Some Measurements of H/D Polarizability Isotope Effects Using Differential Refractometry

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Dedicated to Professor Jacob Bigeleisen on the occasion of his 70th birthday

Refractive index differences between the H and D isomers of some common molecules in the liquid phase were measured between 404.7 and 690.0 nm. The data are combined with information on molar volume isotope effects to yield values for H/D isotope effects on the static polarizability, the vibrational contribution to the static and frequency dependent parts of the polarizability, and the H/D isotope effect on the second moment of the electronic charge distribution. The present results suffice to demonstrate the practicability of this technique to measure the components of the polarizability listed above. However for accurate resolution of the vibrational and second moment contributions, refractive index data of still greater precision will be required.

Introduction

It is a real pleasure to dedicate this paper to Jacob Bigeleisen. The senior author was privileged to spend a postdoctoral appointment with Bigeleisen at Brookhaven National Laboratory in the early sixties. That experience first exposed him to isotope chemistry, now his long-time field of principal interest. Continuing scientific stimulation and personal communication with Professor and Mrs Bigeleisen over the years has been and is very much appreciated by the author and by his wife, Nancy, who once lived just down the street from the Bigeleisen home during the Brookhaven years. Both of us place high value on our relationship with Jake and Grace.

The polarizability of a molecule or collection of molecules is a property which describes the response of electric charge distributions within the molecule(s) to an external electric field. Surprisingly, until a recent discussion by Van Hook and Wolfsberg [1] polarizability isotope effects (PIE's) had not been discussed in terms of a difference development, and no detailed physical interpretation of the origins of the effect was available. Polarizabilities and PIE's can be conveniently measured by determining refractive indices and refractive index differences as a function of wavelength, but differential refractive index data of useful precision are lacking in the literature, especially for molecules in the condensed phase. The present study was undertaken to find out whether refractive index difference measurements with simple equipment would suffice to resolve the different components of the PIE.

Since, in first order, the electronic structure of a molecule is independent of isotopic substitution, PIE's are expected to be small. That effect which does exist is a consequence of isotope effects on vibrational properties. In the usual quantum mechanical calculation of the polarizability one considers the perturbation caused by the interaction of an external electric field with the electric dipoles, both permanent and fluctuating, formed by the charges making up the molecule [2]. In one standard method of calculating the PIE [3, 4] the ground state matrix elements for the perturbation are suitably averaged over the ground state vibration. The resulting IE is a consequence of the isotopic differences in ground state vibrational amplitudes. Accurate wave functions and their gradient are required, and the calculations can become numerically elaborate.

The alternative approach to the PIE [1] begins with a well known result obtained by application of second order perturbation theory and is briefly reviewed here. The frequency dependent mean polarizability of a collection of spatially averaged tumbling liquid or vapor phase molecules is given [2] in terms of the sum over squared transition moments to all upper states, (electronic, vibrational, and other),

$$\alpha(\nu) = (2/3\,\hbar) \sum_n \nu_{n,0} \langle \mu_{n,0} \rangle^2 / (\nu_{n,0}^2 - \nu^2)\,. \qquad (1)$$

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Here $\langle\mu_{n,0}\rangle$ is the electronic dipole transition moment between the ground (0'th) and n'th excited state, $\langle\mu_{n,0}\rangle = \int\psi_n\,\mu\,\psi_0\,\mathrm{d}\tau$, ψ_n and ψ_0 are wave functions, and μ is the dipole operator. Also, $v_{n,0}$ is the frequency corresponding to the energy difference between ground and excited state, and v is frequency of the electromagnetic field probing the effect. We assume that the frequency of the probing light is much higher than the rotational and other low frequencies and there is no physically significant contribution from such low energy states. Equation (1) can then be approximated [2] using closure to give

$$\alpha(v) = (2/3\hbar)\left(\langle\mu_{0,0}^2\rangle - \langle\mu_{0,0}\rangle^2\right) v_n/(v_n^2 - v^2)\,. \qquad (2)$$

