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The Dielectric Constant of Liquid HFC 134a and HCFC 142b[1]

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This paper presents measurements of the dielectric constant of HFC 134a and HCFC 142b, as a function of pressure and temperature, in the temperature range from 200 to 300 K and pressures up to 20 MPa, using a direct capacitance method. The samples used had a stated purity of 99.8 and 99.9 %, respectively. The values of the dielectric constant have a precision of 0.01 % and an accuracy of 0.1 %. The data obtained were correlated as a function of density and pressure. The theory developed by Vedam et al., based on the Eulerian strain, and the Kirkwood equation for the variation of modified molar polarization with temperature and density were applied to analyze the data and to obtain the dipole moment of both refrigerants in the liquid state.

KEY WORDS: density; dielectric constant; dipole moment; HFC 134a; HCFC 142b; Kirkwood equation; refrigerant; Vedam equation.

1. INTRODUCTION

The dielectric constant of environmentally acceptable refrigerants in the liquid state is necessary to study and interpret the electrical properties of these polar fluids and to give operational values for some of the design parameters of machinery used in the air-conditioning and refrigeration industry. Its dependence of temperature, pressure, and density will also permit the application of molecular theories of polar liquids.

These theories are approximate and usually relate the dielectric constant and the molar polarization with density, temperature, polarizability,

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and dipole moment. Several attempts have been made in the past to develop correlating equations for these properties. Of the most successful equations we decided to use the equation of Vedam et al. [1, 2], adapted by Diguet [3], and the Kirkwood modification of the Onsager equation [4–6], as they have been proven to be the most reliable approaches to the problem, and because the experimental data obtained cover a wide range of densities.

In our current program of research on the thermophysical properties of environmentally acceptable refrigerants, we have measured the dielectric constant of HFC 134a and HCFC 142b in the temperature range from 200 to 300 K and with pressures up to 20 MPa using a direct capacitance method. The data on the saturation line have been presented elsewhere, as correlating functions of temperature or density [7].

2. EXPERIMENTS

The experimental setup and its performance have been described in detail by Gurova et al. [7], while the cell has been reported by Mardolcar et al. [8]. The sample handling was also described in Ref. 7. The principal addition to the measuring system was the high-pressure line, composed of a HIP liquid-pressure generator and a Newport Scientific gas compressor and a pressure transducer from Setra Systems with an uncertainty of 0.01 MPa.

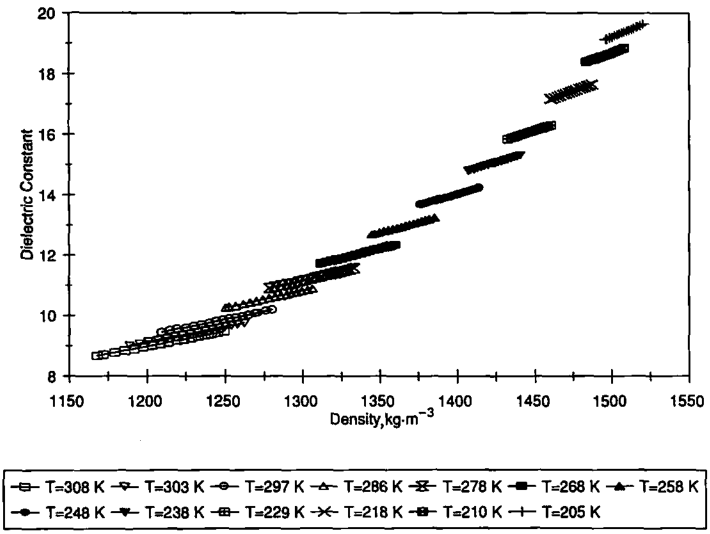

Fig. 1. The dielectric constant of HFC 134a as a function of density, for all the isotherms measured.

