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Abstract

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THE EFFECT OF REPLACING HYDROGEN BY DEUTERIUM ON THE POLARIZABILITY OF MOLECULES

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In a number of works ([1,18]) it was shown that gaseous deuterium compounds have a lower polarizability than their hydrogen analogues. It was also found that replacement of hydrogen by deuterium causes a decrease in the polarizability of certain liquids: water, hydrogen peroxide ([2,10]), benzene, cyclohexane ([3]), and dibromomethane ([4]).

In the present work, the dispersion of light and the density were studied, and the static polarizability (α_0) was calculated, for 12 liquid deuterium compounds and their hydrogen analogues listed in Table 1. The synthesis of $CDCl_3$ is described in ([5]), and that of the deuterioalcohols in ([6]). C_6D_6 and $C_6D_5CH_3$ were prepared as described in ([7]). To obtain CD_3NO_2, nitromethane was repeatedly exchanged with a 0.02 M solution of NaOD in D_2O at 110°. The substances were carefully purified and dried. The density (ρ_4^{20}) and refractive index (n_D^{20}) of the hydrogen compounds agreed with reliable literature data ([8]) with accuracies, respectively, of $1 \cdot 10^{-4}$ g/cm^3 and $1 \cdot 10^{-4}$.

The refractive index was measured with an IRF-23 Pulfrich-type refractometer, with a relative accuracy of $2 \cdot 10^{-5}$, at 293±0.05°K, for the lines: Hα, D, Hg$_3$, Hβ, and Hg$_{c-\phi}$. The static polarizability was obtained by extrapolating to $\nu = 0$ the dependence of $(n^2+2)/(n^2-1)$ on ν^2, where ν is the frequency of light. As Wulf ([9]) showed, for colorless substances and when experimental data for the visible region of the spectrum are used, such extrapolation is theoretically justified. For all the substances we studied, the indicated dependence in the investigated frequency range was linear within the error of measurement of n.

The density was determined with an accuracy of $1 \cdot 10^{-4}$ g/cm^3, every 5°, over the range 20—70° (for chloroform: 10—40°; for methanol: 10—60°). The molar volume (V_x) of a compound with x% D was calculated on the basis of additivity. Table 1 gives values of V_x only for 20°, but the relative difference in the molar volumes of isotopic analogues, with an accuracy of 0.01%, is the same throughout the indicated temperature range.

All 12 deuterium compounds we studied have a lower refractive index and a smaller polarizability than the corresponding hydrogen compounds (Table 1).

The decrease in polarizability upon replacement of hydrogen by deuterium can be explained by the accompanying decrease in the zero-point energy (ε_0) of the atomic vibrations, while the potential curve of the electronic energy and the force constants of the bonds (f) remain practically unchanged (^{10}). In the simplest case of a diatomic molecule, by making certain approximations, it can be shown that the lowering of the vibrational levels of the electronic spectra causes an increase in the energy of the electronic transitions ($\varepsilon_{\mathrm{el}}$) from the ground (0) level to an excited (i) level. Thus, neglecting the difference in electronic energy between the H- and D-compound at identical i-levels and also not taking into account the dif-

Table 1

Isotopic effect in the static polarizability (α_0) and intermolecular dispersion energy (ε_{D}), 293 °K

