SURFACE TENSION AND REFRACTIVE INDEX OF SIX REFRIGERANTS FROM TRIPLE POINT UP TO THE CRITICAL POINT

W. Rathjen and J. Straub

Lehrstuhl A für Thermodynamik
Technische Universität München
Federal Republic of Germany

ABSTRACT

We report measurements on surface tension σ and refractive index n of the refrigerants SF_6 (R 846), CCl_3F (R 11), CCl_2F_2 (R 12), $CClF_3$ (R 13), $CBrF_3$ (R 13B1), and $CHClF_2$ (R 22) throughout the entire temperature range of liquid-vapor equilibrium. The capillary constant a^2 was determined by means of the capillary rise method; the refractive index by measuring the angle of refraction of a light beam passing through a prism and the sample. In order to obtain better information on the liquid-vapor densities which were needed to calculate σ from a^2 but are often inaccurate near the critical and triple point we relate the refractive index n to the Lorentz-Lorenz function LL. The experimental results for a^2, n and σ are presented as functions of temperature. We investigated the validity of simple power laws $a^2 = a_o \mathcal{T}^\phi$ and $\sigma = \sigma_o \mathcal{T}^\mu$ ($\mathcal{T}$ = 1-T/T_c) as well as more exact formulae. For the weakly polar substance a simple power law for σ is a sufficiently accurate approximation (within 1 %) for many purposes. For all substances the temperature dependence of σ can probably be described more accurately by $\sigma = \sigma_o \mathcal{T}^\mu \cdot (1 + b_1 \mathcal{T}^\delta)$. For the substances measured in this work μ is found to be in the range 1.28 < μ < 1.29, b_1 increases with increasing permanent dipole moment and δ is in the range 0.5 < δ < 1.0.

INTRODUCTION

The surface tension σ between the liquid and vapor phases of a pure substance decreases with increasing temperature until the critical point, where the liquid and vapor phases become identical and σ vanishes. At the critical point

$$T = T_c \quad \sigma = 0 \quad \frac{\partial \sigma}{\partial T} = 0 \quad \frac{\partial^2 \sigma}{\partial T^2} = \infty \quad (1)$$

This behaviour is asymptotically described by a simple power law.

$$\sigma = \sigma_o (1 - T/T_c)^\mu \quad (2)$$

According to Guggenheim's formulation (1) of the principle of corresponding states, the exponent μ should have an universal value of μ = 11/9 = 1.22 for all substances. Assuming this value to be true and Eq. (2) to be valid in a wide temperature range a large amount of work has been done in the past to relate the proportionality constant σ_o to the critical state parameters P_c, ρ_c, T_c and to other thermophysical and molecular properties of a specific substance. The resulting equations are often used to calculate surface tension where no experimental data are available.

Modern theories of critical phenomena (2,3,4) support the hypothesis of universality but predict μ = 1.28, a value consistent with new experiments.

Later, we will consider the question what is the form of a universal function σ = f (T) describing the temperature dependence of the surface tension in the entire range of two phase equilibrium.

The surface tension is of considerable significance in technical process like boiling and condensation as well as in the study of phase transition and critical phenomena (particularly through relations to other critical exponents). Thus it is desirable to obtain more experimental information about the surface tension for both technical and scientific reasons. Therefore we have measured the surface tension(and incidentally refractive indices)of six well known refrigerants: SF_6 (R 846), CCl_3F (R 11), CCl_2F_2 (R 12), $CClF_3$ (R 13), $CBrF_3$ (R 13B1) and $CHClF_2$ (R 22). SF_6 is a nearly spherical, nonpolar molecule, whereas $CHClF_2$ has a somewhat high permanent dipole moment. (μ_d = 1.48 D). The influence of the dipole moment is of particular interest in this case.