Table I. Experimental Values of the Dielectric Constant of HCFC 142b

T (K)	P (MPa)	ρ (kg·m^{-3})	ε
	Near 207 K		
206.62	18.23	1336.40	16.355
206.62	17.01	1334.98	16.336
206.62	15.99	1333.73	16.319
206.64	14.98	1332.38	16.301
206.71	14.01	1331.19	16.278
206.73	12.96	1329.90	16.259
206.74	11.95	1328.64	16.241
206.75	10.95	1327.38	16.223
206.76	9.930	1326.10	16.204
206.77	8.980	1324.90	16.186
206.77	8.000	1323.66	16.168
206.77	7.000	1322.36	16.150
206.78	6.000	1321.07	16.131
206.78	4.980	1319.75	16.113
206.78	4.000	1318.46	16.094
206.78	3.000	1317.13	16.076
206.78	1.990	1315.78	16.058
206.78	0.970	1314.40	16.039
206.78	0.310	1313.51	16.028
	Near 214 K		
214.95	17.28	1319.26	15.454
214.96	16.01	1317.65	15.433
214.95	15.00	1316.39	15.418
214.95	14.06	1315.19	15.400
214.95	13.03	1313.86	15.382
214.97	12.02	1312.51	15.362
214.97	10.99	1311.16	15.346
214.96	9.990	1309.86	15.328
214.96	8.980	1308.51	15.310
215.00	8.100	1307.25	15.289
215.02	7.000	1305.72	15.267
215.02	6.000	1304.34	15.249
215.02	4.990	1302.94	15.230
215.02	4.000	1301.55	15.211
215.02	3.010	1300.15	15.192
215.03	1.970	1298.65	15.171
215.05	1.110	1297.36	15.153
215.05	0.490	1296.46	15.142

Table I. *(Continued)*

T (K)	P (MPa)	ρ ($kg \cdot m^{-3}$)	ε
		Near 223 K	
223.22	17.60	1303.89	14.660
223.22	16.50	1302.44	14.642
223.22	15.50	1301.10	14.625
223.22	14.50	1299.75	14.607
223.22	13.50	1298.39	14.590
223.22	12.48	1296.99	14.570
223.22	11.49	1295.61	14.553
223.22	10.48	1294.20	14.534
223.22	9.500	1292.81	14.515
223.22	8.500	1291.38	14.496
223.23	7.490	1289.91	14.476
223.24	6.500	1288.44	14.457
223.24	5.500	1286.96	14.438
223.24	4.490	1285.46	14.419
223.24	3.490	1283.94	14.398
223.24	2.510	1282.46	14.378
223.25	1.500	1280.88	14.357
223.25	0.500	1279.33	14.336
		Near 233 K	
233.66	17.71	1284.28	13.750
233.66	16.51	1282.56	13.729
233.66	15.52	1281.14	13.711
233.66	14.50	1279.65	13.692
233.66	13.51	1278.19	13.673
233.66	12.47	1276.64	13.654
233.66	11.50	1275.19	13.636
233.66	10.50	1273.67	13.617
233.66	9.480	1272.09	13.595
233.66	8.500	1270.57	13.577
233.66	7.510	1269.02	13.557
233.66	6.500	1267.41	13.536
233.66	5.490	1265.79	13.516
233.67	4.520	1264.19	13.495
233.67	3.490	1262.49	13.474
233.67	2.500	1260.83	13.453
233.67	1.500	1259.15	13.431
233.67	0.500	1257.44	13.410

Table I. *(Continued)*

T (K)	P (MPa)	ρ ($\mathrm{kg \cdot m^{-3}}$)	ε
Near 243 K			
242.71	17.25	1266.54	13.021
242.71	15.92	1264.50	12.997
242.71	14.97	1263.03	12.980
242.71	14.00	1261.49	12.962
242.71	12.94	1259.81	12.941
242.71	12.05	1258.38	12.924
242.71	11.00	1256.66	12.902
242.71	10.01	1255.04	12.882
242.71	9.010	1253.37	12.862
242.71	7.990	1251.65	12.841
242.71	7.010	1249.98	12.819
242.71	5.980	1248.18	12.797
242.71	5.040	1246.54	12.777
242.71	3.980	1244.66	12.754
242.71	3.000	1242.89	12.732
242.71	2.000	1241.07	12.710
242.71	0.990	1239.21	12.687
242.71	0.320	1237.96	12.671
Near 252 K			
252.17	17.04	1248.37	12.325
252.17	15.90	1246.48	12.303
252.17	14.90	1244.79	12.284
252.17	13.97	1243.22	12.265
252.17	12.92	1241.40	12.245
252.16	12.01	1239.84	12.226
252.16	10.96	1238.00	12.204
252.16	9.910	1236.12	12.182
252.16	9.020	1234.50	12.163
252.16	8.010	1232.65	12.141
252.16	7.010	1230.79	12.118
252.17	6.040	1228.95	12.096
252.17	4.980	1226.93	12.073
252.17	3.990	1225.00	12.050
252.17	2.970	1223.00	12.026
252.17	2.010	1221.08	12.003
252.17	1.000	1219.04	11.979
252.17	0.320	1217.63	11.962

