The Dielectric Constant of H₂, D₂, and HD in the Condensed Phases*

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Measurements have been made of the dielectric constant in the liquid and solid phases of H₂, D₂, and HD. Precise measurements were made in the liquid phase at saturated vapor pressure and compared with previous data. A study was made of the change in the dielectric constant upon solidification. Measurements were made in the solid phases of H₂ and HD from the solidification point to about 0.02 K. Both solids exhibited temperature-dependent dielectric constants which were rather similar. The magnitude of the temperature dependence was found to be related to the concentration of molecules in the rotational J = 1 state. The dielectric constant of HD was found to change quite dramatically between 1 and 2 K, while H₂ and D₂ show no similar change.

1. INTRODUCTION

There have been several previous measurements¹-² of the dielectric constant ε of the hydrogen molecules H₂, D₂, and HD both in the gas and in the condensed phases. Such measurements yield the average polarizability of the hydrogen molecule if the number density is known accurately and the Clausius–Mossotti equation

\[ \alpha = \frac{3}{4\pi N} \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) \]  

(1)

is valid, where \( \alpha \) is the molecular polarizability and \( N \) is the number density.

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The polarizability so measured is generally the isotropic average of the polarizability parallel to the applied field (\(\alpha_{||}\)) and perpendicular to the applied field (\(\alpha_{\perp}\)).

The homonuclear molecules \(\text{H}_2\) and \(\text{D}_2\) have no permanent dipole moment; however, the heteronuclear molecule \(\text{HD}\) does have a small permanent moment in its rest frame. This moment has been calculated to be of order \(6 \times 10^{-4}\) debye units,\(^3\) which agrees with the value obtained using infrared gas spectra measurements.\(^4\) Since the only previous measurement of the dipole moment of \(\text{HD}\) has been in the gas, it would be of interest to measure this quantity in the solid, where the lack of coincidence of the center of mass and center of charge could modify its value. The interpretation of anomalous dielectric behavior in solid methane\(^5\) (where no permanent dipole moment exists in the rotational ground state) as being due to a cooperative transition of the ferroelectric or antiferroelectric type adds incentive to the investigation of the properties of \(\text{HD}\) in the solid phase.

We report here measurements covering experiments from the liquefaction point through the freezing point to a temperature of about 0.02 K. The measurements were all made using the same capacitance cell; however, for the high-temperature data the cell was cooled by attaching it to a continuous transfer liquid helium refrigerator and for the low-temperature data the cell was attached to a dilution refrigerator.

### 2. EXPERIMENTAL DETAILS

The measurements reported here were performed on a cylindrical guarded capacitance cell made of OFHC copper with volume between the plates of above 5 cm\(^3\) (see Fig. 1). Stycast 2850 GT (Emerson and Cuming, Inc.) was used in the construction of the cell since the expansion coefficients of copper and stycast are similar. Use of the guarded cell in conjunction with a bridge for measuring the capacitance minimized the fringing of the electric field and the effects of wiring capacitance to ground.

For the data taken above 4 K, the capacitance cell was attached to a commercial refrigerator (an Air Products Cryotip) capable of producing temperatures from approximately 2 K to room temperature. Temperature regulation of approximately \(\pm 0.050\) K at the worst was obtained. The high thermal conductivity of the OFHC copper ensured that no significant temperature gradients existed in the cell, except possibly a gradient developed across the hydrogen sample in the gap between the cylinders. Adequate time between different temperature points was allowed to ensure that the entire sample was in thermal equilibrium.