The dipole moment of condensed CH2D2

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THE DIPOLE MOMENT OF CONDENSED CH$_2$D$_2$

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Abstract The permittivities of liquid CH$_4$, CH$_2$D$_2$, and CD$_4$ and those of solid (Kr)$_{1-x}$(CH$_2$D$_2$)$_x$ alloys are presented. At low temperatures Curie laws show up in (Kr)$_{1-x}$(CH$_2$D$_2$)$_x$. From these data the permanent dipole moment of CH$_2$D$_2$ is calcutated to be 4 mD. The liquid state data were analyzed with the Clausius-Mosotti equation. They are consistent with this small dipole moment.

INTRODUCTION

Molecules such as CH$_4$, H$_2$, or NH$_4{}^+$ exhibit a small dipole moment when a part of the protons is substituted by deuterons. The simplest case is hydrogen HD. From the infrared spectrum of this molecule in its gaseous[1] or solid[2] phase, the moment was determined to be of the order of 0.5 mD, depending on the rotational state. Comparable studies on partly deuterated methanes are not available at present, though this group of CH$_4$ derivatives, CH$_3$D, CH$_2$D$_2$ and CHD$_3$, is attractive for several reasons. On the one hand it offers the possibility to develop theoretical concepts for a homologous series of molecules. On the other hand, like partly deuterated species in general, they can be used as dipolar probes in an otherwise nonpolar solid or liquid. With the application of dielectric spectroscopy, the virtually existing, but so far unaccessible low frequency dynamics of the methanes will become detectable.

Among the interesting, often puzzling peculiarities of the condensed methanes is the well know fact that they crystallize into an orientationally disordered state.[3] On cooling, the rotational degrees of freedom vanish successively (at 24.9 and 19.1 K for CH$_2$D$_2$, Refs. 3,4). At the lowest temperatures, the deuteromethanes are ordered almost completely, however, in a complicated manner. The crystal structure of this so called phase III is built

up from several sublattices. And it has so far not been possible to resolve its space group unambiguously.[5] Relatively high rotational constants and low crystal fields[6] should lead to reorientational processes even in phase III. Thus, partly deuterated methanes provide an example where it should principally be possible to study the slow dynamics by dielectric means. By dilution with krypton an orientational glass state can be achieved, as has been reported for $(Kr)_{1-x}(CH_4)_x$ and $(Kr)_{1-x}(CD_4)_x$.[7] It also would be very interesting to study whether the glass transitions can be detected in $(Kr)_{1-x}(CH_2D_2)_x$ by dielectric spectroscopy.

However, in a first step, the dipole moment of these compounds has to be determined. To this end, we will present the permittivities of liquid and solid CH_2D_2 (For the sake of brevity only this isotopic modification will be considered.). The dielectric constant and the molar polarizability of the liquid will be compared to the ones of the nonpolar species, CH_4 and CD_4. These data will demonstrate that the dipole moment of CH_2D_2 is in fact very small. From the permittivities of crystalline $(Kr)_{1-x}(CH_2D_2)_x$ alloys, the permanent dipole moment of CH_2D_2 will be calculated to be 4 mD. The apparent dipole moments differ significantly in the ordered and in the glassy low temperature states.

EXPERIMENTAL

Gases in bottles from various sources were used. The (partly) deuterated methanes CH_2D_2 and CD_4 had a nominal purity of 99%, with approximately 1% of CH_4 impurities. The purity level of the other gases was 99.95% (CH_4) and 99.99% (Kr). The chemicals were (in the case of the alloys with krypton, mixed and) condensed as liquids into a cell of cylindrical design. To homogenize the solid solutions, they were kept at temperatures several degrees below the melting point for at least one hour. The dielectric constants of the samples were measured in the frequency range from 100 Hz to 100 kHz as described previously.[8] Since, within the experimental resolution, the permittivities were independent of the measuring frequencies, we only report data taken at a single frequency, usually 10 kHz.

