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R. Böhmer, U. Giebenhain, Alois Loidl

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Dielectric study of partially isotope-substituted solid and liquid hydrogen and methane

By R. BÖHMER, U. GIEBENHAIN and A. LOIDL
Institut für Festkörperphysik, Technische Hochschule, 64289 Darmstadt, Germany

The solid and liquid phases of hydrogen, n-H_2 and HD, and methane, CHD_3 and CH_3D, have been studied by dielectric measurements. It is found that increasing deuteration has only a minor effect on the molar polarization of hydrogen, but that it leads to a significant decrease of the polarizabilities of the liquid methanes. The dipole moments of the partially isotope substituted molecules have been determined in the solid state. For HD a local field corrected moment of 0·78 mD is found, for CHD_3 and CH_3D the moments are 4·3 and 4·1 mD, respectively.

1. Introduction

Despite the structural simplicity of hydrogen and methane, the quantum solids and liquids formed by these molecules exhibit a wealth of fascinating properties [1, 2]. Particularly the high-pressure phases of hydrogen are currently under intense study primarily in order to detect a metallization transition, the possible observation of which is still discussed [3]. Also such a seemingly simple problem as the determination of the ambient pressure, low-temperature structure of methane, CD_4-III [4], is yet to be solved [5], On the other hand, enormous advances in the understanding of tunnelling excitations and diffusion processes in quantum solids have been achieved in recent years, particularly through the use of neutron scattering [6] and magnetic resonance experiments [7].

Here we report on a dielectric investigation of the quantum systems hydrogen and methane. Owing to their remarkable sensitivity, dielectric techniques are well suited to investigate the orientational response functions of solids formed by partially isotope substituted molecules. The dipole moments of mixed isotope molecules can be extremely small [8]. For example, for hydrogen, HD, from *ab initio* calculations [9–11] and analyses of gas phase infrared (IR) absorption experiments [12–15] dipole transition moments in the range 0·5–0·9 mD have been deduced for the vibrational ground state.

The dipole moment of partially deuterated methane is of the order of 5 mD [16–21] and thus is much larger than that of heteronuclear hydrogen. Previously we have reported from low-frequency dielectric measurements a permanent moment of 4·5 mD for CH_2D_2 [21]. As we will show, for the other mixed isotope methanes, CHD_3 and CH_3D, somewhat smaller moments can be expected.

In the following we present our dielectric results on partially isotope substituted methane and hydrogen molecules in their solid and liquid phases. Comparison will be made with the behaviour in CH_4, CD_4, and H_2, which carry no permanent electric dipole moment.

2. Experimental details

The partially deuterated chemicals were obtained from Medgenix Co. and used without further purification. The isotopic purity of CH_3D and CHD_3 was stated by the supplier to be 99% and 99·6%, respectively. For hydrogen deuteride HD the isotopic purity was 95%. Fully protonated hydrogen was purchased from Linde Co. Since we have taken no special measures to accelerate spin conversion, it can be assumed that the composition of this sample was $(\text{para-H}_2)_{0\cdot 25}(\text{ortho-H}_2)_{0\cdot 75}$, usually called n-$H_2$. The chemicals were condensed as liquids into the dielectric cell which had a geometrical capacitance C_0 of about 51 pF [22]. The capacitance C of the filled cell was measured at 100 kHz using the autobalance bridge HP 4274A. The excitation voltage was 5 V_{rms}. The dielectric permittivity was calculated from $\epsilon(T) = C(T)/C_0(T)$. The minimum sample temperature reached with the home-made ^{4}He cryostat used for this work was about 2·7 K. Measurements were recorded while scanning the temperature with rates of 0·3–0·1 K min^{-1}. However, the results obtained showed no scanning rate dependence. Further experimental details can be found elsewhere [21].