We have used a capillary rise method. The primary experimental quantity we measured is the capillary constant a^2 defined by

$$a^2 = \frac{2 \cdot \sigma}{g (\rho_l - \rho_v)}$$

To calculate σ the liquid vapor density difference must be known. As equations of state are often inaccurate near the critical point we attempted to obtain better data on $\rho_l - \rho_v$ by measuring the refractive index n simultaneously with the capillary constant.

n is related to the density by the Lorentz-Lorenz function LL

$$LL = \frac{1}{\rho} \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \alpha \frac{N_A}{M} \qquad (3)$$

(M = molecular weight, N_A = Avogadros constant, α = polarizability).

LL should nearly be a constant, independent of temperature and density. To the extent that this is true, LL might be determined at temperatures where reliable density data are available. Then Eq. (3) can be used to calculate the density near T_c. This procedure is often used to study the shape of the coexistence curve near T_c. One uses the relations

$$\rho_L - \rho_V = \frac{1}{LL_D} \left[\frac{n^2 - 1}{n^2 + 2}_L - \frac{n^2 - 1}{n^2 + 2}_V \right] \qquad (4)$$

$$\rho_L - \rho_V = \rho_c \, B_0 \, (1 - T/T_c)^{\beta} \qquad (4a)$$

We may ask questions about the behaviour of $\rho_L - \rho_V$ which are similar to those raised about δ. They concern the validity of the one term power law, the value of ß, and a universal form for the function $\rho_L - \rho_V = f(T)$. In this work $\rho_L - \rho_V$ is evaluated only in so far as it is relevant to the calculation of δ (in the range $T_c - T$ 0.5 - 1K). No special effort has been paid to measuring the refractive index closer to the critical point.

EXPERIMENTAL METHOD AND APPARATUS

The capillary rise method applied in this work was proposed by Sugden (5). The principle is sketched in Fig. 1.
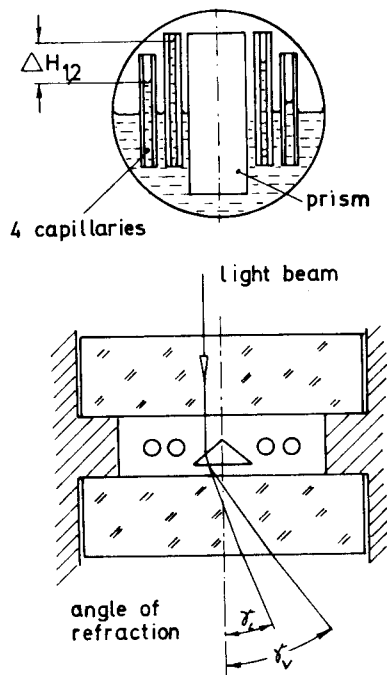

Fig. 1 Schematic view of the experimental method.

The vertical distance ΔH between the interfaces in two capillaries with different internal diameters is measured by means of a cathetometer. Assuming the contact angle to be zero, the height difference ΔH is related to the "capillary constant" a^2 by

$$a^2 = \frac{\Delta H_{1,2}}{1/b_1 - 1/b_2} \qquad (5)$$

where b_1 and b_2 are the radii of curvature at the lowest point of the menisci. They are not measured but must be iteratively evaluated by Sugdens method. The radii of the capillary tubes have been determined by measuring the length and the weight of a certain amount of mercury sucked inside each capillary tube. The constancy of the radius of each tube has been checked by ascertaining that the length of the column of mercury does remain constant when measured at different positions within the tube. In this way the radii could be determined with an accuracy of 0.0002 mm. The reading precision of the cathetometer was better than 0.002 mm. The principal error is due to the subjective localization of the meniscus in a capillary tube: $\Delta(\Delta H) \leq 0.01$ mm. The possible maximum error can be summarized in Eq. (6)

$$\Delta a^2 = 4.8 \cdot 10^{-3} \cdot a^2 + 1.2 \cdot 10^{-3} \, mm^2 \quad (6)$$

The first term refers to the uncertainty in the capillary radii and the second to $\Delta(\Delta H)$, which is the most important term as $T \rightarrow T_c$.