Substance	D, atomic %	n_D	V, cm^3/mol	$\alpha_0 \cdot 10^{24}$, cm^3	$\frac{\varepsilon_{\mathrm{D,H}} - \varepsilon_{\mathrm{D,D}}}{\varepsilon_{\mathrm{D,H}}} \times 100$
C_6H_6	0	1.50110	88.87	9.950	0.41
C_6D_6	91	1.49909	88.69	9.896	
$C_6H_5CH_3$	0	1.4968	106.29	11.705	0.47
$C_6D_5CH_3$	76	1.4945	106.18	11.652	
CH_3NO_2	0	1.38166	53.65	4.670	1.00
CD_3NO_2	96	1.37945	53.66	4.640	
$CHBr_2CHBr_2$	0	1.63773	116.42	16.018	0.26
$CDBr_2CDBr_2$	80	1.63631	116.42	15.991	
$CHCl_3$	0	1.44590	80.17	8.258	0.30
$CDCl_3$	98	1.44492	80.19	8.244	
$CH_2OHCHOHCH_2OH$	0	1.47397	73.02	7.751	0.71
$CH_2ODCHODCH_2OD$	96	1.47149	73.13	7.730	
CH_2OHCH_2OH	0	1.43197	55.74	4.473	0.58
CH_2ODCH_2OD	97	1.42994	55.82	4.464	
CH_3OH	0	1.32863	40.48	3.191	0.54
CH_3OD	70	1.32759	40.54	3.186	
C_2H_5OH	0	1.36139	58.36	5.010	0.42
C_2H_5OD	98	1.36060	58.45	5.006	
$CH_3(CH_2)_2OH$	0	1.38542	74.79	6.805	0.37
$CH_3(CH_2)_2OD$	99	1.38445	74.89	6.800	
$(C_3H_7)_2CHOH$	0	1.37758	76.55	6.836	0.36
$(C_3H_7)_2CHOD$	99	1.37672	76.67	6.834	
CH_3COOH	0	1.37200	57.24	5.038	0.43
CH_3COOD	98	1.37090	57.27	5.028	

difference in rotational energy, in view of the fact that in absolute magnitude it is small in comparison with the difference in vibrational energy, we obtain:

$$\Delta\varepsilon_{\mathrm{el}} = \varepsilon^{0,i}_{\mathrm{el,D}} - \varepsilon^{0,i}_{\mathrm{el,H}} = (\varepsilon_{0,\mathrm{H}} - \varepsilon_{i,\mathrm{D}})^{0} - (\varepsilon_{0,\mathrm{H}} - \varepsilon_{0,\mathrm{D}})^{i}. \tag{1}$$

Since, neglecting terms of higher powers, we have $(^{10})$:

$$\varepsilon_{0,\mathrm{H}} - \varepsilon_{0,\mathrm{D}} = \frac{1}{2} h\omega_{0,\mathrm{H}}(1-\zeta) - \frac{1}{4} h\omega_{0,\mathrm{H}}\chi_0(1-\zeta^2) =$$

$$= \frac{h}{4\pi}\mu_{\mathrm{H}}^{-1/2} f^{1/2}\left(1 - \zeta - \frac{\chi_0}{2} + \frac{\chi_0}{2}\zeta^2\right),$$

where μ is the reduced mass, χ_0 is the anharmonicity coefficient, and $\zeta = (\mu_{\mathrm{H}}/\mu_{\mathrm{D}})^{1/2}$, then from (1) we find:

$$\Delta\varepsilon_{\mathrm{el}} = \frac{h}{4\pi}\mu_{\mathrm{H}}^{-1/2}\left[(f^0)^{1/2} - (f^i)^{1/2}\right]\left[(1-\zeta) - \frac{\chi_0}{2}(1-\zeta^2)\right]. \tag{1'}$$

Since $f^0 > f^i$; $(1-\zeta)$ and $(1-\zeta^2)$ are positive quantities of the same order, while χ_0 is of the order of 0.01 $(^{10})$, then, according to $(1')$, we have

$$\Delta\varepsilon_{\mathrm{el}} > 0 \quad \text{or} \quad \nu_{i,\mathrm{D}} > \nu_{i,\mathrm{H}}, \tag{2}$$

where ν_i is the frequency of the electronic transition.

The consequences of (2) are probably also valid for a polyatomic molecule. This opinion is apparently held by Ingold, Raisin, and Wilson $(^{11})$, since, in explaining the decrease in the polarizability of benzene upon replacement of hydrogen by deuterium, they present, in a more approximate form, essentially the same arguments as those given above for a diatomic molecule. Urey and Teal $(^{12})$ explain the greater polarizability of heavy water, as compared with ordinary water, also by the fact that $\nu_{i,\mathrm{D}} > \nu_{i,\mathrm{H}}$.