3. Results and discussion

3.1. *Hydrogen*

The dielectric constants of the liquid hydrogens, H_2 and HD, studied in this work increased almost linearly with decreasing temperatures in agreement with previous dielectric investigations [23–25]. Using the densities ρ of these liquids as tabulated by Woolley *et al.* [26] we have determined the molar polarizations P according to

$$P = V_m(\epsilon - 1)/(\epsilon + 2). \tag{1}$$

Here $V_m = m/\rho$ is the molar volume and m the molar mass. We find $P(H_2) = (2{\cdot}010 \pm 0{\cdot}010)\,\text{cm}^3$ and $P(\text{HD}) = (2{\cdot}018 \pm 0{\cdot}003)\,\text{cm}^3$† in good agreement with previous experimental [23, 25] and theoretical [27] determinations. It should be noted and is also confirmed by results on D_2 [25] that the molar polarization is practically independent of the degree of deuteration.

On solidifying, the dielectric constants increased by about 4%. In contrast to a previous report [25] this effect was quite reproducible and therefore well defined values for the dielectric constants were obtained in the solid states. Using the molar volumes of n-H_2 (22·91 cm^3) and of HD (20·58 cm^3) [1] together with the electronic contributions to the permittivities yields $P(H_2)/P(\text{HD}) = 1{\cdot}025 \pm 0{\cdot}005$.

Our measurements on the hydrogen solids confirm that at low temperatures ($2{\cdot}7\ \text{K} < T < 10\ \text{K}$) the dielectric constant of HD varies much more rapidly than that of the homonuclear hydrogens [25, 28]. However, in contrast to the investigation of Constable *et al.* [25] our results for hydrogen deuteride turned out to be reasonably reproducible.

Dielectric constants for HD as measured in three different runs are shown in figure 1. The slight variation of ϵ seen in all samples is expected for solids containing molecules that carry small permanent dipole moments. The temperature dependence of ϵ indicates the presence of non-centrosymmetric molecules that

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† 1 cm^3 of polarizability ≈ $1{\cdot}112\,65 \times 10^{-16}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^2$.

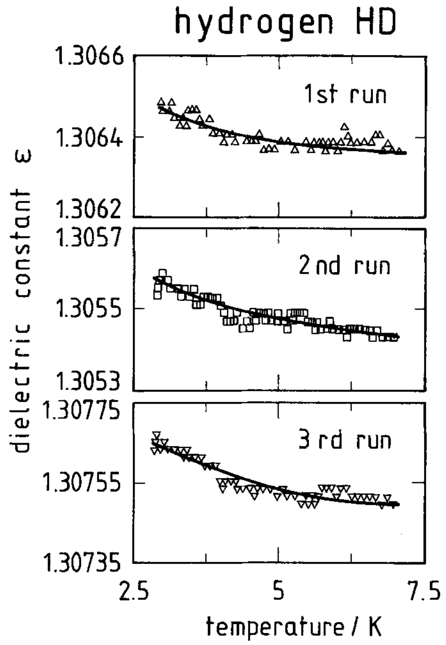

Figure 1. Dielectric constant of three different HD crystals which have been produced from the same liquid. Solid lines are fits using (2).

perform reorientations with a rate larger than the measuring frequency and can be described by the Curie law,

$$\epsilon = \epsilon_{\infty} + 4\pi C/T. \tag{2}$$

The solid lines shown in figure 1 are least square fits using (2) and have yielded the high frequency permittivity $\epsilon_{\infty} = 1{\cdot}306 \pm 0{\cdot}001$ and the Curie constant $C = (49{\cdot}1 \pm 8{\cdot}8)\ \mu\mathrm{K}$. From the Curie constant the dipole moment can be calculated according to [21]

$$\mu = [(27k_B C)/N]^{-1/2}(\epsilon_{\infty} + 2)^{-1}, \tag{3}$$

if the local electric fields are accounted for by applying the Lorentz correction. Using a number density $N = 2{\cdot}926 \times 10^{22}\ \mathrm{cm}^{-3}$ [29] a dipole moment of $\mu = (0{\cdot}76 \pm 0{\cdot}07)$ mD† was obtained (neglecting the local fields would give a moment of 0·84 mD). The effective moments increase by a factor of 1·026 if we take into account the nominal isotopic purity of HD. Hence the final value of the local field corrected electric dipole moment is $\mu = 0{\cdot}78$ mD.