Here $\langle\mu_{0,0}\rangle$ is the dipole moment averaged over the ground state, and $\langle\mu_{0,0}^2\rangle$ is the second moment of the electronic charge distribution also averaged over the ground state. v_n is now a suitably averaged excitation, sometimes taken as the frequency corresponding to the energy difference to ionization. Actually there is little realistic expectation that the parameter v_n will coincide exactly with any of the various excitation frequencies or with the ionization potential. Also complications will ensue unless $v_n^2 \gg v^2$ over the entire range of measurement, and we incorporate that assumption into the present formalism. Therefore the present analysis is limited to molecules which are not colored and/or which have little or no vibronic intensity in the visible region.

To express PIE, due account must be taken of isotope effects on all terms; one obtains in first order (i.e. neglecting all higher order isotope effects)

$$\Delta\alpha(v)/\alpha(v) = \frac{\Delta\langle\mu_{0,0}^2\rangle - 2\langle\mu_{0,0}\rangle\,\Delta\langle\mu_{0,0}\rangle}{\langle\mu_{0,0}^2\rangle - \langle\mu_{0,0}\rangle^2} - (\Delta v_n/v_n)\,\frac{(v_n^2 + v^2)}{(v_n^2 - v^2)}\,. \qquad (3)$$

The final approximations leading to (4) recognize that $v_n^2 \gg v^2$, so expansion of the denominator of the second term is warranted, and [5] that $\langle\mu_{0,0}^2\rangle \gg \langle\mu_{0,0}\rangle^2$. This second approximation is exact for nonpolar molecules where $\langle\mu_{0,0}\rangle = 0$.

$$\Delta\alpha(v)/\alpha(v) = \Delta\langle\mu_{0,0}^2\rangle/\langle\mu_{0,0}^2\rangle - (\Delta v_n/v_n) \cdot (1 + 2v^2/v_n^2)\,. \qquad (4)$$

The connection between the PIE and the refractive index isotope effects is made through the Lorenz-Lorentz equation [2]

$$f(n) = (n^2 - 1)/(n^2 + 2) = \alpha N/(3\varepsilon_0)\,, \qquad (5)$$

where n is the refractive index, N the number density of molecules and ε_0 the permittivity of the vacuum. Differentiation with respect to isotope and combination with (4) yields

$$\Delta f(n)/f(n) = [\Delta\langle\mu_{0,0}^2\rangle/\langle\mu_{0,0}^2\rangle - \Delta V/V - \Delta v_n/v_n] - (2v^2/v_n^2)(\Delta v_n/v_n)\,, \qquad (6)$$

which is of the form $\Delta f(n)/f(n) = A + Bv^2$, with slope and intercept given by

$$B = -(2/v_n^2)(\Delta v_n/v_n) = 2(\Delta\mathrm{ZPE} - \Delta\mathrm{VIB})/v_n^3 \qquad (7)$$

and

$$A = \Delta\langle\mu_{0,0}^2\rangle/\langle\mu_{0,0}^2\rangle - \Delta V/V - \Delta v_n/v_n = \Delta\langle\mu_{0,0}^2\rangle/\langle\mu_{0,0}^2\rangle - \Delta V/V + Bv_n^2/2\,. \qquad (8)$$

In the last part of (7) we take account of the fact that the isotope effect on the average transition frequency must account for vibrational differences in both the ground state (denoted here as ΔZPE, the isotopic difference in zero point energies) and the average excited state (denoted here as ΔVIB). (Notice $v_n = v_{ne} + \mathrm{VIB} - \mathrm{ZPE}$ so $\Delta v_n = v_n(h) - v_n(d) = \Delta\mathrm{VIB} - \Delta\mathrm{ZPE}$, with v_{ne} the frequency corresponding to the energy difference between the origins of the ground and average excited states). To evaluate ΔVIB one recognizes that in theory average upper state vibrational excitations for H and D substituted molecules are available from the distributions of Franck-Condon factors [1]. Also, in (6) and (8) $\Delta V/V = -\Delta N/N$ is the molar volume isotope effect (MVIE), which in many cases is available from the literature. The goal of the present paper is to measure isotopic differences in refractive index to test the development reviewed above.

