Influence of Isotopologue Dipole Moments on Precision Dielectric-Constant Measurements

Allan H. Harvey

National Institute of Standards and Technology,
Boulder, CO 80305, USA

allan.harvey@nist.gov

Measurements of the relative permittivity (static dielectric constant) of fluids such as methane have been interpreted with the assumption of zero dipole moment. This assumption is not strictly true, due to the presence of isotopologues with small, nonzero dipole moments. We investigate the significance of this effect by analyzing the effect of the dipole of CH_3D on the static dielectric constant of methane. It is found that the isotopologue effect is more than two orders of magnitude smaller than the uncertainty of the best existing measurements. Similar estimates for other compounds such as H_2 and CO_2 produce even smaller effects. Therefore, the interpretation of these measurements with a dipole moment of zero remains valid.

1. Introduction

Measurements of the static dielectric constant (relative permittivity) of fluids have a variety of uses in metrology. Many of these applications exclusively employ noble gases, such as dielectric-constant gas thermometry [1]. However, measurements of molecular species (>1 atom) are also of interest, for example in studies of humidity [2] and natural gas [3].

In the early 2000s, Moldover and coworkers [4, 5, 6] published highly accurate capacitance-based measurements of the dielectric constant of several common gases, including the major components of natural gas, at pressures up to 7 MPa. For nonpolar fluids, the static dielectric constant ε is described by the Clausius-Mossotti equation:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \rho A_\varepsilon, \tag{1}$$

where ρ is the molar density and A_ε is proportional to the mean zero-frequency polarizability of an isolated molecule. Additional terms of higher order in density can be added to the right-hand side of Eq. (1) [1, 7], but extrapolating dielectric-constant data to zero density can yield accurate values of A_ε (and thence the molecular polarizability). Alternatively, if the polarizability is known, accurate dielectric measurements can determine the molar density. In the studies of Moldover and coworkers [4, 5, 6], A_ε for nonpolar gases such as N_2, CH_4, C_2H_6, CO_2, and H_2 was typically determined with a relative standard uncertainty on the order of 5×10^{-5}.

However, the assumption that the dipole moment is zero is not strictly true for "nonpolar" molecular fluids. The moment is identically zero by symmetry only if the fluid is isotopically pure. Isotopic substitution, for example the substitution of an ordinary hydrogen atom (^{1}H) by an atom of deuterium (^{2}H, usually written D), can create a species with a nonzero dipole moment. Two effects contribute to this. First, the unequal nuclear masses create asymmetry in the electron distribution when higher-order effects beyond the Born-Oppenheimer approximation are considered; this happens for example in the HD molecule. Second, and more significant when it occurs, for molecules with more than one intramolecular bond the different reduced masses of the bonds (for example, a C-D bond versus a C-H bond in CH_3D) cause asymmetry in the vibrationally averaged molecular geometry and lead to a dipole moment.

Because of the high precision of recent dielectric-constant measurements, it is plausible that the small dipole moments of naturally occurring isotopologues could influence the results. In this brief note, we analyze this question, focusing on the case of CH_3D in methane.

2. Analysis

For describing the low-density behavior of the static dielectric constant of polar fluids, an additional term must be added to Eq. (1); this is sometimes called the Debye-Langevin equation [8]:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \rho \left(A_\varepsilon + \frac{A_p}{T} \right), \tag{2}$$

where T is the absolute temperature. The quantity A_p is related to the average of the square of the molecular dipole moment p by

$$A_p = \frac{N_A \langle p^2 \rangle}{9 \varepsilon_0 k}, \tag{3}$$

where N_A is the Avogadro constant, ε_0 is the electric constant (permittivity of free space), and k is the Boltzmann constant. In Eqs. (2) and (3) and the remainder of this paper, we have used the symbols p and A_p for dipole-related quantities instead of the μ and A_μ used in previous work [3, 5]; this is to avoid confusion with the use of μ for the magnetic permeability in refractive-index gas metrology [7]. For a mixture of n components (whether different chemical compounds or isotopologues), the average appearing in A_p is given by

$$\langle p^2 \rangle = \sum_{i=1}^{n} x_i p_i^2 , \tag{4}$$

where x_i is the mole fraction and p_i the dipole moment of species i. To evaluate the significance of isotopologue dipole moments, the magnitude of the A_p term in Eq. (2) must be compared to the uncertainty with which A_ε is known. This calculation requires the mole fractions x_i and dipole moments p_i of the species with nonzero dipole moments.