In order to compare this dipole moment with literature results, in table 1 we have compiled the transition dipole moments from IR investigations of gaseous HD and from theoretical calculations. Originally Blinder [9] had calculated a moment of 0·567 mD, which subsequently was claimed by Trefler and Gush to be in agreement with their experimental results [12]. But *ab initio* calculations carried out later have yielded significantly larger moments [10, 11]. The apparent disagreement between the early IR investigations and the more refined theories has been resolved by Nelson and Tabisz [13]. These authors showed, that by neglecting destructive interference

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† 1 D ≈ $3{\cdot}335\,64 \times 10^{-30}$ C m.

Table 1. Experimental (e) and theoretical (t) determinations of the dipole moment of HD.†

$J \leftarrow J+1$ with $J =$	μ/md		Reference	
0	0·585	t	Blinder	[9]
0, 1, 2, 3	0·588	e	Trefler and Gush	[12]
0, 1, 2, 3	0·839	t	Wolniewicz	[10]
0, 1, 2, 3	0·829	t	Ford and Browne	[11]
1, 2, 3	0·905	e	Nelson and Tabisz	[13]
3, 5, 6	0·882	e	Essenwanger and Gush	[14]
0, 1, 2, 3	0·811	e	Lu, Tabisz and Ulivi	[15]
—	0·78 ± 0·07	e	This work	

† In [9–15] the dipole moments have been determined from rotational transitions in the fundamental (0–0) vibrational band or from *ab initio* calculations. Where available the results for the lowest lying absorption bands in the R-branch have been averaged over several rotational levels J as indicated.

effects, they are able to reproduce the results of Trefler and Gush [12]. However, by taking into account these effects in a proper manner, an average moment of about 0·85 mD is obtained [13–15]. Thus, the dipole moment of solid HD determined in this work is compatible with the more recent theoretical calculations and with the experimental determinations carried out for gaseous HD

3.2. *Methane*

The liquid methanes $CH_{4-n}D_n$ exhibit an almost linear variation of the dielectric constant with temperature. Results for $n = 1$ and $n = 3$ (with n being the number of deuterons) are shown in figure 2. In order to calculate the molar polarizations, the molar volumes are required. These are known for CH_4 and CD_4 only [30, 31]. However, there are indications that the densities of the mixed isotope methane liquids lie between those of the isotopically pure ones [32, 33]. Thus, in the temperature range relevant here, we have calculated the molar volume (in cm^3) according to $V_m = 24{\cdot}095 - 0{\cdot}095n + 0{\cdot}1235T$ with temperature T given in Kelvin [21].

The molar polarizations of the liquid methanes have been determined using (1) and are presented in figure 3. Our results for CH_4 are in good agreement with those

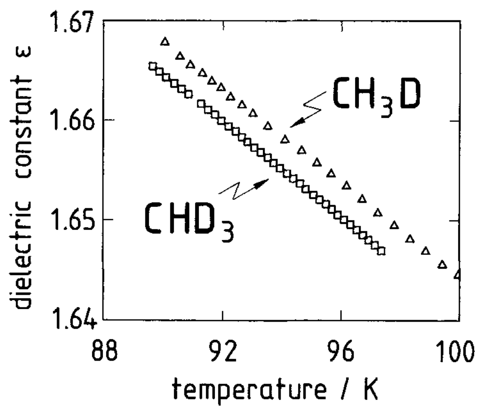

Figure 2. Dielectric constant of the methanes CHD_3 and CH_3D in their liquid states.

