0.08	29.5±0.9		
363.15	b	4.32±0.53	0.2	−2.0 [1]	1.272	6.91±0.09	29.3±0.9		
$(CHCl_3/CDCl_3)_l$ [1]	1.68±0.08	0.16±0.20	0.4	−0.2±0.1 [1]	d	1.5±0.2	c	c	1.3
$(C_2H_2Br_4/$ $C_2D_2Br_4)_l$ [1]	1.69±0.05	0.40±0.13	0.3	0.0±0.1 [1]	d	1.7±0.2	d	d	1.3
$(CH_3NO_2/$ $CD_3NO_2)_l$ [1]	2.3±0.5	−4.2±0.1	1.5	−0.2±0.1 [1]	d	2.1±0.6	d	d	6.7
$(C_6H_6/C_6D_6)_l$ [1]	3.2±0.2	0.44±0.52	1.2	2.1±0.1 [36]	d	5.3±0.4	c	c	6.1
$(C_6H_5CH_3/$ $C_6D_5CD_3)_l$ [1]	3.8±0.1	1.32±0.40	0.3	1.5±0.2 [34]	0.722	5.3±0.3	4.8±1.4	0.5±1.7	6.8
$(C_6H_{12}/C_6D_{12})_l$ [1]	8.55±0.06	1.84±0.17	0.4	2.2±0.2 [35]	1.27	10.8±0.3	11.7±1.1	−0.9±1.4	10.9
$(C_6H_5NH_2/$ $C_6H_5ND_2)_l$ [1]	2.3±0.3	0.2±0.5	1.1	−1.4±0.2 [1]	d	0.9±0.4	c	c	1.6
$(C_6D_3H_2NH_2/$ $C_6D_3H_2NH_2)_l$ [1]	1.6±0.1	−0.46±0.12	0.3	−0.1±0.2 [1]	d	1.5±0.3	d	d	1.6
$(CH_3OH/CH_3OD)_l$ [1]	2.65±0.18	0.26±0.48	1.1	−1.5±0.1 [37]	d	1.5±0.3	c	c	2.0
$(C_2H_5OH/$ $C_2H_5OD)_l$ [1]	1.68±0.14	0.62±0.38	0.9	−1.5±0.2 [1]	d	0.2±0.3	c	c	1.2
$(n\text{-}C_3H_7OH/$ $n\text{-}C_3H_7OD)_l$ [1]	2.13±0.07	0.31±0.30	0.5	−2.2±0.4 [1]	d	−0.1±0.5	c	c	0.9
$(i\text{-}C_3H_7OH/$ $i\text{-}C_3H_7OD)_l$ [1]	1.29±0.03	1.04±0.30	0.3	−3.0±0.4 [1]	d	−1.7±0.5	c	c	0.9
$((CH_2OH)_2/$ $(CH_2OD)_2)_l$ [1]	3.72±0.18	1.53±0.26	0.6	−1.4±0.2 [1]	d	2.3±0.4	c	c	2.2
$(CH_3COOH/$ $CH_3COOD)_l$ [1]	2.41±0.20	0.65±0.40	0.9	−0.6±0.2 [1]	d	1.8±0.4	c	c	1.0

[a] 5% uncertainty assigned to v^*.
[b] See text.
[c] Cannot be obtained at useful precision from present data. The uncertainty in both $\Delta v^*/v^*$ and $\Delta d_{00}^2/d_{00}^2$ is in excess of 50%.
[d] Not available.
[e] Corrected from the experimental value immediately above using currently accepted VPIE data (see text).
[f] Calculated following Denbigh [31], from the bond polarizabilities and isotope effects given in Table 6 as deduced from the parenthesized values at the top of this column, Table 5.

one from an earlier calculation reported by Kolos and Wolniewicz [20]. They found $\langle r_{00}^2 \rangle_H = 2.6132$ and $\langle r_{00}^2 \rangle_D = 2.5935$; $\Delta \langle r_{00}^2 \rangle / \langle r_{00}^2 \rangle = 0.0075$.