Experimental, Results

Refractive index difference between the H and D substituted compounds described below were measured at room temperature using a Brice-Phenix [6] differential refractometer dating from the early 1950's. To illuminate the samples we used a mercury lamp fitted with a set of Oriel (Oriel Corp., Stratford, CT) interference band pass filters and made measurements at 404.7, 435.5, 514.5, 576.7 and 690.0 nm. The refractive index difference between sample and reference is accurately proportional to the horizontal displacement, Δd, of a vertical slit image, $\Delta n = k(\lambda)\,\Delta d$. We calibrated to find $k(\lambda)$ at each wave length by measuring slit image displacements for dilute KCl solutions referenced to pure H_2O, and employed least squares fits to the highly accurate and precise refractive index data of Kruis [7] to calculate the proportionality constants, after first fitting literature data [8] on the refractive index of water, n_0, and apparent molar volumes [9] of KCl/H_2O solutions, ϕ_v, both at 298.15 K. M is the molarity of the KCl solution, the units employed by the original author [7].

$$n_0 = \sum_{i=0}^{3} A_i (v^2)^i , \tag{9a}$$

$$\phi_v = \sum_{i=0}^{4} B_i M^{i/2} , \tag{9b}$$

$$(n^2-1)/(n^2+2) - (n_0^2-1)/(n_0^2+2) = (M/1000) \cdot \left[\sum_{i=0}^{2} C_i (v^2)^i - ((n_0^2-1)/(n_0^2+2))\, \phi_v \right] : 0.1 < M < 0.8 . \tag{9c}$$

The A_i, B_i, and C_i parameters are reported in Table 1. Equations (9a), (9b), and (9c) are readily solved for $\Delta n = n - n_0$ and calibration factors obtained. We found an rms error of about 0.2% on the determination of any single $k(\lambda)$, an rms error of 0.4% on the average of all $k(\lambda)$'s, and have used the grand average $k = 0.9952 \times 10^{-2}$ unit per cm of image displacement in the work reported below. To calculate that average, calibrations at 690.0 nm were weighted $1/2^2$ those at other wave lengths because of eye-strain at that wave length.

Table 1. The parameters of (9a), (9b) and (9c).

i	A_i $(10^{-28}\ \mathrm{Hz}^2)^i$	B_i $(\mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{M}^{-i/2})$	C_i $((10^{-28}\ \mathrm{Hz}^2)^i\ \mathrm{cm}^3\ \mathrm{M}^{-1})$
0	1.321761	26.860	10.9651
1	5.26672E-04	1.86800	1.19801E-02
2	−4.81590E-06	−0.34806	4.56817E-05
3	3.96848E-08	0.60529	–
4	–	−0.18110	–

Refractive index differences were measured for the H/D isomers of the compounds listed in Table 2. The D-labelled compounds were each of nominal isotopic purity 99+% D; both H and D isomers were analytical grade reagents and used as received from the manufacturer. About 1.5 ml of the H-isomer was placed in each side of the cell, allowed to thermally equilibrate for 15 to 30 minutes, and the image displacement recorded at each wave length at both cell orientations in order to establish a zero reading. The sample on one side of the cell was then replaced with D-isomer and the procedure repeated. The image displacement corresponding to Δn was taken as the difference of differences. Each determination was repeated a minimum of five times and then converted to Δn using k determined as described above. To calculate $\Delta f(n)/f(n)$, for every protio species listed in Table 3 we least squares fitted refractive index data from the literature [10–12] to a one term dispersion relation of standard form,

$$(n^2-1)/(n^2+2) = v_n D/(v_n^2 - v^2) \tag{10}$$

then used the smoothing parameters v_n and D to obtain n at each experimental wavelength, finally obtaining $\Delta f(n)/f(n) = \{6n^2/[(n^2-1)(n^2+2)]\}\ (\Delta n/n)$. These

Table 2. H/D isotope effects at room temperature (25 ± 1 °C).
$\Delta f(n)/(f(n) = \{6n^2/[(n^2-1)(n^2+2]\}\ (\Delta n/n)$, $(n^2-1)/(n^2+2) = Dv_n/(v_n^2 - v^2)$.

