

Measurement of the Dipole Moments of Seven Partially Fluorinated Hydrocarbons with a Radiofrequency Reentrant Cavity Resonator

A. R. H. Goodwin^{1,2} and J. B. Mehl^{1,3,4}

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Equilibrium dipole moments of gaseous pentafluorodimethyl ether (HFE-125), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,2,2,3-pentafluoropropane (HFC-245ca), 1,1,1,2,2-pentafluoropropane (HFC-245fa), and 1,1,1,2,2,3,3,4-octafluorobutane (HFC-338mccq) were obtained from the resonance frequency of a reentrant cavity at temperatures between 250 and 373 K. The electronic contributions to the polarization were determined for each fluid from liquid-phase optical index of refraction measurements at 297 K.

KEY WORDS: dipole moment; dielectric constant; electromagnetic resonator; refrigerant; reentrant cavity.

1. INTRODUCTION

In this paper we report dipole moments for seven gaseous substances, listed in Table I, at temperatures between 250 and 373 K, a range which includes the normal boiling temperature for each substance and is below the critical temperature. All of the substances studied have multiple conformers. Some were found to have temperature-dependent dipole moments. For brevity, the substances are referred to by the numbering scheme used by the refrigeration industry, as listed in Table I [1]. To the best of our

¹ Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, U.S.A.

² Present address: Center for Applied Thermodynamic Studies, University of Idaho, Moscow, Idaho 83844-0905, U.S.A.

³ Also Department of Physics and Astronomy, University of Delaware Newark, Delaware 19711-2570, U.S.A.

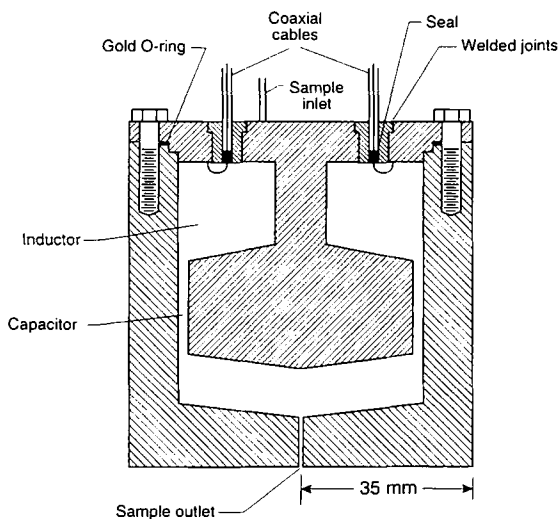
⁴ To whom correspondence should be addressed.

Table 1. Chemical Name and Refrigerant Number

Chemical name	Refrigerant number
Pentafluorodimethyl ether	HFE-125
1,1,1,2,3,3,3-Heptafluoropropane	HFC-227ea
1,1,1,2,3,3-Hexafluoropropane	HFC-236ea
1,1,1,3,3,3-Hexafluoropropane	HFC-236fa
1,1,2,2,3-Pentafluoropropane	HFC-245ca
1,1,1,2,2-Pentafluoropropane	HFC-245fa
1,1,1,2,2,3,3,4-Octafluorobutane	HFC-338mccq

knowledge, the dipole moments of these substances have not been reported previously.

The dipole moments were deduced from measurements of the resonance frequency of a radiofrequency reentrant cavity. The operation of the resonator, shown in Fig. 1, may be understood by considering an equivalent circuit of a capacitor in series with an inductor. The capacitor is formed by the gap between the lower, bulbous extension of the lid and the cylinder. The inductance is associated with current flow between the inner and the outer sections along a path encircling the upper toroidal section. A full analytical model of the resonator, described elsewhere [2], takes into account the finite size of the components by modeling the coaxial sections of the apparatus as waveguides and, also, includes the effects of