The measurements of the refractive index were carried out at a wavelength, $\lambda = 5.461 \cdot 10^{-5}$ cm with a mercury vapor lamp. The light passes through an adjustable slit on a collimating telescope. The parallel beam which emerges then passes through the sample. An autocollimating telescope, which was connected to optical circular table, was used to position the prism and to observe the angle of refraction. The precision of angle measurement was better than $\pm$ 2", corresponding to an uncertainty within $\Delta n/n < 10^{-4}$. The overall uncertainty is estimated to be within $\Delta n/n < 3 \cdot 10^{-4}$. The temperature has been measured with a 100 Ω platinum resistance thermometer calibrated by means of a standard thermometer, which was previously calibrated at the Physikalisch-Technische Bundesanstalt, Braunschweig.

The precision of the temperature measurement is better than 1 mk, the relative accuracy is better than 0.01 K for temperatures above room temperature and 0.05 K at very low temperatures.

The apparatus developed to work at temperatures from -190 K to + 200 K and pressures up to 120 bar is shown in Fig. 2 The most essential elements are:
- a stainless steel pressure vessel (1) with high strength copper flanges, windows of fused quartz (4) and in the center four capillaries (2) and a prism (3). The internal diameter is 48 mm,

- a vacuum housing of aluminium (7)

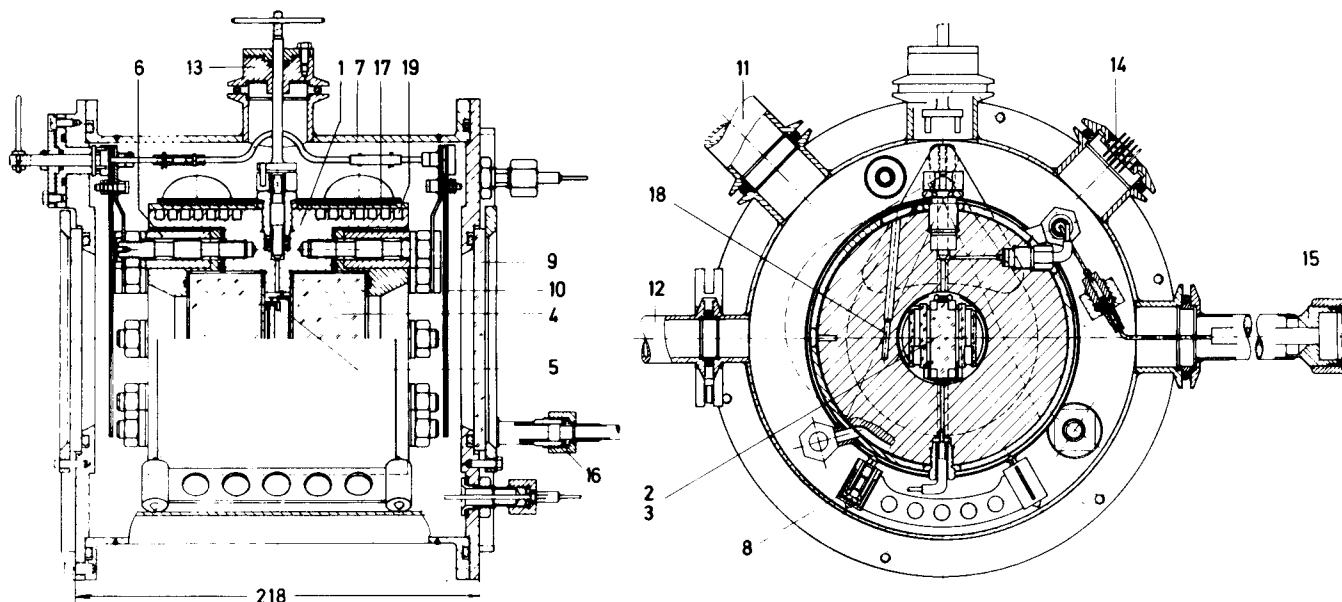- a movable and heatable radiation shield (10).