Table I. *(Continued)*

T (K)	P (MPa)	ρ ($kg \cdot m^{-3}$)	ε
		Near 263 K	
262.99	16.96	1227.79	11.596
262.98	15.90	1225.88	11.575
262.98	14.90	1224.04	11.555
262.98	14.00	1222.37	11.536
262.98	12.99	1220.46	11.515
262.98	11.98	1218.53	11.494
262.98	10.98	1216.59	11.471
262.98	10.00	1214.67	11.450
262.98	9.000	1212.67	11.427
262.98	8.090	1210.83	11.405
262.99	7.030	1208.63	11.379
262.99	5.980	1206.43	11.354
262.99	5.000	1204.35	11.330
262.99	3.990	1202.18	11.305
262.99	3.010	1200.02	11.280
262.99	2.010	1197.80	11.255
262.99	1.000	1195.51	11.229
262.99	0.320	1193.94	11.212
		Near 273 K	
272.85	17.62	1210.36	10.998
272.84	16.00	1207.20	10.964
272.85	14.97	1205.12	10.942
272.84	13.98	1203.13	10.920
272.84	12.99	1201.10	10.899
272.84	11.99	1199.01	10.876
272.84	10.99	1196.88	10.854
272.84	10.00	1194.75	10.830
272.84	9.000	1192.56	10.806
272.83	8.000	1190.34	10.782
272.83	6.950	1187.96	10.756
272.83	6.010	1185.79	10.732
272.83	4.980	1183.37	10.707
272.83	4.000	1181.02	10.681
272.83	3.010	1178.71	10.656
272.82	2.000	1176.14	10.628
272.82	1.000	1173.61	10.599
272.82	0.320	1171.85	10.582

Table I. *(Continued)*

T (K)	P (MPa)	ρ (kg · m^{-3})	ε
	Near 283 K		
283.83	18.15	1190.63	10.369
283.82	16.99	1188.17	10.343
283.82	16.00	1186.02	10.320
283.82	15.07	1183.97	10.299
283.82	13.98	1181.53	10.274
283.81	12.99	1179.29	10.252
283.81	12.04	1177.09	10.229
283.81	11.01	1174.66	10.204
283.81	10.03	1172.31	10.179
283.81	9.010	1169.81	10.153
283.80	8.010	1167.34	10.128
283.80	7.010	1164.79	10.102
283.80	6.000	1162.17	10.073
283.80	4.980	1159.47	10.046
283.80	4.010	1156.84	10.018
283.80	3.000	1154.06	9.9883
283.80	2.010	1151.27	9.9582
283.80	1.000	1148.35	9.9282
283.80	0.320	1146.36	9.9084
	Near 293 K		
293.55	17.25	1170.01	9.8140
293.54	16.03	1167.14	9.7846
293.54	15.05	1164.77	9.7606
293.54	14.06	1162.34	9.7376
293.54	13.06	1159.84	9.7119
293.54	12.06	1157.28	9.6865
293.54	11.05	1154.65	9.6601
293.54	9.960	1151.76	9.6294
293.54	9.080	1149.36	9.6054
293.54	7.990	1146.35	9.5758
293.54	7.080	1143.78	9.5504
293.54	6.060	1140.81	9.5203
293.54	5.130	1138.07	9.4922
293.54	3.950	1134.49	9.4568
293.54	3.050	1131.69	9.4290
293.53	1.980	1128.30	9.3946
293.53	1.030	1125.20	9.3632
293.53	0.330	1122.85	9.3400