We now focus on methane, CH_4, which preliminary examination of available information suggested would have the largest isotope effect because H/D substitutions tend to produce the most asymmetry and CH_4 has four opportunities for substitution.

While there is significant natural variability in the isotopic composition of methane in natural gas, typical values for the deuterium content [9] are about 20 % depleted in D compared to Standard Mean Ocean Water, giving an atom fraction of D of approximately 0.0125 %. Since each methane molecule has four hydrogen atoms that could be substituted with deuterium, the corresponding mole fraction of CH_3D is

approximately 0.05 %, or $x_{CH_3D} = 0.0005$. The fraction of D is small enough that the effect of multiply substituted species such as CH_2D_2 can be neglected.

For the dipole moment of CH_3D, Hollenstein *et al.* [10] list their own measured values and several literature results, ranging in debye units from roughly 0.0055 D to 0.0057 D (1 D $\approx$ 3.335 641 $\times$ 10^{-30} C m). We adopt a value of 0.0056 D for this analysis.

Substituting these values in Eq. (4) produces $\langle p^2 \rangle = 1.6 \times 10^{-8}$ D^2. Conversion to SI units and substitution in Eq. (3) yields $A_p = 1.0 \times 10^{-4}$ cm^3 K mol^{-1}. The abovementioned dielectric measurements were performed at temperatures near 300 K, meaning that the contribution of the dipolar term (A_p/T) in Eq. (2) is roughly 3×10^{-7} cm^3 mol^{-1}. The value of A_ε for methane is approximately 6.5 cm^3 mol^{-1} [5], meaning that the relative contribution of the dipolar term is on the order of 5×10^{-8}, three orders of magnitude smaller than the relative uncertainty of A_ε.

This is only a semiquantitative estimate, since there is significant uncertainty in the CH_3D mole fraction. However, even under the most "pessimistic" assumptions, the relative contribution of the dipolar term would be no larger than 1×10^{-7}, which is more than two orders of magnitude smaller than the relative uncertainty of A_ε. It is safe to say that, within the precision of current experiments, the small amount of polarity in methane due to the deuterated species can be neglected.

Other substances can be examined in similar ways. We do not find a measured dipole moment for singly deuterated ethane, but the small dipole moment (~0.01 D) of CH_3CD_3 [11] suggests that the relative dipolar contribution to the dielectric constant of ethane is of similar magnitude to that for methane. For HD, both experiment [12] and theory [13] indicate a dipole moment near 0.0009 D, which produces an effect (A_p roughly a factor of 80 smaller than for methane) that is negligible compared to the uncertainty of A_ε for H_2 [6]. The dipole moment of $^{16}O^{12}C^{18}O$ is approximately 0.0012 D [14], small enough for its effect on the dielectric constant of CO_2 to be negligible ($A_p \approx 3 \times 10^{-5}$ cm^3 K mol^{-1}) despite the relatively high (approximately 0.2 %) natural abundance of ^{18}O. Diatomic molecules such as $^{16}O^{18}O$ and $^{14}N^{15}N$ would be expected to have dipole moments smaller than that of HD, because the post-Born-Oppenheimer effects that produce the moment are inversely proportional to the nuclear masses.

3.   Conclusions

We have used literature values of dipole moments and isotopic abundances to analyze the effect of naturally occurring isotopologues on precise measurements of the static dielectric constant. For methane, this effect is more than two orders of magnitude smaller than the uncertainty of the best existing measurements. The effect is even less significant for other common gases. Therefore, the analysis of state-of-the-art dielectric-constant data [4, 5, 6] for these "nonpolar" gases with the assumption of zero dipole moment is valid.

Improvements continue to be made for gas-phase dielectric measurements in metrology [1, 15, 16], so it is possible that future experiments will achieve lower uncertainties. If the relative uncertainty is reduced by more than one order of magnitude, the effect of isotopologues could become significant, and the framework developed in this paper could be used to assist in data analysis. This framework would also be useful if precision dielectric-constant measurements were made on a sample that was artificially enriched in minor isotopes.

4. References

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About the author: Allan H. Harvey is a chemical engineer in the Applied Chemicals and Materials Division at NIST, where he develops models for thermophysical properties of pure fluids and mixtures, with an emphasis on aqueous systems and systems of importance for metrology. The National Institute of Standards and Technology is an agency of the U.S. Department of Commerce.