The validity of (2) is confirmed by experimental data. Thus, Ingold and Wilson $(^{13})$ found for C_6D_6 and C_6H_6 in the fluorescence spectrum of benzene that $\nu_{i,\mathrm{D}}$ is greater than $\nu_{i,\mathrm{H}}$ by approximately 200 cm^{-1}. Herzberg and Schmid $(^{14})$, on the basis of predissociation phenomena in the CH and CD spectra, came to the conclusion that the energy levels of combinations of atomic terms in CD lie approximately 350 cm^{-1} higher than in CH. Franck and Wood $(^{15})$ established that the long-wavelength absorption limit of D_2O lies farther from the ultraviolet region than that of H_2O, and consequently $\nu_{i,\mathrm{D}} > \nu_{i,\mathrm{H}}$. It was also shown for methane $(^{16})$ and ammonia $(^{17})$ that $J_{\mathrm{D}} > J_{\mathrm{H}}$, where J is the ionization potential.

The polarizability of a molecule is expressed by the dispersion formula $(^{22})$

$$\alpha = \frac{2}{h} \sum \frac{\nu_i P_i^2}{\nu_i^2 - \nu^2}, \tag{3}$$

where P_i^2 are the probabilities of electronic transitions, and ν is the frequency of the incident light. In view of the identity of the electron shells of isotopic compounds, $P_{i,\mathrm{D}}^2 \approx P_{i,\mathrm{H}}^2$. Therefore, according to (3), for the polarizability α_i at level i we obtain:

$$\frac{\alpha_{i,\mathrm{D}}}{\alpha_{i,\mathrm{H}}} = \frac{\nu_{i,\mathrm{H}} - \nu^2/\nu_{i,\mathrm{H}}}{\nu_{i,\mathrm{D}} - \nu^2/\nu_{i,\mathrm{D}}}. \tag{4}$$

Since $\nu_{i,\mathrm{H}} < \nu_{i,\mathrm{D}}$, and for colorless substances $\nu_i > \nu$, it follows from (4) that $\alpha_{i,\mathrm{D}} < \alpha_{i,\mathrm{H}}$. Hence, probably, in general

$$\alpha_\mathrm{D} < \alpha_\mathrm{H} \tag{5}$$

in agreement with the experimental data (^{1}).

Substituting into (4) the expansion of the quantity $(\nu_{i,\mathrm{D}} - \nu^2/\nu_{i,\mathrm{D}})^{-1}$ in a series, we obtain:

$$\frac{\alpha_{i,\mathrm{D}}}{\alpha_{i,\mathrm{H}}} = \frac{\nu_{i,\mathrm{H}}}{\nu_{i,\mathrm{D}}} - \nu^2 \left(\frac{1}{\nu_{i,\mathrm{H}}\nu_{i,\mathrm{D}}} - \frac{\nu_{i,\mathrm{H}}}{\nu_{i,\mathrm{D}}^3} \right) - \nu^4 \left(\frac{1}{\nu_{i,\mathrm{H}}\nu_{i,\mathrm{D}}^3} - \frac{\nu_{i,\mathrm{H}}}{\nu_{i,\mathrm{D}}^5} \right) -$$

$$-\nu^6 \left(\frac{1}{\nu_{i,\mathrm{H}}\nu_{i,\mathrm{D}}^5} - \frac{\nu_{i,\mathrm{H}}}{\nu_{i,\mathrm{D}}^7} \right) - \dots - \nu^{2n} \left(\frac{1}{\nu_{i,\mathrm{H}}\nu_{i,\mathrm{D}}^{2n-1}} - \frac{\nu_{i,\mathrm{H}}}{\nu_{i,\mathrm{D}}^{2n+1}} \right) - \dots \tag{6}$$

In (6) all factors multiplying ν^{2n} have a common form, and, since $\nu_{i,\mathrm{D}} > \nu_{i,\mathrm{H}}$, these factors are positive. In view of this, and since in the right-hand side of (6) all terms beginning with the second are subtracted from $(\nu_{i,\mathrm{H}}/\nu_{i,\mathrm{D}})$, the difference between α_D and α_H increases with increasing ν. This also agrees with experimental literature data and with our data.