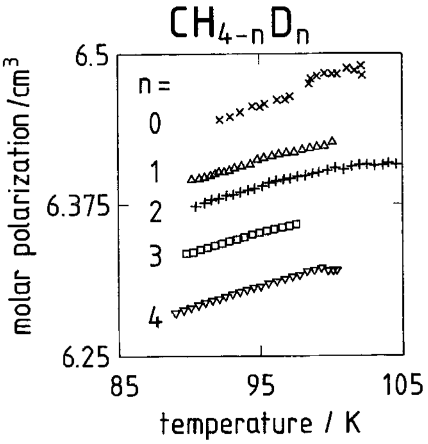

Figure 3. Molar polarizations of all five isotopic modifications of methane. For $n = 1$ and $n = 3$ the polarization was calculated using (1) and the data shown in figure 2. Results for the liquids with $n = 0$, 2, and 4 were taken from [21].

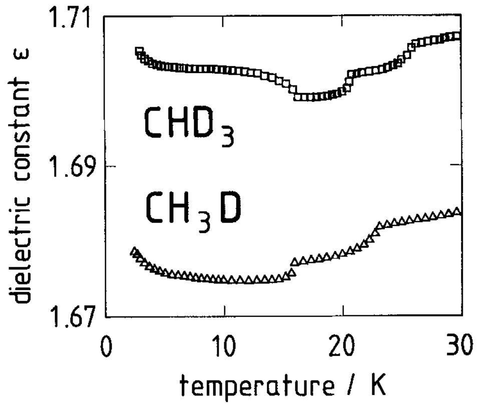

Figure 4. Dielectric constants of solid CH_3 and CH_3D as a function of temperature.

by Amey and Cole [34], but about 3% smaller than those by Straty and Goodwin [31] due to the systematically larger dielectric constants reported by the latter authors.

Strikingly and in contrast to the behaviour observed for the hydrogens the polarization decreases significantly upon deuteration. This decrease can be explained by the fact that the C–D bond is shorter than the C–H bond [35]. This effect is responsible not only for the higher densities of the deuterated liquids but also leads to a change in the intermolecular potentials effectively making the C–D bond less polarizable than the C–H bond [36].

The low-temperature dielectric constants of CHD_3 and CH_3D are shown in figure 4. Several solid state phase transitions show up at 23·1 and 15·7 K ($n = 1$) and at 26·0 and 20·8 K ($n = 3$) which, within the experimental uncertainty of our results (±0·2 K), are in good agreement with calorimetric results [2] confirming the high purity of our samples. Additionally, in several cooling runs of CHD_3, a discontinuity in ϵ showed up in the vicinity of 16 K. The origin of this anomaly, which was not

Table 2. Dipole moments of isotope-substituted methanes.

	C/mK	ϵ_∞	μ/mD	Method	Reference
CH_3D	1·23	1·679	4·1	Dielectric	This work
			4	Theory	[16]
			5·68	Infrared	[17]
			5·66	MB[a]	[18]
CH_2D_2	1·51	1·692	4·5	Dielectric	[21]
			14	MW[b]	[20]
CHD_3	1·37	1·702	4·3	Dielectric	This work

[a] MB, molecular beam electric resonance.

[b] MW, microwave spectroscopy.

detectable during heating, is unclear at present. It is noted that also for CD_4 irregular dielectric behaviour has been observed in the solid state [21].

For temperatures below about 10 K the dielectric constants of both methane solids studied here show a Curie-type of behaviour, indicating the presence of permanent electric dipole moments. Using (2) and (3) and taking $N = 2·008 \times 10^{22}\,\mathrm{cm}^{-3}$ [33] for the number densities of the methanes at low temperature we have calculated the dipole moments 4·1 mD ($n = 1$) and 4·3 mD ($n = 3$) from the best fits. The dipole moments of the partially deuterated methanes are compiled in table 2 together with various results from the literature. The moment obtained in the present work for $n = 1$ is in good agreement with the theoretical calculations by Gangemi [16]. The experimental determinations for $n = 1$ and $n = 2$ in the gas phase using IR absorption and molecular beam resonance techniques (MB) have yielded somewhat larger moments (see table 2). This may be due to the fact that sometimes vibrationally excited states were investigated for which enhanced dipole moments are to be expected [19].