Table I. *(Continued)*

T (K)	P (MPa)	ρ $(kg \cdot m^{-3})$	ε
	Near 303 K		
303.75	13.07	1138.92	9.1698
303.75	12.07	1136.06	9.1440
303.75	11.08	1133.19	9.1174
303.76	10.01	1129.98	9.0845
303.76	9.040	1127.03	9.0569
303.76	8.110	1124.14	9.0297
303.76	7.050	1120.75	8.9980
303.76	6.100	1117.65	8.9695
303.76	5.150	1114.45	8.9391
303.76	4.050	1110.66	8.9020
303.76	3.090	1107.25	8.8693
303.76	2.060	1103.48	8.8343
303.76	1.070	1099.74	8.7985
303.76	0.400	1097.16	8.7730

Measurements were made on HFC 134a and HCFC 142b samples of stated purity 99.8 or 99.9% (Solvay Fluor und Derivative, Gmbh) at an average of 12 isotherms separated by 10 K, in steps of 1 MPa, from slightly above the saturation pressure to 20 MPa.

The values of the experimental data which were obtained at a frequency of 10 kHz with an estimated precision of 0.01% and an accuracy better than 0.1% will be published elsewhere for HFC 134a [9]. Data for HFC 142b are presented here. The density of 134a from the equation of state developed by Tillner-Roth and Baher [10], while for 142b it was obtained by an universal correlation scheme for the refrigerants developed by Fialho and Nieto de Castro [11]. The density was determined with an estimated uncertainty less than 1% for reduced temperatures lower than 0.8. Figure 1 shows the dielectric constant of HCFC 134a as a function of density, for all the isotherms, where a structure similar to the dependence of the thermal conductivity of liquids is found. Table I gives the data obtained for HCFC 142b as a function of pressure for each isotherm.

3. DISCUSSION

The dependence of the dielectric constant on density was studied using the formalism of Vedam et al. and Diguet [1–3]. Vedam and Chen [2] have found that the Eulerian representation of strain in liquids under pressure is very convenient to describe the optical and electrical properties of liquids, because the increase in pressure only rearranges the molecules, decreasing the "free volume" available to them and conditioning their movement. Following these authors we have used the relation between $\varepsilon^{1/2}$ and the Eulerian strain Σ, defined as

$$\Delta = \varepsilon^{1/2}(\rho) - \varepsilon^{1/2}(\rho_0) = A'\Sigma + B \tag{1}$$

with

$$\Sigma = \frac{1}{2}\left[1 - \left(\frac{\rho}{\rho_0}\right)^{1/2}\right] \tag{2}$$

where ρ_0 is a reference density, chosen in this work to be the saturation density at each isotherm. This linear dependence of Δ on Σ was encountered in several organic fluids, but it was not tested for the same fluid over wide ranges of temperature and pressure. From the data obtained it can be concluded that the derivative $(\partial\varepsilon/\partial P)_T$ is always positive, $(\partial\varepsilon/\partial T)_P$ is always negative. The derivative $(\partial\varepsilon/\partial\rho)_T$ is also always positive. Figures 2 and 3 show the variation of the function Δ with the eulerian strain Σ for HFC 134a and HCFC 142b. It can be shown that the variation is linear, with a negative slope $(A' < 0)$ and a value of the intercept about the same for all the temperatures, and $B \approx 0$. This fact is consistent with Eq. (1), and minor deviations from the linearity should be attributed to the combined

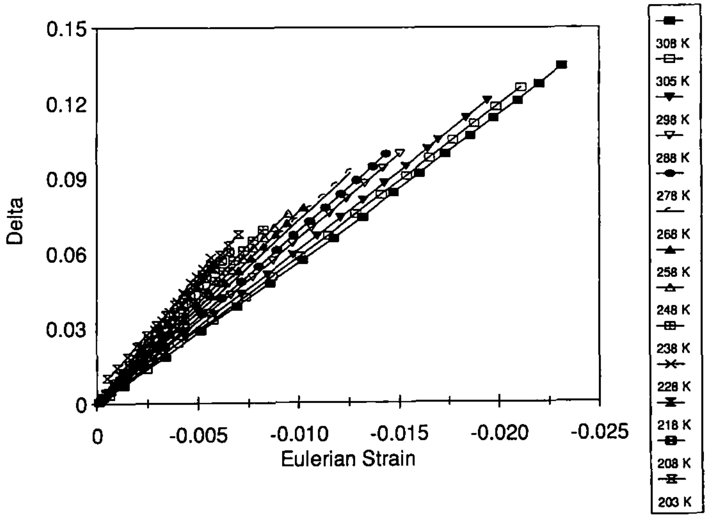

Fig. 2. The function Δ as a function of the Eulerian strain for HFC 134a.