Fig. 2 Apparatus, (1) pressure vessel, (2,3) capillaries and prism, (4) windows, (5) sealing, (6) compensation of thermal expansion, (7) aluminium housing, (8) prop, (9) windows, (10) radiation shield, (12) handling of valve, (14) electrical contacts, (15) LN$_2$ - inlet, (16) N$_2$ - outlet, (17) electrical heating, (18) thermometer well, (19) bifilar canals.

At low temperatures the pressure vessel is cooled by a controlled stream of nitrogen flowing through bifilar channels (19). At high temperatures the vessel is heated electrically (17). An electronic control circuit holds the temperature constant to within $\pm$ 1 mk. Isothermal conditions which are essential especially near the critical point are achieved by heating the radiation shield such that no temperature differences is measured between shield and vessel. In order to eliminate heat transfer to the housing by conduction and convection the housing is evacuated to less than 10^{-7} bar.

The sealing elements (5) consist of teflon coated Viton-O-rings or metal-O-rings.

EXPERIMENTAL RESULTS AND DATA ANALYSIS

In Table 1 the characteristic data of the investigated substances are compiled.

Table 1   Some characteristic data of the measured gases

Gas	mol. weight	dipole moment Debye	T_s [1] °C	T_c °C	P_c bar	ρ_c g/cm^3
SF$_6$ (R846)	146.o2	0	-5o.6	45.48	37.72	o.734
CCl$_3$F (R11)	137.38	o.68	-111	198	44.9	o.554
CCl$_2$F$_2$ (R12)	12o.92	o.7o	-158	111.78	42.4	o.558
CClF$_3$ (R13)	1o4.47	o.65	-181	28.778	38.2	o.578
CBrF$_3$ (R13B1)	148.93	o.65	-168	67.o35	4c.63	o.745
CHClF$_2$ (R22)	86.48	1.48	-16o	96.12	5o.33	o.525

1) except for SF$_6$ no data of the triple point could be found therefore the melting temperature are given.

Exept for CCl$_3$F the critical temperatures have been measured in this work by visual observation of the reappearance of the meniscus. The relative uncertainty is less than 0.015 K.

In general the measurement were carried out from near triple point until $(T_c - T) >$ 0.5 - 1 K. Because of a failure of a seal the experimental run for CCl$_3$F could only be performed up to T_c - T = 13 K. (185 °C).

The purity of the gases as delivered by Hoechst Company is stated to be 99.98 %. They were further purified by freezing in liquid nitrogen and pumping out non-condensable gases.

The thermophysical properties are taken from Ref. (6-12). The primary experimental results namely the capillary constant a^2 and refractive index n are plotted in Fig. 3 and 4. The data are given in the appendix.

The functional representation of the data is given in two steps: First, to obtain information on the critical exponents and amplitudes the data are fitted to one term power laws in successively extended temperature ranges. Secondly more complicated functions are used to fit the data from critical point to triple point.

To evaluate the coefficients and exponents in the functions linear and nonlinear least squares techniques are applied as proposed by Bevington (13) and van der Voort (14). The essential quantities to test the goodness of fit are

$$\chi^2 = \sum_{i=1}^{M} W_i \left(y_{i,exp} - y(\alpha_{\nu}, x_i) \right)^2 = minimum \quad (7)$$