**Fig. 1.** Cross section through the reentrant cavity.

dissipation by surface currents and the effective capacitance associated with waveguide discontinuities and the lower open space in the cavity. When the resonator is filled with a gas of relative permittivity (dielectric constant), ϵ_r , the resonance frequency f_0 is given by

$$(2\pi f_0)^2 \approx \frac{1 - 2\pi R_t C_4 f_0 \epsilon_r}{\epsilon_r [L_t(C_4 + C_t/3) + L_c C_c + L_c(C_t^2/3 - C_c C')/C_4]} \quad (1)$$

where the symbols L , C , and R designate inductance, capacitance, and resistance, respectively. The major terms are the inductance $L_t \approx 5.9$ nH associated with the toroidal region and the capacitance $C_4 \approx 30$ pF, whose main component $C_1 \approx 24$ pF comes from the bulbous, small-gap portion of the resonator. The other terms, which are defined in the full description of the theory [2], have approximate numerical values $L_c \approx 0.18$ nH, $C_t \approx 0.6$ pF, $C' \approx 2.3$ pF, $C_c \approx 4.3$ pF, and $R_t \approx 12$ m Ω . The capacitances and inductances [Eq. (1)] depend on the resonator dimensions and hence on the temperature and pressure. The capacitance C_1 is particularly sensitive to pressure. It was determined experimentally by calibration with helium, whose dielectric constant is well-known. The other capacitances and the inductances in Eq. (1) are less sensitive to dimensional changes. Values determined directly from mechanical measurements were used in data analysis. These were corrected for thermal expansion of the resonator using a value of the coefficient of thermal expansion determined in the helium calibration. A typical resonance frequency is 375 MHz.

Equation (1) is the first component of the theoretical model. The second component is the dependence of the relative permittivity on the pressure p , which is given by the series expansion [4]

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = A_e \left(\frac{p}{RT} \right) + (B_e - BA_e) \left(\frac{p}{RT} \right)^2 + \dots \quad (2)$$

where A_e is the molar polarizability. The second dielectric virial coefficient B_e was neglected in the analysis. For the polar substances investigated in this work, the molar polarizability was expressed by the Debye equation [4]

$$A_e = A_e^{\text{at}} + A_e^{\text{el}} + \frac{N_A \mu^2}{9\epsilon_0 k_B T} \quad (3)$$

where A_e^{at} and A_e^{el} are the atomic and electronic contributions, respectively, N_A is the Avogadro constant, k_B the Boltzmann constant, and μ the dipole moment, which itself may have a temperature dependence.

The electronic contribution to the molar polarizability is obtained from measurements of the optical index of refraction n through the relationship

$$A_e^{\text{el}} = \frac{n^2 - 1}{n^2 + 2} \quad (4)$$

The atomic contribution A_e^{at} was estimated as 20% of A_e^{el} [3, 5, 6].

2. EXPERIMENTAL PROCEDURE

2.1. Reentrant Cavity

The apparatus has been described in detail elsewhere [2]. Only the most important features are described here. The reentrant rf resonator, shown in Fig. 1, was machined from yellow brass (65% copper, 35% zinc) to the nominal dimensions provided below. The parts met at an interlocking step. The step ensured accurate concentric alignment of the parts when they were bolted together. The assembled resonator was sealed with a gold O-ring; thus, its outer shell acted as a pressure vessel. The lower part was a hollow cylinder closed at the bottom. It had an internal radius of 25 mm and a wall thickness of 10 mm. The upper part of the resonator served as a lid to the cylinder and had a bulbous coaxial extension into the cavity. Near its top, the extension to the lid had an outer radius of 5 mm and an effective length of 18.5 mm. The region between the narrow part of the extension and the outer cylinder formed the inductor L_1 . The bulbous portion of the extension had an outer radius of 24 mm and a length of 20 mm. An annular gap about 1 mm wide separated the bulbous extension of the lid from the inner surface of the cylinder. This portion of the cavity forms an annular capacitor of magnitude $C_1 \approx 24$ pF. The capacitance C_4 which appears in Eq. (1) is the sum of C_1 plus contributions from fringing fields and the large gap at the bottom of the cavity. The assembled resonator has an internal volume of approximately 60 cm³.