System	$v_n^2/(10^{-28}\ \mathrm{Hz}^2)$	$Dv_n/10^{-28}\ \mathrm{Hz}^2)$	$10^3\ \Delta f(n)/f(n)^a$ ($\lambda = c/v$)/nm				
			404.7	435.5	514.5	576.7	690.0
C_6H_6/C_6D_6	638.2	180.43	4.19 (1)	4.04 (1)	3.77 (2)	3.63 (4)	3.47 (2)
$C_6H_5CH_3/C_6D_5CD_3$	649.8	182.89	4.69 (1)	4.60 (1)	4.36 (1)	4.39 (1)	4.20 (1)
C_6H_{12}/C_6D_{12}	1144.2	289.62	9.51 (1)	9.46 (1)	9.14 (2)	9.03 (1)	8.78 (1)
CH_3OH/CH_3OD	1201.1	240.47	4.35 (1)	4.34 (2)	4.10 (4)	4.03 (3)	3.75 (2)
CH_3OH/CD_3OD	1201.1	240.47	9.60 (1)	9.44 (1)	9.02 (2)	8.87 (2)	8.39 (3)
C_2H_5OH/C_2H_5OD	1192.6	259.02	2.50 (2)	2.48 (2)	2.31 (3)	2.25 (2)	2.08 (2)
CH_3COOH/CH_3COOD	1107.2	245.42	1.48 (2)	1.43 (2)	1.24 (1)	1.18 (2)	0.87 (1)
CH_3COOH/CD_3COOD	1107.2	245.42	3.66 (2)	3.63 (1)	3.27 (1)	3.19 (1)	2.87 (1)
$CHCl_3/CDCl_3$	1041.3	271.00	1.61 (2)	1.65 (2)	1.61 (3)	1.59 (1)	1.54 (1)
CH_2Cl_2/CD_2Cl_2		b	4.34 (1)	4.28 (1)	4.12 (1)	4.09 (1)	3.99 (1)
CH_3CN/CD_3CN	1181.9	246.14	3.13 (1)	3.07 (1)	2.94 (2)	2.89 (2)	2.83 (1)
$(CH_3)_2CO/(CD_3)_2CO$	1044.4	224.10	7.18 (1)	7.15 (1)	6.89 (2)	6.82 (2)	6.67 (3)
$(CH_3)_2SO/(CD_3)_2SO$		b	1.31 (1)	1.27 (1)	1.16 (1)	1.19 (1)	1.13 (1)

[a] Parenthetical entries indicate standard deviation in last significant figure.
[b] Dispersion relation not available; data to right are values of $10^3\ \Delta n$.

Table 3. Least squares analysis of the refractive index isotope effects in Table 2.
$\Delta f(n)/f(n) = \{6n^2/[(n^2-1)(n^2+2)]\}(\Delta n/n) = A + B \cdot v^2$.