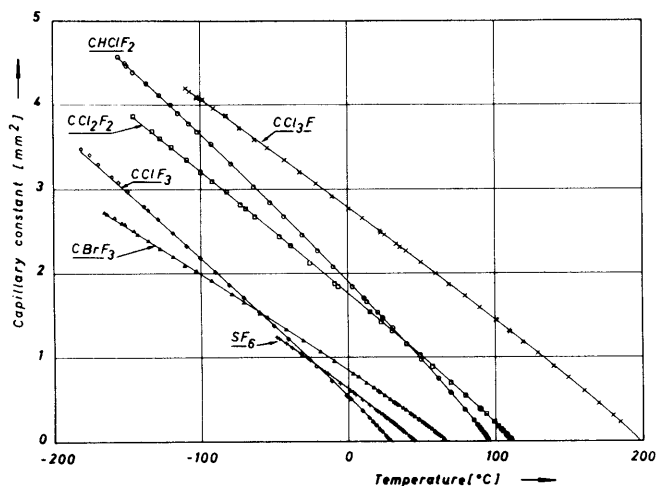$$\chi_\mu^2 = \chi^2 / (M - N) \quad (7a)$$

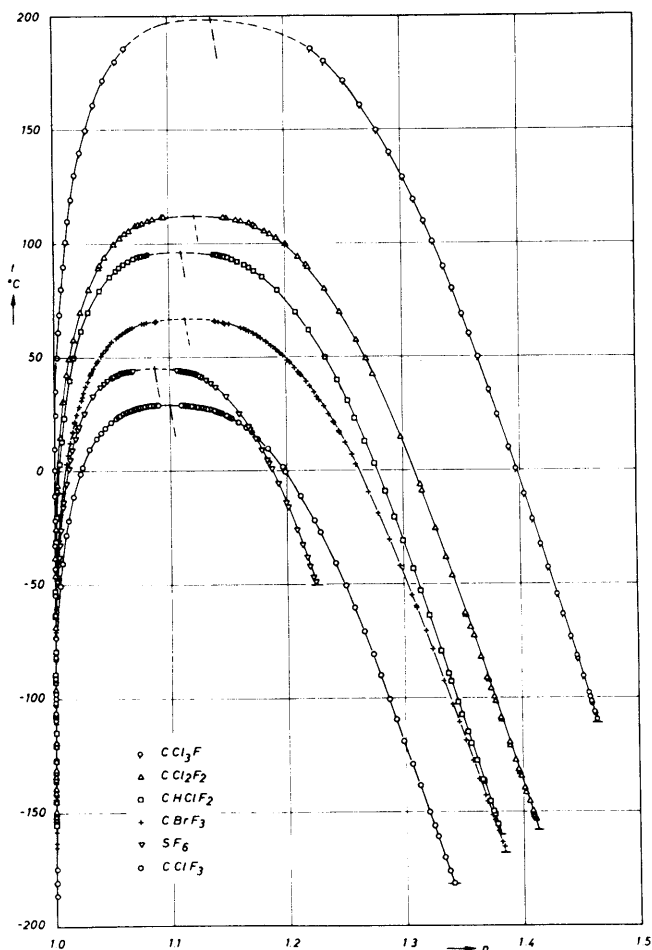Fig. 3 Capillary constant a^2 as function of temperature

Fig. 4 Refractive index n as function of temperature

M = number of data points y_i, N = Number of parameter a_ν to be optimized, W_i = weighing factor, Yiexp experimental value, y (a_ν,x_i) fitting function, x_i independent variable. As weighing factor we used

$$W_i = 1 / \delta_i^{\,2} \qquad (8)$$

where $\delta_i^{\,2}$ signifies the variance of a particular data point; δ_i (the standard deviation) is given for instance by Eq. (6). The influence of the standard deviation δ_i (T) can be assumed to be negligible. The influence of the uncertainty of T_C is evaluated by varying T_C in its range of uncertainty. To discuss errors we introduce three quantities: (1) The standard deviation of the fit (SD) defined by

$$SD^2 = \frac{1}{M-N} \sum (y_{iexp} - y_{calc.})^2 \qquad (9)$$

(2) the relative standard deviation (SD_r) or mean relative error defined by

$$SD_r^2 = \frac{1}{M-N} \sum \left(\frac{y_{iexp} - y_{calc.}}{y_{calc.}} \right)^2 \qquad (10)$$

and (3), the standard deviation of the parameter a_ν defined by

$$SD^2(a_\nu) = \sum \left[\delta_i^{\,2} \left(\frac{\partial a_\nu}{\partial y_i} \right)^2 \right] \qquad (11)$$

The results of the analysis are reported in the next sections.