The two electrical feedthroughs were formed from stainless-steel, PTFE-insulated, coaxial cables that were sealed into the lid with high-pressure conical fittings machined from nylon. Seals of exceptionally high electrical resistivity are not required. The dimensional stability of the seals is also not critical. The coupling loops in the resonator were approximately semicircles, 5 mm in diameter, oriented in a plane through the axis of the resonator to maximize coupling to the (azimuthal) magnetic field in the toroid.

The resonance frequencies f_0 and half-widths g were obtained from measurements of the complex transmission coefficient $w(f)$ with a network

analyzer. When the network analyzer excited the resonator at 0 dBm, the signal detected at resonance was -14 dBm. The complex transmission coefficient w was measured at a series of frequencies f_i (typically 51 to 201) in an approximate range $f_0 - 2g < f_i < f_0 + 2g$. The theoretical resonance function

$$w(f) = \frac{Af}{F^2 - f^2} + B \quad (5)$$

was then fit to the data $w_i(f_i)$. The complex constants in Eq. (5), $F = f_0 + ig$, A , and B , were determined in the fit. The rms residuals of the fits were typically 0.05% of the maximum amplitude. The resonance frequency f_0 and half-width g were typically obtained with precisions of about 3×10^{-7} and 5×10^{-4} , respectively.

2.2. Temperature Measurement

The rf resonator was suspended inside a stirred fluid bath that was thermostated to within 3 mK. The temperature was determined with a resolution of 0.01 K with an industrial-grade stainless-steel sheathed platinum resistance thermometer, which was calibrated on ITS-90. The sensing element was located in the stirred fluid near the cell.

2.3. Pressure Measurement

For the resonator calibration with helium, pressures were measured with a fused-quartz Bourdon-tube differential pressure gauge. The manufacturer's calibration data indicated that the gauge had a full scale of 10 MPa and was linear to 1×10^{-5} . This gauge was calibrated against another gauge whose accuracy was directly traceable to a piston gauge. The zero-pressure indication of the gauge varied by up to 1 kPa between isotherms; this drift was accounted for separately. The reference port of the gauge was continuously evacuated by a mechanical vacuum pump, and the pressure monitored with a thermocouple vacuum gauge so that the gauge was effectively operated as an absolute device. A quartz pressure gauge was used for the dipole moment measurements of HFC-227ea, HFC-236ea, and HFC-245ca. This gauge has a precision of 0.01 kPa and an accuracy, as stated by the manufacturer, of 0.3 kPa. It was mounted in the thermostat fluid with the sensing element in the same plane as the center of the capacitor. When we compared this device to a fused-quartz Bourdon-tube differential pressure gauge, we found differences of 4.29 kPa at pressures between 0.1 and 6 MPa. When this offset was accounted for, the discrepancies

Table II. Sample Purity^a

Substance	P_1	GC analysis	P_2
HFC-227ea	0.998	0.001 air	0.999
HFC-236ea	0.992	0.001 air and one unknown 0.004	0.996
HFC-245ca	0.998	0.001 air	0.999
HFE-125	0.991	0.0085 air and two unknowns	0.9995
HFC-236fa	0.9957	5 unknowns	0.9957
HFC-245fa	0.995	6 unknowns	0.995
HFC-338mccq	0.973	0.02 air and 6 unknowns	0.997

^aSupplier-stated mole-fraction purity P_1 , mole fractions observed in the GC measurements, and estimated purity P_2 as used in our measurements, based on the assumption that volatile impurities were removed by degassing.

were reduced to less than 0.1 kPa, a level more than adequate for our purpose and well within the manufacturer's quoted accuracy. A simpler gas-handling system was used for the more limited measurements on HFC-338mccq, HFE-125, HFC-236fa, and HFC-245fa. For these substances, the pressure was measured directly with a transducer which had a nominal accuracy, according to the manufacturer, of 0.7 kPa. It was regularly calibrated when gas samples were changed. The sample upper pressure was limited to about 60% of the vapor pressure in order to avoid systematic errors arising from condensation on the apparatus walls.