System	$10^{-3} A$	10^{33} B Hz^{-2}	$10^9 \sigma^2$	$10^3 \Delta V/V$	$10^3 \Delta\alpha/\alpha$	(ΔZPE−ΔVIB) cm^{-1}	$10^3 \Delta\langle d^2\rangle/\langle d^2\rangle$
C_6H_6/C_6D_6	3.08±0.10	2.01±0.26	5.9	2.1 ±0.2[a]	5.2±0.3	540± 70	−1.2±0.8
$C_6H_5CH_3/C_6D_5CD_3$	3.97±0.07	1.31±0.16	2.5	1.5 ±0.2[b]	5.5±0.3	360± 43	1.2±0.5
C_6H_{12}/C_6D_{12}	8.44±0.07	2.05±0.17	2.5	2.2 ±0.2[a]	10.6±0.3	1323±110	−1.1±1.0
CH_3OH/CH_3OD	3.52±0.10	1.63±0.26	6.0	−1.64±0.03[d]	1.9±0.2	1130±180	−7.9±1.6
CH_3OH/CD_3OD	7.89±0.13	3.21±0.33	9.8	2.64±0.05[d]	10.5±0.2	2227±229	−8.8±2.0
C_2H_5OH/C_2H_5OD	1.90±0.06	1.16±0.15	2.0	−1.8 ±0.3[c]	0.1±0.3	797±103	−6.8±0.9
CH_3COOH/CH_3COOD	0.67±0.11	1.57±0.28	6.6			963±171	
CH_3COOH/CD_3COOD	2.52±0.10	2.21±0.27	6.2			1357±165	
$CHCl_3/CDCl_3$	1.52±0.03	0.22±0.09	0.7	−0.2 ±0.2[c]	1.3±0.1	121± 50	0.2±0.5
CH_3CN/CD_3CN	2.66±0.01	0.84±0.03	0.1			570± 20	
$(CH_3)_2CO/(CD_3)_2CO$	6.39±0.05	1.50±0.14	1.6	2.9 ±0.3[h]	9.3±0.4	843± 79	1.5±0.8
Gas phase data as fitted in reference [1].							
H_2/D_2[e]	13.7 ±0.1	1.61±0.09	0.2		13.7	1167	3.7
CH_4/CD_4[f]	16.2 ±0.1	2.24±0.07	0.1		16.2	1492	3.1
H_2O/D_2O[g]	6.8 ±0.4	2.76±0.44	0.2		6.8	1610	−8.0

[a] Ref. [17], [b] Ref. [18], [c] Ref. [12], [d] Ref. [19], [e] Ref. [13], [f] Ref. [14], [g] Ref. [15], [h] Ref. [20].

values and their standard deviations (for five measurements of Δd in each case) are reported in Table 2. The v_n^2 and Dv_n parameters of (10) are also found in the table.

In Table 3 we report the parameters obtained by least squares fitting of the data in Table 2 to (6); the resolution of the least squares parameters into the vibrational, MVIE, and second moment contributions; the values derived for the static PIE's; and the associated statistical errors in fits and derived parameters. For purposes of comparison Table 3 also contains similar fits to literature data for several of the permanent gases. Previous condensed phase measurements [12] were not precise enough to give accurate values for B in fits to (6) and therefore do not permit resolution into vibrational and second moment contributions as described above. However they are precise enough to permit meaningful comparisons of the intercepts.

Discussion

Comparisons of static PIE's $(\Delta\alpha/\alpha)_s$, for the liquids studied in this work with earlier but less precise results from the literature [12] show agreement within experimental error. In [1] it was demonstrated that static PIE data can be rationalized in terms of a group contribution scheme. The present results, in good agreement with earlier ones, fit nicely into that scheme. Solution of (6) and (7) shows $(\Delta\alpha/\alpha)_s = A + \Delta V/V$. The relative error in the determination of the intercepts, δA, when combined with the uncertainty in literature MVIE's is reasonably small (about 5% of $\Delta\alpha/\alpha$ for the present data, on the order of 20% for the literature [12] data). The relative errors in the slopes, δB, are larger. They generally range between 10 and 20% for the present data, but are much larger for the literature data [1, 12], so large, in fact, that it is not warranted to employ those measurements of B to resolve vibrational and second moment contributions to the PIE.