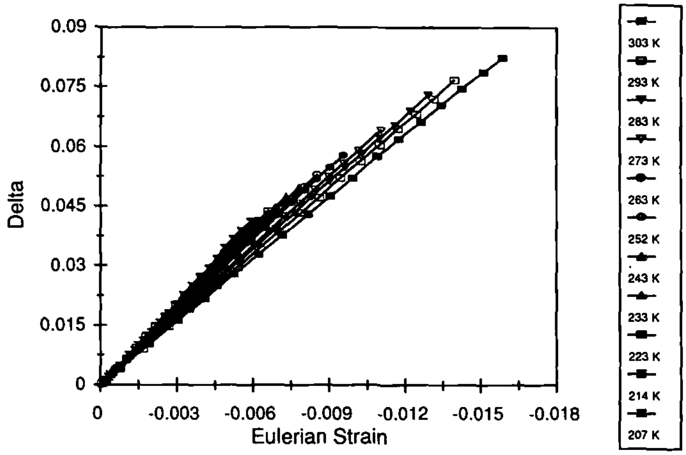

Fig. 3. The function Δ as a function of the Eulerian strain for HCFC 142b.

Table II. Values of the Constants A' and B of Vedam Equation

Fluid	T (K)	ρ_{sat} ($kg \cdot m^{-3}$)	$\varepsilon(\rho_{sat})$	$-A'$	10^4B
HFC 134a	203	1495.03	19.130	10.3405	−1.6
	208	1482.01	18.388	9.68167	−8.3
	218	1458.90	17.156	9.30890	−0.4
	228	1430.34	15.783	8.88645	52
	238	1405.87	14.790	8.48800	−3.8
	248	1375.05	13.668	8.05141	−2.6
	258	1343.09	12.691	7.64962	−1.7
	268	1310.38	11.733	7.32014	−2.0
	278	1277.84	10.913	6.92887	−4.6
	288	1249.75	10.270	6.62559	−3.1
	298	1209.33	9.4551	6.22193	−6.7
	305	1186.69	9.0099	5.99905	−10
	308	1167.44	8.6770	5.82585	−13
HCFC 142b	207	1313.20	16.023	7.08613	4.0
	214	1295.87	15.132	6.89657	1.0
	223	1278.61	14.327	6.68391	1.2
	233	1256.65	13.399	6.51492	1.1
	243	1237.44	12.664	6.39219	1.5
	252	1217.09	11.956	6.22345	1.3
	263	1193.45	11.205	6.07949	2.0
	273	1171.37	10.576	5.82471	1.7
	283	1146.00	9.9037	5.65656	2.4
	293	1122.70	9.3384	5.50930	0.4
	303	1097.16	8.7730	5.21603	3.7

inaccuracies of the dielectric constant measurements and the equations of state used to calculated the densities, especially the accuracy of ρ_{sat} for HCFC 142b. Table II presents the values of the constants A' and B, with the values of density and dielectric constant for the saturation temperature. These values can be used to calculate the dielectric constant of the refrigerants studied at any density, with an estimated accuracy of 0.1 %. It can also be seen that A' has a very regular and smooth variation with temperature.

From the theory of molecular polarisability developed by Kirkwood [5], which uses the definition of the Onsager local field in a liquid assembly of permanent dipoles [4], it is possible to correlate the dielectric constant of the polar liquid with the apparent dipole moment μ^* through the equation

$$\frac{(\varepsilon-1)(2\varepsilon+1)}{9\varepsilon}\left(\frac{M}{\rho}\right)=\frac{N_0}{3}\left(\alpha+\frac{\mu^{*2}}{3\varepsilon_0 k_B T}\right) \tag{3}$$