2.4. Sample Purity

The manufacturer's stated minimum purity for each sample is listed in Table II together with the results of our gas chromatographic (GC) measurements on these materials. The GC analyses were performed with a thermal-conductivity detector and a Chromsorb B4 packed column.⁵ Before use, each material was transferred from the supplier's container into a vacuum sublimation cell where it was degassed at the temperature of either liquid nitrogen or a mixture of dry ice and acetone. Prior to transfer to the resonator, the HFC-245ca, HFC-227ea, and HFC-236ea samples were transported in the gas phase to a vessel which contained a grade 0.4-nm molecular sieve that had been baked at 500 K previously. The samples were then transferred into a dry, evacuated storage vessel from

⁵ In order to describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.

which they were transferred in the gas phase into the reentrant cavity. The other samples were degassed but not treated in the molecular sieve. Table II lists the probable purity level for the fluids as used in the resonator. Prior to commencing a measurement sequence, the resonator and gas-handling system were evacuated with a rotary vacuum pump until the pressure indicated by a thermocouple gauge in the pumping line had been below 1 Pa for 24 h.

2.5. Refractive-Index Measurements

The electronic contribution to the polarizability for each sample was obtained from the amount-of-substance density and the optical index of refraction. The latter was either determined with an apparatus described by Chae et al. [7] or obtained from published values [8]; in both cases the refractive index was obtained from measurements of the angle between two emerging beams of visible light from a He-Ne laser (wavelength = 628 nm).

3. RESULTS AND ANALYSIS

The major component of the capacitance of the resonator is determined by the small gap at the bulbous portion; thus it is particularly sensitive to the dilation of the resonator that occurs when the resonator is filled with a fluid at high pressures. The dependence of the capacitance upon pressure and temperature was determined from measurements of the frequency when the cavity was filled with helium. The polarizability of He is small and known to a high accuracy from the calculation of Weinhold [9]. The details of the calibration are reported elsewhere [2]. The molar polarizability of argon was measured as a check of this calibration. Our value, which has been reported elsewhere, differed by less than 0.02% from the experimental value reported by Bose and Cole [10].

When the resonator contains a pressurized sample, the resonance frequency shifts both because of the dilation of the cavity and because of the dielectric effects of the fluid. The fractional decrease in the resonance frequency due to dilation is about 84×10^{-6} at 300 K and 300 kPa. The fractional increase due solely to the dielectric properties of the fluid is, from Eqs. (1) and (2), $A_e p / (2RT)$, which has a typical magnitude of 3×10^{-3} at 300 K and 300 kPa for the refrigerants studied in this work. Thus, the dielectric effect is much larger than the dilation effect, and uncertainties in the dilation correction are not a major source of uncertainty in the determination of dipole moments.

The data reduction requires values of the gas density. These were obtained as follows. For HFC-245ca, HFC-338mccq, and HFE-125 the

densities were estimated with the virial equation of state correct to the second virial coefficient B . For HFC-245ca and HFC-338mccq, $B(T)$ was estimated from a model proposed by Weber [11]. The values obtained for HFC-245ca varied between $-640 \text{ cm}^3 \text{ mol}^{-1}$ at 330 K and $-550 \text{ cm}^3 \text{ mol}^{-1}$ at 350 K. For HFC-338mccq the estimated virial coefficients varied from $-1610 \text{ cm}^3 \text{ mol}^{-1}$ at 330 K to $-1130 \text{ cm}^3 \text{ mol}^{-1}$ at 350 K. For HFE-125 $B(T)$ was obtained from the acoustic measurements of Hurly [12]. For HFC-236fa, HFC-245ca, HFC-227ea, and HFC-236ea, the densities were determined with the equation of state software package REFPROP 4.2 [13]. Liquid densities, required for the optical index of refraction measurements, were obtained from published data [8] except for HFC-227ea and HFC-338mccq, which were provided by Defibaugh prior to publication [14].

3.1. Electronic and Atomic Polarizabilities

The electronic and atomic contributions in Eq. (3) were required for the analysis. They were determined as described below. The values so determined were held fixed in all fits.