For the static polarizability ($\nu = 0$), from (4) we have:

$$\left(\frac{\alpha_{i,\mathrm{D}}}{\alpha_{i,\mathrm{H}}} \right)_0 = \frac{\nu_{i,\mathrm{H}}}{\nu_{i,\mathrm{D}}}. \tag{7}$$

At moderate temperatures, a consequence of relation (5) is a decrease in the intermolecular dispersion energy (ε_D) when hydrogen is replaced by deuterium.* Thus, according to the formula of Slater and Kirkwood (^{23})

$$|\varepsilon_{\mathrm{D}}| = \frac{3eh}{8\pi r^6}\left(\frac{n\alpha_0^3}{m}\right)^{1/2}, \qquad (8)$$

where n is the total number of electrons in the outer shells of the atoms comprising the molecule, m and e are the mass and charge of the electron, and r is the distance between molecules. In the first approximation, $(r_H/r_D)^3 = V_H/V_D$. Therefore

$$\frac{\varepsilon_{\mathrm{D,D}}}{\varepsilon_{\mathrm{D,H}}} = \left(\frac{V_H}{V_D}\right)^2 \left(\frac{\alpha_{0,\mathrm{D}}}{\alpha_{0,\mathrm{H}}}\right)^{3/2}. \qquad (9)$$

As is seen from Table 1, calculation by (9) showed that, for the substances studied,

$$|\varepsilon_{\mathrm{D,D}}| < |\varepsilon_{\mathrm{D,H}}| \quad \text{(intermediate temperatures)}. \qquad (10)$$

This is due to the fact that at intermediate temperatures the relative difference in the value of $\alpha^{3/2}$ of isotopic analogues is greater than such a difference in the values of V^2, so that, according to (9), the sign of the ratio $(\varepsilon_{\mathrm{D,D}}/\varepsilon_{\mathrm{D,H}})$ is determined by the sign of the ratio $(\alpha_{0,\mathrm{D}}/\alpha_{0,\mathrm{H}})$.

Consequence (10) is in agreement with the fact that replacement of hydrogen by deuterium causes a lowering of the critical temperature (^{24}), if it is not in the region of low temperatures, and also with the fact that deuterium compounds have a greater compressibility than their hydrogen analogues (^{6}), if the low-temperature region is excluded.

However, at low temperatures the molar volume is sharply affected by the change in the amplitude of the zero-point vibrations of the molecules. Therefore, for D_2 and H_2 near 19.5°K, for example, V_D is smaller than V_H by 17% (^{19}), and for He^4 and He^3 (^{20}) at 2°K, V_4 is smaller than V_3 by 29%. In these cases the difference in the value of ε_D for isotopic analogues, according to (9), is determined mainly by the difference in the values of V, and

$$|\varepsilon_{\mathrm{D,D}}| > |\varepsilon_{\mathrm{D,H}}| \quad \text{(low temperatures)}. \qquad (11)$$

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* Bell (^{18}) also proposes another approach to the consequence of (5). He qualitatively relates (5) to the fact that, owing to the anharmonicity of zero-point atomic vibrations, the increase in the mean internuclear distance, relative to its value at the minimum of the potential curve, is smaller in the case of a D compound than in an H compound.

Thus, if the values of V and α_0 (^{21}) for He^4 and He^3 corresponding to 2°K are substituted in (9), we obtain that $|\varepsilon_{D,4}|$ is greater than $|\varepsilon_{D,3}|$ by 45%. It is interesting that the result of this very approximate calculation agrees well with the experimental data on the heat of vaporization of He^4 and He^3 (^{20}): at 2°K, respectively, 22.2 cal/mol* and 11.1 cal/mol.

Consequence (11) also corresponds to the fact that D_2 and He^4 have a higher critical temperature than, respectively, H_2 and He^3 (^{24}).

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* This value refers to HeI; however, in the present case this apparently has no substantial significance. As is known, the heat of the λ-transition in liquid helium is negligible, and between 1.75° and 3.5°K the heat of vaporization changes only within 4%.

Note: Figure translations are in progress. See original paper for figures.

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