The isotope effect on the energy parameter, $\Delta v^*/v^*$, is less straightforwardly estimated. Remember v^* is an electronic excitation energy from the ground state to an average excited state at a given internuclear separation, averaged appropriately over the ground sate zero-point vibrational function. We shall assume that the variation in the energy of the ground state with

internuclear separation can be described in the harmonic approximation in terms of a force constant $\varkappa$ and the coordinate, R, which measures the displacement from equilibrium. For the average excited state we expect a somewhat smaller dependence of the energy on the displacement coordinate, but for want of any specific information will assume no R dependence at all. We obtain

$$v^* = E^* - E_{ground} = E^* - (E_0 + \varkappa R^2/2). \quad (18)$$

We now average v^* over the zero-point vibrational wavefunction of the ground electronic state and remember the virial theorem [10] for harmonic oscillators to obtain

$$v^* = E^* - E_0 - \varkappa \langle(R)^2\rangle/2$$
$$= (E^* - E_0) - ZPE/2, \qquad (19)$$

where ZPE is the zero-point vibrational energy of the ground state. Thus

$$\Delta v^*/v^* = -\Delta(ZPE/2)/(E^* - E_0 - ZPE/2)$$
$$\approx -\Delta(ZPE/2)/v^*. \qquad (20)$$

In the denominator it is sufficient to take $v^* \approx E^* - E_0$,

$$\Delta\alpha/\alpha = (\Delta d_{00}^2/d_{00}^2 + \Delta(ZPE/2)/v^*)$$
$$+ (\Delta(ZPE)/v^*)(v^2/v^{*2}). \qquad (21)$$

For $v^* = 1 \times 10^5$ cm^{-1} (about the average excitation energy for H_2), $\Delta(ZPE)/v^* = 0.0064$ (the IE on the ground state ZPE is 638 cm^{-1}), $\Delta\alpha/\alpha = (0.0052 + 0.0032) + 0.64 \times 10^{-12} v^2$. This result is compared with experiment and with the earlier calculation in Table 3. The calculated static isotope effect (Table 3, calc. II a) is about 40% below the experimental value for the closure calculation, and about 40% higher than experiment for the Lyman/Werner state-to-state calculation (Table 3, calc. I) (20% lower than experiment if no IE is assumed on excited state potential energies above the Lyman and Werner bands). The coefficients of the frequency dependent terms are lower than experiment for the closure calculation, but higher for the state-to-state calculation. It is interesting to note that had we taken $\Delta v^*/v^* = -\Delta(ZPE)/v^*$, instead of employing (20) to evaluate $\Delta v^*/v^*$, both intercept and slope would be much more nearly in agreement with experiment (cf. Table 3, closure calc. II b). In fact the agreement would be essentially quantitative, but we find no theoretical rationale for such averaging. To sum up: considering the precision of the d_{ij} calculations [15, 17, 19, 20], the uncertainty in the closure approximation, and uncertainty in the other approximations which have been employed, we conclude that agreement between calculation and experiment is reasonable. In the closure calculation we assumed no IE whatsoever on E^*, the averaged upper states potential energy, but without giving any detailed justification for that assumption. The assumption is extreme.
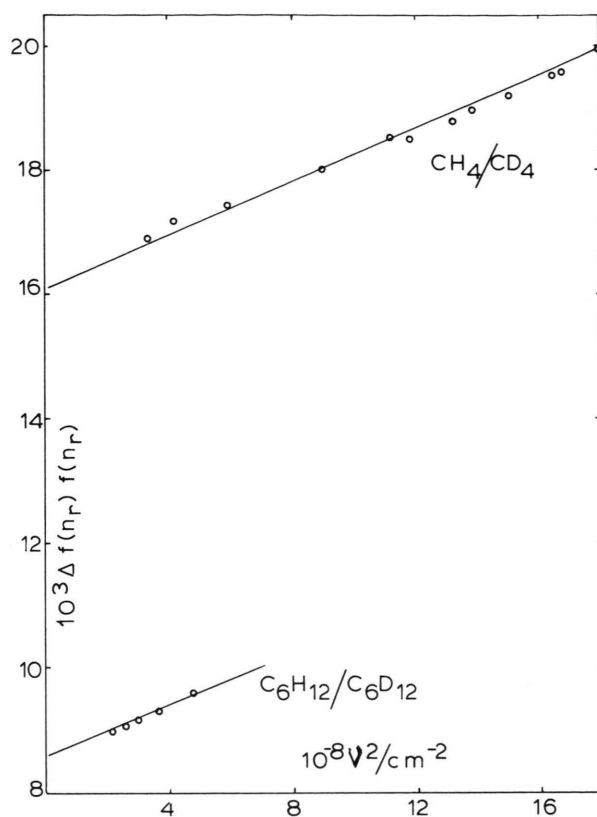