Capillary constant a^2

In order to test the validity of the one term power law

$$a^2 = a_o^2 \; \mathcal{T}^{\,\phi} \qquad (12)$$

$\mathcal{T} = (1 - T/T_c)$, the experimental data have been fitted to the linearized Eq. (12).

$$\ln a^2 = \ln a_o^2 + \phi \ln \mathcal{T} \qquad (13)$$

The temperature range of the approximation is successively extended from near T_C to $\mathcal{T}_{max} = 0.01, 0.1 \ldots 0.68$ (triple point of CCl_2F_2). In Fig. 5 it is clearly to be seen that except for $CHCLF_2$ and very close to T_C ($\mathcal{T} \rightarrow 0$) where the scatter is too large, in extending the temperature range of the fit ϕ remains constant, thus indicating that for these 5 nonpolar or weakly polar substances Eq. (12) is valid in the entire temperature range. For the polar
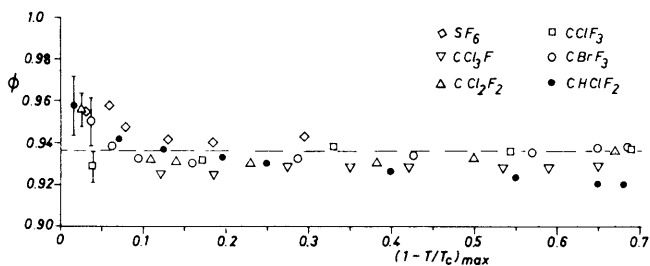

Fig. 5 Variation of the exponent ϕ on extending the temperature range of the fit.

substance $CHClF_2$ ϕ systematically decreases from $\phi = 0.942$ $(0.003 < \mathcal{T} < 0.07)$ to $\phi = 0.92$ $(0.003 < \mathcal{T} < 0.68)$. Therefore in Eq. (12) a second term must be added. The general form of this two term function was assumed to be

$$a^2 = a_o^2 \, \mathcal{T}^\phi (1 + a_1^2 \, \mathcal{T}^{\phi_1})$$ (14)

First we attempted to optimize ϕ_1 but no reasonable and comparable results were obtained. Therefore ϕ_1 was fixed to be 1. The most probable parameter of Eq. (14) and (12) are listed in Table 2.

For the weakly polar substances, the addition of a second term decreases ϕ only slightly. The change is comparable to the standard deviation for ϕ. The average error SD_r is improved only for $CHClF_2$. This is to be expected because the data for this fluid show large deviations from a one term power law.

Refractive indices, shape of the coexistence curve

The main purpose of the refractive index measurements was to obtain the parameter B_O and β of Eq. (4) which should be used near T_c. Therefore first the parameter B_{on} and β of Eq. (15)

$$\left(\frac{n^2-1}{n^2+2}\right)_L - \left(\frac{n^2-1}{n^2+2}\right)_V = B_{on} \cdot \mathcal{T}^\beta$$ (15)

were determined in successively extended temperature ranges. It turned out that in the relevant temperature range $0.002 < \mathcal{T} < 0.1$ β remains nearly constant and the deviations of the experimental values from Eq. (15) are within experimental error. This indicates that a simple power law is suitable to describe the shape of the coexistence curve in these limits. B_{on} and β are listed in Table 4.

It is noteworthy that despite the differences in permanent dipole moment among the various fluids in comparable temperature ranges, the exponent β has nearly the same value of $0.341 < \beta < 0.347$ ($0.002 < \mathcal{T} < 0.09$). CCl_3F can not be included in this comparison due to the lack of data near T_c. The uncertainty in T_c is probably greater than 0.1 K.