Vibrational and second moment contributions to the PIE are reported in Table 3. Although comparisons with previous condensed phase results from the literature are not useful (see above), resolutions of gas phase PIE's for H_2/D_2 [13], CH_4/CD_4 [14], and H_2O/D_2O [15] into vibrational and second moment contributions are included at the bottom of Table 3. These gas phase data are much more precise than those previously available for liquid phase compounds [1, 12]. Examination of Table 3 shows that the vibrational term, ΔZPE−ΔVIB, is positive. Except for hydrogen it is significantly smaller than that estimated from a simple ZPE model. The vibrational contribution to the static PIE can be calculated from the dispersion parameter for the protio compound, v_n, and B of (7), $(\Delta ZPE - \Delta VIB)/v_n = B v_n^2/2$. In all cases it is the largest contributor to PIE. The simple ZPE model assumes a high level density in the excited state and little or no isotope effect on the Franck-Condon excitation factors; in that case $\Delta ZPE - \Delta VIB \cong \Delta ZPE$. For H/D substitution at carbon, $\Delta ZPE \cong 3000\ (1-1/\sqrt{2}) \cong 880\ cm^{-1}$ or 2.6×10^{13} Hz per bond substituted, which is much larger than the values of ΔZPE−ΔVIB reported in the table, (except for the case of H/D substitution on an alcoholic OH group or water, and for hydrogen). This simple observation, alone, demonstrates that quantitative understanding will demand analysis of excited state vibrational effects. PIE is a probe for that information.

Electronic second moment isotope effects for the compounds listed in Table 3 are generally negative. Especially good agreement is found between OH/OD substituted compounds where $10^3\, \Delta\langle\mu^2\rangle/\langle\mu^2\rangle = -8 \pm 1$. To calculate the isotope effect in first approximation we speculate that the isotope effect should scale with vibrational amplitude. In that case $\Delta\langle\mu_{0,0}^2\rangle/\langle\mu_{0,0}^2\rangle$ should be positive for homonuclear diatomics and simple polyatomics, (where the center of mass is independent of isotope – CH_4/CD_4 for example), and this is so. For H_2/D_2 the effect deduced from the refractive index measurements [1, 12, 13] (Table 3) is in reasonable agreement with accurate quantum mechanical calculation. If the center of mass depends on isotopic substitution, however, second moment isotope effects can easily be inverse. As an example consider water; the molecular center of mass lies further out along the line bisecting the DOD angle than it does along that bisecting HOH. The electronic center of interaction and the center of mass do not coincide, and $e\langle r^2\rangle$, referenced to the center of mass, shows an inverse isotope effect. This likely accounts for the negative values of $\Delta\langle\mu_{0,0}^2\rangle/\langle\mu_{0,0}^2\rangle$ observed for the hydrogen bonded molecules in Table 3. An exactly similar argument was used by Dutta-Choudhury and Van Hook [16] to rationalize the small and inverse MVIE's for condensed phase waters and ices. As well, it likely accounts for the negative (or small positive) values of $\Delta\langle\mu_{0,0}^2\rangle/\langle\mu_{0,0}^2\rangle$ for most of the other compounds in Table 3. However the negative values found for benzene, which is centrosymmetric, and cyclohexane, nearly so, are confusing.

Conclusion

Differential measurements of isotopic differences in refractive index when coupled with data on MVIEs yield useful information on polarizability isotope effects (PIE). If carried out at high precision, such measurements can be employed to resolve the various contributions to the PIE. In the approximation used in this paper these can be labelled as vibrational (generally the larger) and second moment contributions. The experiments we have described, although carried out carefully, used outdated equipment without thermostatting. Even so they permitted an approximate but still useful resolution of the PIE into its components. With modest elaboration we estimate an improvement of about an order of magnitude in experimental precision to be possible. This would permit the experimental definition of H/D IE's on second moments with good precision and may eventually lead to resolution of the vibrational contribution into its ground and upper state components. At that level of precision careful comparison with detailed theoretical calculation will become appropriate.

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