Fig. 1. H/D isotope effects for two hydrocarbons. $\Delta f(n_r)/f(n_r) = (6n_r^2/(n_r^2 + 2)(n_r^2 - 1))\Delta n_r/n_r$ is plotted vs. $v^2/(\text{cm}^{-1})^2$. Upper curve CH_4/CD_4, gas phase [12]. Lower curve C_6H_{12}/C_6D_{12}, liquid phase, 293.15 K [1].

Summary, H_2/D_2 Analysis

The development above has demonstrated that PIE's and their frequency dependence can be calculated, albeit approximately, by properly averaging the transition moment/transition energy ratio over the ground state vibration. The analysis of H_2/D_2 data has served the useful purpose of testing this formalism for the PIE and demonstrating its validity. It has shown that both the static and dynamic parts of PIE are vibrational in origin. The second part of the paper deals with application to other molecules. These, unlike hydrogen, are too complicated to permit elaborate theoretical calculation of the PIE in an economic fashion.
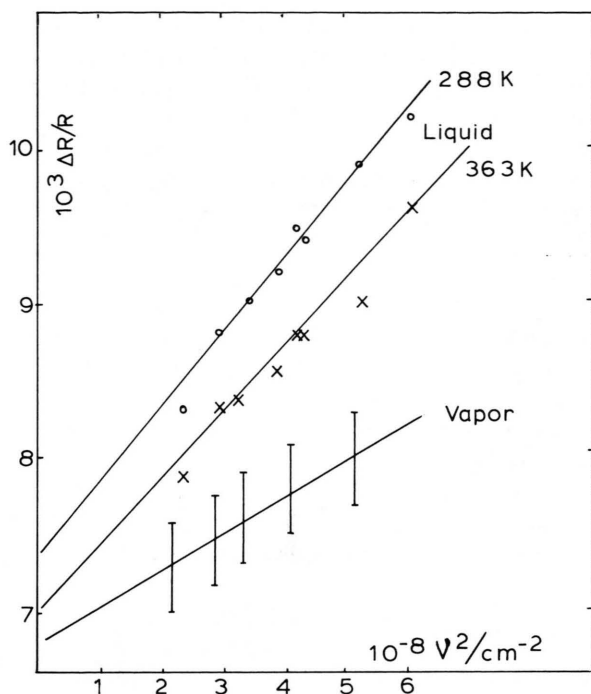
Fig. 2. Molar refractivity isotope effects for the system H_2O/D_2O. $\Delta R/R = \Delta f(n_r)/f(n_r) + \Delta V/V$ is plotted vs. $v^2/(cm^{-1})^2$. The lowermost curve is for the vapor [23] as corrected (see text). The upper curves are for the liquids at 15 and 90 °C [13].

Polarizability Isotope Effects from Refractive Indices

Table 5 reviews data on frequency dependent refractive index isotope effects from least squares fits with (11). For these fits, $\Delta f(n_r)/f(n_r) = A + m v^2$, with $m = -(2/v^{*2})(\Delta v^*/v^*)$ and $A = \Delta d_{00}^2/d_{00}^2 - \Delta V/V + m v^{*2}/2$. The parameter v^{*2} (column 6) has been estimated from least squares fits of refractive index data for the protio compound to the Drude equation [21], written in the form $((n_{rH}^2-1)/(n_{rH}^2+2)) = \Theta/(v^{*2}-v^2)$, Θ a constant. The form is equivalent to that obtained with the closure approximation, above. The static PIE is $(\Delta\alpha_0/\alpha_0) = A + \Delta V/V$, and the isotope effect on the second moment is $\Delta d_{00}^2/d_{00}^2 = \Delta\alpha_0/\alpha_0 - m v^{*2}/2$ (see Table 5). The first seven entries in Table 5 refer to our least squares analysis of the gas phase interferometric measurements of Larsen and coworkers ((H_2/D_2) [12], (CH_4/CD_4) [12, 22], (HCl/DCl, HBr/DBr, and H_2S/D_2S) [12]) and the Cuthbertsons [23] (H_2O/D_2O). Plots of similar data reported by Frivold and coworkers [24] for H_2/D_2, CH_4/CD_4, HCl/DCl, NH_3/ND_3, H_2S/D_2S and