The electronic contribution to the polarizability was calculated from the optical index of refraction and the liquid density, as expressed in Eq. (4). The results are listed in Table III. The electronic contribution did not exceed 33% of the total polarizability under any conditions in the present work.

In the absence of spectroscopic information, the atomic contributions were estimated by an empirical rule suggested by Meyer and Morrison [3, 5, 6]. They measured the sum of the atomic and electronic contributions to A_e for 10 substances with temperature-independent dipole moments. Their results may be summarized by the rule $A_e^{\text{at}}/A_e^{\text{el}} \approx 0.2 \pm 0.1$

Table III. Electronic Contributions to the Polarizability of the Refrigerants

Substance	$A_e^{\text{el}} (\text{cm}^3 \cdot \text{mol}^{-1})$
HFC-227ea	15.9
HFC-236ea	15.7
HFC-245ca	15.2
HFE-125	12.6
HFC-236fa	17.2
HFC-245fa	15.4
HFC-338mccq	20.4

(mean and standard deviation). This rule was used to estimate A_c^{at} for the substances investigated in this work.

3.2. Dipole Moments

The data were analyzed in two ways. In the first method, the theoretical expression for the resonance frequencies as a function of pressure, as determined from Eqs. (1), (2), and (3), was fit to experimental resonance frequencies along each isotherm. There were two free parameters in each fit: the dipole moment and the zero-pressure value of the capacitance C_1 . The dipole moments determined from the isotherm fits are listed in Table IV and displayed as functions of temperature in Fig. 2. The dipole moment of HFC-227ea was measured at 15 temperatures between 250 and 373 K. The results, which have a mean and standard deviation of 1.456 ± 0.002 , do not show a significant temperature dependence. The dipole moments of HFC-236ea and HFC-245ca appear to have linear temperature dependences over the full range of measurements. Some temperature dependence is also evident in the more limited data taken with HFE-125, HFC-236fa, and HFC-245fa. The two measurements of HFC-338mccq suggest a weaker temperature dependence.

Table IV. Dipole Moments μ (D) at Temperatures T for the Refrigerants Investigated:
1 D = 3.33564×10^{-30} C · m

Substance	T (K)	μ (D)	T (K)	μ (D)	T (K)	μ (D)
HFE-125	330.00	1.513	339.98	1.517	350.01	1.522
HFC-227ea	250.03	1.457	260.01	1.453	269.98	1.452
	280.01	1.455	290.00	1.455	299.99	1.457
	309.99	1.457	320.00	1.458	330.02	1.458
	340.06	1.459	350.10	1.459	360.17	1.454
	370.24	1.454	373.26	1.455	330.04	1.454
	340.07	1.454	350.11	1.454		
HFC-236ea	273.20	1.121	280.02	1.130	290.00	1.159
	299.98	1.187	309.99	1.211	320.00	1.233
	330.02	1.254	340.06	1.275	350.10	1.295
HFC-236fa	329.98	1.982	350.03	1.981		
HFC-245ca	280.01	1.718	290.00	1.727	299.99	1.743
	309.99	1.747	320.00	1.754	330.02	1.762
	340.06	1.771	350.10	1.779		
HFC-245fa	329.97	1.574	339.98	1.581	350.03	1.586
HFC-338mccq	329.96	1.880	350.03	1.857		