In this equation M is the relative molar mass of the liquid, N_0 is the Avogadro number, α is the molecular polarizability of the molecule, ε_0 the electrical permittivity of vacuum, and k_B the Boltzmann constant. The apparent dipole moment $\mu^* = g^{1/2}\mu$, where μ is the dipole moment in the ideal-gas state and g is the Kirkwood correlation parameter. This parameter measures the restrictions to rotation imposed by a cage of molecules in a given molecule. Kirkwood, on the basis of a quasicrystaline model, defined this parameter g as

$$g=\frac{\mu^{*2}}{\mu^2}=1+\sum_{i=1}^{\infty} z_i\langle\cos\gamma_i\rangle \tag{4}$$

where z_i is the number of neighbors to the central molecule under consideration in the ith coordination shell, and $\langle\cos\gamma_i\rangle$ is the average cosine angle γ formed by the dipole moments of molecules in the ith shell with the dipole of the central molecule. For liquids of high dielectric constant $\varepsilon \propto g\mu^2$, and g and μ depend on the structure of the liquid. For non-polar or nonassociated liquids $g \approx 1$, but for polar liquids it may considerably differ from unity. Although possible, g has rarely been calculated rigorously, so we have opted to calculated it from the experiment.

The value of μ^* was calculated for both refrigerants, by a linear regression of the Kirkwood function as a function of $1/T$. It is noteworthy that the value of this function was independent of the density within the error of the density calculations. Figure 4 shows the corresponding plot and Table III the values obtained for μ^* and g, using the values of μ taken

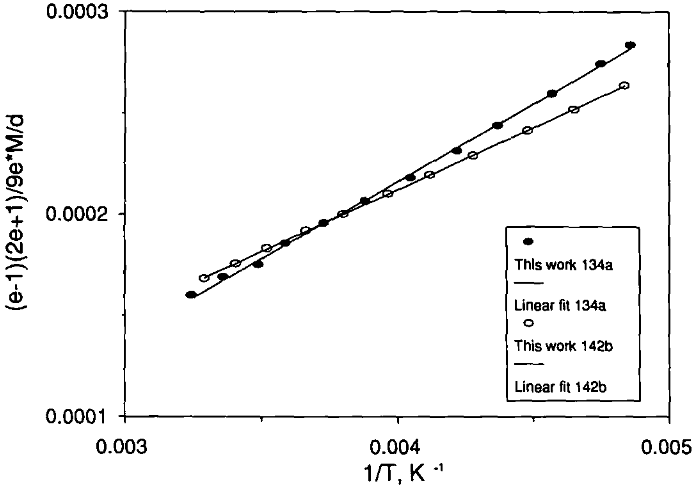

Fig. 4. The Kirkwood function $[(\varepsilon-1)(2\varepsilon+1)/9\varepsilon](M/\rho)$ for both refrigerants as a function of $1/T$.

after the work of Meyer and Morrison [12]. The value of g obtained for HFC 134a is greater than the one obtained for HCFC 142b. HFC 134a, 1,1,1,2-tetrafluoroethane, is a quasi-symmetrical molecule, while HCFC 142b, 1,1-difluoro-1-chloroethane, is highly asymmetric. This will make the rotation in the liquid phase easier for this last molecule, which is confirmed by the determination of a smaller correlation coefficient g. The result is coincident if we interpret on the basis of the apparent dipole moment, much greater for HFC 134a.

Pople [13] applied Kirkwood theory to liquid water, assuming a structure consisting of a water molecule hydrogen bonded to four neighbors and found a value of $g = 2.6$. The values obtained for both refrigerants are close to this value, but these compounds have a value of the dipole moment in the gaseous phase much bigger than that of water.

Table III. Dipole Moments and Kirkwood Correlation Factor for HFC 134a and HCFC 142b in the Liquid State. Units in Debye

Fluid	μ^*	μ [12]	g
HFC 134a	3.54	2.06	2.96
HCFC 142b	3.17	2.14	2.20

4. CONCLUSIONS

The use of the concept of Eulerian strain seems to be completely successful for the interpretation of the dependence of the dielectric constant on density. However, there is some theoretical work yet to be done in order to obtain accurate information about the molecular properties of the polar liquids studied. The choice of the reference density is very important and the possibility of determining universal behavior is encouraging from the results presented in Figs. 2 and 3. In addition, and because $B \approx 0$, it may be possible to use Vedam relation as a predictive tool for dielectric constants of refrigerants.

The use of Kirkwood theory was much more rewarding, as we could obtain values of the apparent dipole moments in the liquid phase, which are consistent with the present knowledge of the molecular structure of both molecules in the liquid phase.

Interpretation of similar results for other refrigerants will be presented in the near-future.

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