H_2Se/D_2Se showed intolerably high scatter and will not be further discussed except for the data on NH_3/ND_3 (see Table 5). The first seven sets of isotopic isomers were measured [12, 22] at equal (low) pressures; so for these gas phase data $\Delta V/V = 0$. Refractive indices of dilute vapors lie close to unity. The uncertainty in the high precision measurements is less than 1 part in 10^7 but, even so, the uncertainties in least squares slope and intercept translate to an approximate 5 to 10% uncertainty in $(2/v^{*2})(\Delta v^*/v^*)$. Clearly, however, within these limits the slope-intercept measurements of $(\Delta\alpha_0/\alpha_0)$ and $\Delta v^*/v^*$ are consistent with theoretical expectations (see previous section where the H_2/D_2 case is discussed and further discussion below).

Proceeding down Table 5, we defer discussion of the data on H_2O/D_2O, and turn attention to refractive index data reported by Rabinovitch [1] for a variety of liquids at 293.15 K. A precision of 1 in 10^5 is claimed, and that claim is consistent with the uncertainties found in the least squares parameters reported in columns 2 and 3. However the isotope effects are small, so the relative error in the fitting parameters m and A, particularly m, is large. In many cases, the present data are not precise enough to resolve the characteristic energy $(\Delta v^*/v^*)$ and second moment $(\Delta d_{00}^2/d_{00}^2)$ contributions to PIE with useful precision. For example the relative error in m for the $C_6H_5NH_2/C_6H_5ND_2$ or n-C_3H_7OH/n-C_3H_7OD data exceeds 100% and implies large relative uncertainties in $(\Delta v^*/v^*)$ and $(\Delta d_{00}^2/d_{00}^2)$ even though their linear combination $(\Delta\alpha_0/\alpha_0)$ as determined from intercept and molar volume isotope effect (MVIE) is established with better precision. Other compounds in the table behave similarly. Smith and Van Hook [25] have recently reported differential refractive index (RI) measurements of modestly improved precision on a number of H/D isotopic pairs of liquids, but results of much higher precision will be required to yield usefully precise values of $(\Delta v^*/v^*)$ and $(\Delta d_{00}^2/d_{00}^2)$. The Smith and Van Hook results are incorporated in Table 5.

We now consider the water data of Mehu and Johannin-Giles [13] and the Cuthbertsons [23] as summarized in Table 5. For the liquid the RI's for H_2O and D_2O at nine wavelengths between 6438 and 4047 A have been reported [13] at 5 degree intervals between 288.15 and 363.15 K. Molar refractivities, $R = V_m(n^2-1)/(n^2+2)$, where V_m is the molar volume of the fluid and n the experimental RI, were calculated

from the RI data using V_m data recommended by Kell [26]. Preliminary fits to (11) at individual temperatures showed that both intercept and slope depended on temperature and phase. We fit the entire set of liquid data to a modified form of (11) derived after examining the form of the preliminary fits to liquid and vapor.

$$
\begin{aligned}
\Delta f(n_r)/f(n_r) + \Delta V/V &= \Delta R/R \\
&= \Delta d_{00}^2/d_{00}^2 - (\Delta v^*/v^*)(1 + \Delta a\, t) \\
&\quad - (\Delta v^*/v^*)(2/v^{*2})(1 + \Delta a\, t)\, v^2 .
\end{aligned}
\tag{22}
$$