LIQUID METHANES

The permittivities of the methanes CH_4, CH_2D_2 and CD_4 in their liquid states are presented in Fig. 1. They increase approximately linearly with decreasing temperatures. Only the data for CH_4 can be compared with literature values.
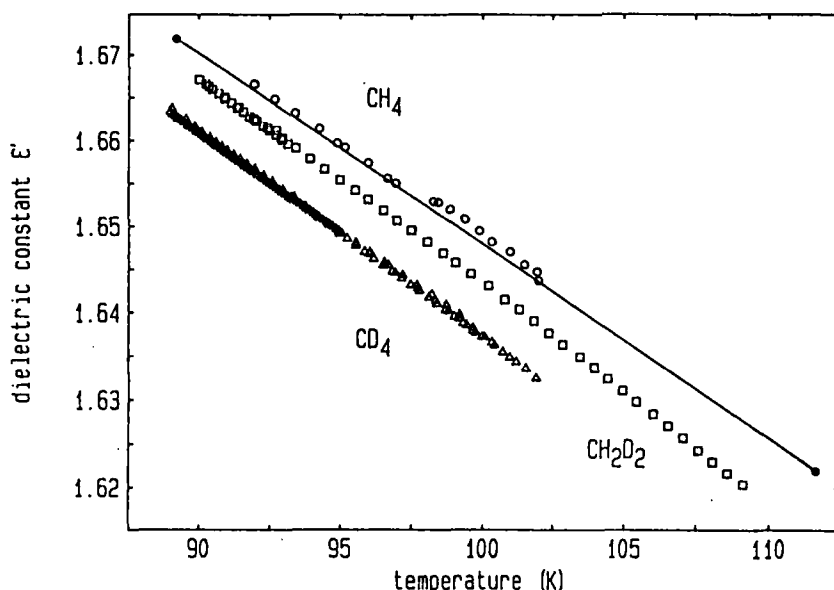
FIGURE 1   The permittivity of liquid CH_4, CH_2D_2, and CD_4 obtained in this work (open symbols). The dielectric constant of CH_4 was also measured by Amey and Cole[9] (● and straight line).

The agreement with the results obtained by Amey und Cole[9] is excellent as can be seen in Fig. 1. Dielectric constants measured by McLennan et al.[10] are roughly 3% larger and are not included in Fig. 1. The absence of any Curie-type of behavior in the permittivity of CH_2D_2 indicates that, in the liquid state, the contribution of the permanent dipole moment to the total polarization is negligible. Hence, the Clausius-Mosotti equation may be used to calculate the molar polarizability

$$P = (\varepsilon - 1)/(\varepsilon + 2) \times M/d. \tag{1}$$

To our knowledge, the density has only been determined for liquid CH_4. However, upon deuteration the variation of the lattice constants (± 1%, Ref. 11) is much smaller as compared to that of the molar weight M (> 10%). In a first approximation, the ratio M/d evaluated for CH_4 is thus applicable to the deuterated species, too. The polarization P resulting from the calculations using Eq. (1) is shown in Fig. 2. If it is assumed that the deuterated liquids exhibit a slightly higher density as the fully protonated one, then the differences in P tend to disappear. The decrease of P with temperature was already demonstrated to occur in gaseous and liquid CH_4.[12,9] However, at the melting point the polarization calculated from the present data is smaller as the one given by Amey and Cole[9] (P = 6.456 cm³), who use a smaller density than the one reported by Keyes et al.[13] (d = 0.4586 g/cm³). The nonzero dielectric virial
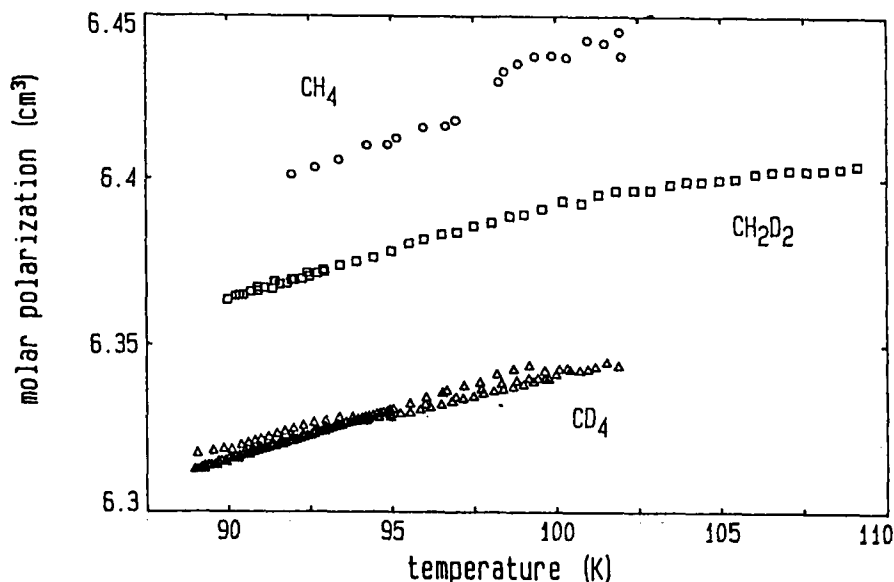
FIGURE 2 The temperature dependent molar polarization of various isotopic modifications of liquid methane.