One of the main objectives of this work was to find out how the dipole moments of the different methane modifications depend on the degree of deuteration. In order to avoid difficulties associated with comparing results that have been determined using different experimental techniques we will use the dipole moments obtained from our systematic dielectric studies. It is noted that although the absolute values of the dipole moments from this work may be inaccurate up to about 10%, the relative uncertainty of the ratio of any two dipole moments is not larger than 3%.

The dipole moments for both methane modifications investigated in this work are smaller than that of CH_2D_2 ($\mu = 4·5$ mD [21]). Using a simple bond-dipole model the difference in the moments for $n = 2$ on the one hand and for $n = 1$ and $n = 3$ on the other hand is expected to be 15·5%, as explained in the following.

In the bond-dipole model moments of magnitude μ_{CD} and μ_{CH} are assigned to the C–D and C–H bonds, respectively. Furthermore the moment vectors associated with two adjacent bonds are assumed to enclose the ideal tetrahedral angle of $\vartheta = 109·47^\circ$, irrespective of the degree of deuteration. Thus the dipole moment of CH_2D_2 is given by $\mu(2) = 2\cos(\vartheta/2)|\mu_{\mathrm{CD}} - \mu_{\mathrm{CH}}| = 1·155|\mu_{\mathrm{CD}} - \mu_{\mathrm{CH}}|$. For CH_3D elementary geometrical considerations yield $\mu(1) = |\mu_{\mathrm{CD}} - 3\mu\cos(180^\circ - \vartheta)|$. Since $3\cos(180^\circ - \vartheta)$ equals unity one finds $\mu(1) = |\mu_{\mathrm{CD}} - \mu_{\mathrm{CH}}|$ and furthermore $\mu(3) = \mu(1)$.

Neither the experimentally observed enhancement of $\mu(2)$ as compared to $\mu(1)$ or $\mu(3)$ nor the inequality of $\mu(1)$ and $\mu(3)$ are predicted. Therefore we are led to suggest that the tetrahedral angles in all partially isotope-substituted methane modifications are non-ideal [37]. In order to check this conjecture high-resolution IR experiments would be most helpful since the existence of deviations from the ideal tetrahedral symmetry should lead to additional, presumably rather weak absorption bands.

4. Conclusions

Low-frequency dielectric measurements have been carried out for the quantum liquids and solids n-H_2, HD, CHD_3, and CH_3D. The liquid hydrogens are characterized by molar polarizations of about 2 cm^3, almost independent of the degree of deuteration. In the solid state the polarization of n-H_2 is 2·5% larger than that of HD. The differences of the charge and the mass distributions in HD give rise to a Curie behaviour in the permittivity below about 9 K. The Curie constant yielded a Lorentz field corrected dipole moment of $\mu = (0{\cdot}78 \pm 0{\cdot}07)$ mD. This value is in good agreement with the transition dipole moment inferred from IR absorption measurements of HD in its electronic and vibrational ground state [13–15].

The molar polarizations of the liquid methanes are now measured for all five isotopic modifications and are found to exhibit a marked decrease upon deuteration. The permanent dipole moment $\mu(1)$ determined from the solid state permittivity of CH_3D is in good agreement with the theoretical calculations by Gangemi [16], but significantly smaller than the transitions moments determined in gas phase experiments [17, 18]. According to a simple bond dipole model the moment $\mu(2)$ of CH_2D_2 should be larger than those of the other deuterated methanes by a factor of $(4/3)^{1/2} = 1{\cdot}155$. However, the experimentally observed dipole moment ratios $\mu(2)/\mu(1) = 1{\cdot}10 \pm 0{\cdot}03$ and $\mu(2)/\mu(3) = 1{\cdot}05 \pm 0{\cdot}03$ as reported in this work are smaller than expected by these simple considerations. This suggests the existence of slight departures of the tetrahedral angles from their ideal values in the partially isotope substituted methanes.

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