Here t is the Celsius temperature, Δa is a fitting parameter, and the other symbols take up their previous meaning. Least squares analysis yielded $\Delta d_{00}^2/d_{00}^2 = (-22.4 \pm 0.9) \times 10^{-3}$, $(\Delta v^*/v^*) = (-29.9 \pm 0.9) \times 10^{-3}$, and $\Delta a = (2.41 \pm 0.21) \times 10^{-4}\,C^{-1}$, with $v^* = 1.129 \times 10^5\,cm^{-1}$ obtained from a fit to a one-term dispersion relation (Drude equation). Although for most substances the molar refractivity is apparently temperature and phase independent [21], the data show this is not the case for water. The reason is probably connected with the very large frequency shift in the OH/OD stretching frequencies of water which occur on condensation. For example at 313.15 K the total ZPE shift on condensation for the two OH stretching frequencies is about 330 cm^{-1} to the red, but that phase frequency shift depends on temperature (because of the temperature dependence of the extent of hydrogen bonding). Van Hook [27] has demonstrated consistency between spectroscopic [28] and vapor pressure isotope effect (VPIE) measurements using temperature dependent OH stretching frequencies, $\Delta(\Sigma v_{OH})/\delta T = 1.4\,cm^{-1}\,C^{-1}$. To introduce temperature dependence into the present formalism and arrive at (22), we recognized that to reasonable approximation one can replace Δv^* by $\Delta v^*(1 + \Delta a t)$ and v^* by $v^*(1 + a t)$ and assume $\Delta a \ll a$. Equation (22) is first order in isotopic difference, so terms involving "a" cancel. The least squares derived value of "Δa" is equivalent to $\Delta v^* = (0.8 \pm 0.1)\,cm^{-1}\,C^{-1}$ and correlates nicely with value of 1.4 $cm^{-1}\,C^{-1}$ cited above [27]. On the other hand we have not attempted a rationalization at the molecular level for the large inverse IE on d_{00}^2. Smith and Van Hook [25] point out that in first approximation $\Delta d_{00}^2/d_{00}^2$ should scale with the vibrational amplitude IE in qualitative agreement with the development in the earlier part of this paper. For water, however, the center of mass is isotope dependent and lies further out along the line bisecting DOD than it does for HOH. The center of charge and

the center of mass do not coincide, and $\langle d_{00}^2 \rangle$ referenced to the center of mass rather than the center of charge shows an inverse IE. A closely related argument was used by Dutta-Choudhury and Van Hook [29] to rationalize the inverse MVIE's observed for the condensed phase waters and ices. The effect appears to be common to non-centro-symmetric molecules (see Table 5).

The vapor phase molar refractivity data of Cuthbertson and Cuthbertson [23], after correction using presently accepted VPIE data [30], yield PIE's in good agreement with the liquid phase measurements (Table 5). (The Cuthbertsons established vapor concentrations in their interferometer cell by liquid-vapor equilibration.)

Bond Polarizability Isotope Effects

To test the consistency of the static PIE's reported in Table 5, static bond PIE's were calculated from the data for hydrogen, methane, water, ammonia, and hydrogen chloride and bromide (i.e. from the parenthesized values at the top of the last column of Table 5), and are reported in Table 6. Using the bond polarizabilities recommended by Denbigh [31], together with tabulated values for α, and employing the estimation scheme described by Denbigh and elaborated by Hirschfelder, Curtiss and Bird [2], static polarizabilities and their PIE's were calculated for the liquid phase compounds listed at the bottom Table 5. The results are reported in the last column of Table 5. The average deviation $\langle |PIE(\text{estimated}) - PIE(\text{expt.})| \rangle$ is 0.0008 and compares favorably with experimental error. Thus, the usefulness of this correlation scheme is established. From the bond polarizabilities in Table 6 one can in principle calculate PIE's for the majority of organic C, O, N, H/D compounds. (To exemplify consider cyclohexane. From [2], page 949, $\alpha(CH) = 6.5$ and $\alpha(CC) = 6.4 \times 10^{-25}\,mol^{-1}\,cm^3$ so for $c\text{-}C_6H_{12}$ $\alpha = 12 \times 6.5 + 6 \times 6.4 = 116.4 \times 10^{-25}$ (expt. $= 116.1 \times 10^{-25}$), while the IE (Table 4) is $\Delta\alpha =$

Table 6. Bond polarizability isotope effects.