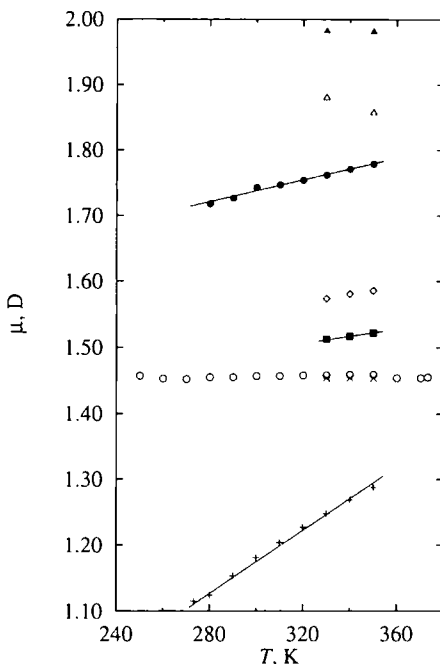


Fig. 2. Dipole moments of HFE-125 (■), HFC-227ea (○, ×), HFC-236ea (+), HFC-236fa (▲), HFC-245ca (●), HFC-245fa (◇), and HFC-338mccq (△), as determined in this work. The symbols were obtained by separate fits to each isotherm. The straight lines are representations of three of the data sets obtained from the second method of data analysis, as explained in the text.

The nearly linear temperature dependence of the dipole moment suggested a second analysis method, for which the dipole moment was assumed to be a linear function of temperature

$$\mu(T) = \mu_1 + \mu_2 t \quad (6)$$

where t is the numerical value of the Celsius temperature. This equation was used in a fit of the model to the entire set of resonance frequencies for each material. The experimental resonance frequencies were fit to the model with four free parameters: μ_1 , μ_2 , and two parameters describing the (linear) temperature dependence of the resonator capacitance at zero pressure. This analysis yielded a “best” linear representation for the dipole moment. The approach worked well for three refrigerants. The values of μ_1

Table V. Values of the Parameters μ_1 and μ_2 in Eq. (6) for Three Refrigerant Substances

Substance	μ_1 (D)	μ_2 (D)
HFC-236ea	1.110	0.0024
HFC-245ca	1.716	0.00083
HFE-125	1.481	0.00054

and μ_2 so determined are listed in Table V. However, the method worked poorly for HFC-227ea and HFC245fa. The measurements on HFC-227ea were performed in two separate sequences. The data from the two sequences were somewhat inconsistent, possibly due to variations in chemical purity. (Minor hysteresis of the resonator dimensions was occasionally observed; however, it did not contribute significantly to the uncertainty in the dipole moment or the observed scatter of the data.) For HFC-227ea, three isotherms were repeated; the results are shown with different symbols in Fig. 2. In each case, the two independent determinations of the dipole moment agree within 0.3%.

The largest uncertainty in the dipole moments is due to the assumptions made in estimating A_v^{at} as $(0.2 \pm 0.1) A_v^{cl}$. Here the number after the \pm sign is the standard deviation of the ratios in the data base from which this empirical rule is derived. It is no more than a plausible assumption that similar ratios for other substances will fall into the same range. The effects of an uncertainty of this magnitude on the dipole moments was estimated by reanalyzing all the data with A_v^{at} equal to $0.1A_v^{cl}$. This change increased the average dipole moments determined from the fits by 0.02 D for HFC-245ca and HFE-125 and by 0.03 D for the other five substances. This is a systematic effect. The data can be corrected at a later time if more accurate values of A_v^{at} become available.

Another source of systematic error is the method used for estimating the densities. Because the data were limited to pressures well below the saturated vapor pressure, the differences between the densities used and the densities estimated from the ideal-gas law had a maximum value of 5% for HFE-125 and HFC-338mccq, a maximum of 3% for HFC-245fa, and a maximum of 2% for all other substances investigated. As long as the equations of state have even moderate accuracy, it is thus clear that the effects of density uncertainty on the dipole moments will be much less than 1%. Finally, the uncertainty in the dilation of the apparatus is equivalent to an uncertainty in the dipole moment of order 0.0001 D.

In summary, the major contribution to the standard error in the dipole moments is the uncertainty due to the use of the empirical rule for

estimating the atomic contribution to the polarizability. The magnitude of this contribution is 0.02 D for HFC-245ca and HFE-125 and 0.03 D for the other substances. The total polarization is determined with much lower uncertainty. For this reason, and to facilitate future correction of these data if better estimates of the atomic contribution to the polarization become available, the dipole moments are listed in Table IV with an extra digit.

For each of the molecules studied in this work there are numerous conformers. In the absence of spectroscopic evidence, we were not able to identify the dominant species.

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