coefficient, which is responsible for the decrease of the polarization with temperature, was attributed to dipole moments which were induced by the octopole moments of the surrounding molecules.[12]

SOLID $(Kr)_{1-x}(CH_2D_2)_x$ ALLOYS

For dipoles reorienting freely on the experimental timescales, the dielectric constant is expected to follow a Curie law

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

This kind of behaviour is in fact observed in the $(Kr)_{1-x}(CH_2D_2)_x$ solid solutions. Fig. 3 shows the data for several concentrations normalized to their dielectric constants in the high frequency limit $\epsilon_\infty = 1.70$ ($\pm$ 0.04). The magnitude of the 1/T-effects is increasing with the dipole concentration. This is also expected from the Lorentz-field corrected Curie constant

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

which scales with the dipole density N. For six samples with $x \le 0.8$ one finds $C/x = 1.2$ mK. Solving Eq. (2) for μ and taking into account the densities of methane and krypton, a dipole moment of 4 mD is calculated. This result is in accord with rough estimates from bond moments.[14] The difference of these quantities for C-D and C-H, as determined from a number of covalent bonds,
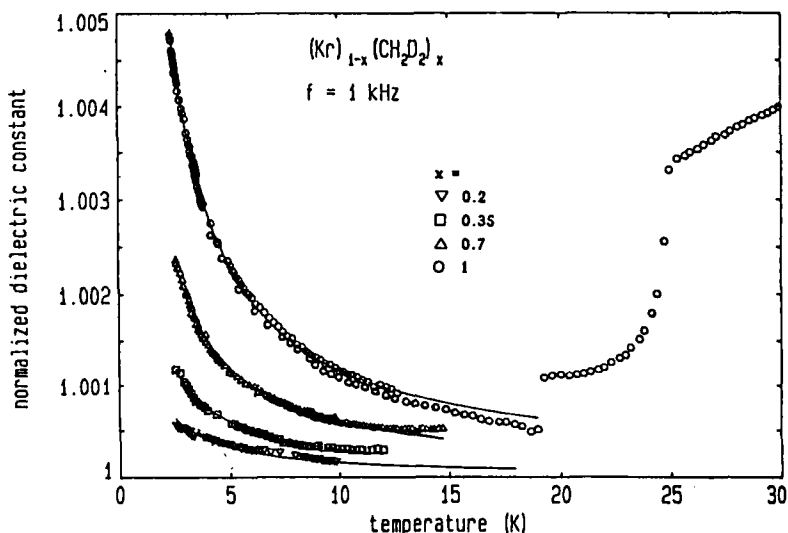

FIGURE 3   The normalized dielectric constants $\varepsilon'/\varepsilon_\infty$ of $(Kr)_{1-x}(CH_2D_2)_x$ solid solutions vs temperature. The high temperature data of the mixed crystals have been ommitted for clarity. The sudden changes in the permittivity of pure CH_2D_2 mark the occurence of phase transitions. Solid lines are fits to Curie laws as described in the text.

and hence the moment of a hypothetical linear D-C-H molecule is 10 mD. This is only slightly larger than the moment of CH_2D_2.

For dipole concentrations $x \approx 0.8$, the Curie constant is larger than expected from the relation above. It amounts to $C = 1.5$ mK for pure CH_2D_2, yielding an apparent moment of 4.5 mD. To understand the difference between these moments of pure and (sufficiently) diluted CH_2D_2 it has to be noted that the crystals with $x < 0.8$ are orientationally disordered down to the lowest temperatures.[15] Samples with higher methane concentrations freeze into an orientationally ordered state.[16] The local electric fields due to the ordering of the molecules can produce significant contributions to the dielectric constant.[17] Whether this effect is responsible for all of the enhancement of the dipole moment in the antiferrorotational state of CH_2D_2 can be answered only after a detailed determination of the structure of phase III.

CONCLUSIONS

From the dielectric constants of the isotopic modifications CH_4, CH_2D_2, and CD_4 the liquid state polarizabilities were calculated. Methane CH_2D_2 exhibits a permanent dipole moment of $\mu = 4$ mD. The apparent μ of CH_2D_2 in its low temperature antiferrorotational state is roughly 10% larger. This is presumably due to the enhancement of local fields, or, in other words, due to octopole induced dipole moments. The magnitude of the reported moment is still large enough to allow for sensitive dielectric measurements. Our results thus show that the use of partly deuterated molecules (or ions) opens new perspectives on the investigation of otherwise nonpolar solids.

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