Bond	$10^3\,(\Delta\alpha_0/\alpha_0)$	$10^{25}\,\Delta\alpha_0/cm^3$
HH/DD	13.7	0.11
CH/CD	16.2	0.10
OH/OD	7.2	0.064
NH/ND	12	0.089

Table 7. H/D virial coefficient isotope effects.

	$(2\pi N \sigma^3)$[a] $cm^3 mol^{-1}$	$(\varepsilon/k)/K$ [a]	$10^3 (\Delta\alpha/\alpha)$ [b]	$10^4 (\Delta\sigma/\sigma)$ [c]	T/K	$-\Delta B = -(B_H - B_D)$ $cm^3 mol^{-1}$ (calc., this work)	$-\Delta B$ Exp. (ref.)
CH_4/CD_4	85 ± 6	156 ± 6	16.2	3.5	200	1.3	3 [4, 5]
					300	0.5	2
					400	0.3	1
C_2H_6/C_2D_6	178 ± 8	205 ± 5	13.9	3.0	200	4.1	6 [5]
					300	3.2	3
					400	1.1	1
					500	0.9	0
C_2H_4/C_2D_4	221 ± 21	167 ± 8	9.9	2.0	200	2.9	4 [5]
					300	1.3	3
					400	0.7	1
					500	0.5	0
$(CH_3)_4C/(CD_3)_4C$	595 ± 38	242 ± 8	12.2	1.5	300	20	20 [5]
					400	13	11
					500	11	9
C_6H_6/C_6D_6	1483 ± 61	196 ± 3	5.3	0.75	300	15	
					400	10	
					500	8	≤ 8 [39]
C_6H_{12}/C_6D_{12}	2130 ± 46	176 ± 2	10.9	0.8	300	58	
					400	38	

[a] From (23) by least squares.
[b] See Table 5 and text.
[c] See text and/or [32].

$12 \times 0.104 \times 10^{-25} mol^{-1} cm^3$, so $\Delta\alpha_0/\alpha_0 = 1.25/116$ $= 0.0107$ (expt. 0.0108).)

Other Properties, Including Virial Coefficient and Molar Volume Isotope Effects

A number of important physical properties, for example the London dispersion contribution to the second virial coefficient, scale with polarizability. With a reliable method available to estimate PIE's, useful estimates of isotope effects on these properties become available [4, 5].

The Virial Coefficient Isotope Effect (VCIE)

The Sutherland potential combines a simple dispersion attractive term with a hard sphere cut-off to model intermolecular interaction. The strength of attraction is proportional to α^2, $\Phi(dis) = - K \alpha^2/r^6$ $= -(\varepsilon \sigma^6/r^6)$, the negative sign implies attraction, ε is the well depth, and σ the size parameter. The repulsive contribution is such that $\Phi = \infty$ for $r < \sigma$. The second virial coefficient is [2]

$$B = (2\pi N \sigma^3/3)(1 - 3(\varepsilon/kT)(1 + \varepsilon/(16 kT)) - ...), \quad (23)$$

so

$$\Delta B/B = (3 \Delta\sigma/\sigma - 3(\varepsilon/kT)(2\Delta\alpha/\alpha - 6\Delta\sigma/\sigma) + ...))/ \\ (1 - 3(\varepsilon/k) - ...) \quad (24)$$

because $\Delta\varepsilon/\varepsilon = 2\Delta\alpha/\alpha - 6\Delta\sigma/\sigma$. The Sutherland potential is crude, but in first approximation it suffices to estimate virial coefficient isotope effects using the difference formalism. With $\Delta\alpha/\alpha$ calculated as in the section above, and with $\Delta\sigma/\sigma$ estimated from mean square amplitudes for the gas phase molecules following Bartell and Roskos [32], or for more massive molecules from $\Delta V/V$ [6, 29, 30, 32–37] not too far from the triple point, the VCIE's reported in Table 7 were calculated. The table compares calculated and experimental VCIE's for those four hydro/deuterocarbons [4, 5] where comparison with experiment is possible, and gives a calculated VCIE for one other compound. Because VCIE scales as $(2\Delta\alpha/\alpha - 6\Delta\sigma/\sigma)$, the relative error in the calculation is large; we have estimated it as 25%. Within that uncertainty, however, the calculated and experimental values (which are also imprecise) are in good agreement in both sign and magnitude. VCIE's are small and difficult to measure. For all except the most exacting requirements, the

present method of estimation gives useful results while avoiding the large investment in time and capital which high accuracy PVT measurements imply. In the development, we have deliberately avoided treatment of H-bonded systems which are not expected to be satisfactorily described with the Sutherland potential.

Estimation of Molar Volume Isotope Effects

Equation (11) shows at zero frequency that $\Delta f/f = (\Delta d_{00}^2/d_{00}^2 - \Delta v^*/v^* - \Delta V/V)$. The parameters $\Delta v^*/v^*$ and v^* can be obtained if refractive index data of useful precision are available over a range of frequencies. If $\Delta V/V$ is available from other experiments the data can be used to measure the IE on electronic second moment. Alternatively a suitably reliable estimate of $\Delta d_{00}^2/d_{00}^2$ may be available from calculations or correlations with data on other compounds (or from vapor phase RI measurements where $\Delta V/V = 0$). In that case it is possible to obtain both PIE and $\Delta V/V$ from a single series of refractive index measurements. With differential refractometry on liquid samples it is possible to measure isotopic differences in the sixth or even seventh significant figure of the refractive index. Such measurement is about two orders of magnitude better than the data for $\Delta V/V$ reviewed in Table 5 and should correspond to $\approx \pm 0.0001$ in $(\Delta \alpha_0/\alpha_0)$ and $\Delta v^*/v^*$. $\Delta V/V$'s for H/D substitution typically are of the order 10^{-3} and are established by high precision densitometry to at best ± 0.0001. From Table 5 we note that $\Delta d_{00}^2/d_{00}^2$ and $\Delta v^*/v^*$ are commensurate in size. Thus, by coupling differential RI and densitometric MVIE, the IE on electronic second moment can be determined. Alternatively, if gas phase differential RI measurements are possible, $(\Delta V/V = 0)$; so $\Delta d_{00}^2/d_{00}^2$ can be determined directly. If the PIE is independent of phase, $\Delta d_{00}^2/d_{00}^2$ can be transferred to the condensed phase to yield $\Delta V/V$'s with a precision equal to or better than those now available from high precision densitometry. This approach, however, is restricted to molecules where the isotopic substitution is in non-hydrogen-bonded positions, vide supra.

The Vapor Pressure Isotope Effect

The VPIE is the IE on the equilibrium between the condensed and dilute gas phases [30]. In the theoretical analysis of VPIE, vibrational frequency shifts consequent to the phase change must be considered for all $3n$ normal modes. For the internal frequencies, Wolfs-

berg [8] has shown the van der Waals dispersion interaction between two molecules leads to a zero point energy shift proportional to terms involving ground electronic state infrared intensities and vibrational polarizability. That ZPE shift arises from a contribution of excited vibrational states within the electronic ground state to the molecular polarizability, and this contribution to the polarizability has been ignored in this paper. The contribution from excited electronic states is related to the electronic polarizability in the development in this paper. It, too, can be re-expressed in terms of a set of zero point energy shifts characterizing the phase change. For methane, where the integrated IR intensity is modest, Fang and Van Hook [4] have shown the electronic ground state IR contribution to the IE's to be small compared to the contribution from electronic polarizability.

In addition to the ZPE shift in internal frequencies, VPIE analysis must take proper account of the quantization of the external motions of the interacting molecules within the well defined by the intermolecular potential (i.e. account for hindered rotation and translation) [30]. This leads to a positive contribution to the overall VPIE, opposite in sense to that from the dispersion interaction treated above via the PIE. For relatively light molecules the external contribution can be significant. For that reason the VPIE, and other IE's on thermodynamic activity and related properties, do not scale in simple proportion to the PIE. (IE's on the thermodynamic activity and its derivatives are straightforwardly related to VPIE using standard thermodynamic procedures [30].)

Remark. The connections between the MVIE, VCIE and/or VPIE, and the PIE have been argued for many years [3–5, 7, 8, 30]. The present analysis points out that the PIE, an effect of vibrational averaging, gives rise to an IE on the van-der-Waals interaction. Thus, the analysis offers a straightforward description of the physical origin of the PIE and of some of its physical consequences.

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