As we intend to use Eq. (4) near T_c to determine $\rho_L - \rho_V$ we will have to show, that it is justified to consider the Lorentz-Lorenz function, as defined by Eq. (4) to be constant in a small temperature range.

Table 2 Result of the linear and nonlinear approximation of the capillary constant a^2 in the entire temperature range $0.003 < \mathcal{T} < (T_c - T_t)/T_c$

Gas	a_o^2 mm^2	$SD(a_o^2)$	ϕ	$SD(\phi)$	a_1^2	$SD(a_1^2)$	SD_r %	χ_μ^2
S F_6	3.9313	0.015	0.943	0.0017	–	–	1.71	0.97
	3.9387	0.069	0.944	0.005	-0.00224	0.0032	1.7	1.06
C Cl_3 F (R11)	6.2337	0.0075	0.928	0.001	–	–	0.400	1.04
	6.1975	0.046	0.9261	0.0031	0.00835	0.010	0.406	1.06
C Cl_2 F_2 (R12)	5.6146	0.012	0.936	0.0017	–	–	1.4	1.2
	5.4533	0.050	0.9261	0.0033	0.0463	0.0144	1.65	0.94
C Cl F_3 (R13)	4.8465	0.018	0.9379	0.0013	–	–	1.37	1.6
	4.7430	0.0355	0.9346	0.0028	0.0472	0.011	1.21	1.06
C Br F_3 (R13B1)	3.8785	0.0058	0.9380	0.001	–	–	0.92	1.45
	3.7576	0.023	0.927	0.0023	0.04688	0.01	0.933	1.0
CH Cl F_2 (R22)	6.551	0.014	0.921	0.0015	–	–	3.29	1.79
	6.8416	0.0317	0.9359	0.002	-0.0647	0.0066	1.98	1.0
	6.8592	0.059	0.937	0.003	$\mathcal{T} <$	0.1	3	1.4

In Table 3 LL_D - values are compiled for different temperatures. These values were determined from Eq. (4), with $\varrho_l - \varrho_v$ calculated from equations of state given in the literature.

Table 3   Values of the LL-function LL_D for different temperatures. LL in cm^3/g

$T_C - T$ K	S F_6	C Cl_3 F	C Cl_2 F_2	C Cl F_3	C Br F_3	CH Cl F_2
o(LL_C)	0.07925	0.16153	0.14143	0.11375	0.09989	0.13824
10	0.07964	0.1600	0.1413	0.11364	0.09806	0.13749
20	0.07983	0.15995	0.1410	0.1136	0.09795	0.13745
50	0.07767	0.15978	0.1390	0.1135	0.09752	0.13682
100	-	0.15892	0.13844	0.1127	0.09666	0.13545
T_t	0.07754	0.15712	0.13744	0.1125	0.09747	0.13591
LL_{Dm} (o-10K)	0.079445 ±0.0002	0.1608 ±0.0008	0.14137 ±0.00007	0.1137 ±0.00005	0.09898 ±0.00098	0.1379 ±0.0004
LL_{Lit}	0.0775[1]		0.1392[2]	0.1151[2]	0.09792[2]	0.13773[2]

1) perfect gas 0^oC, 1 bar, Ref.(15) ; 2) perfect gas Ref.(16)

At T_C ($T_C - T = 0$) a value of the Lorentz-Lorenz function was determined by extrapolating the quantity
$$1/2 \left[(n_l^2-1)/(n_l^2+2) + (n_v^2 - 1)/(n_v^2 + 2) \right]$$
to T_C and then devided by the most probable critical density (Table 1). Thus we are assuming the rectilinear diameter is a straight line. In this way we obtained a value for LL at the critical point which we call LL_C.

In Table 3 it is to be seen, that the change of the LL-function down to T_t is indeed quite small, less than 3.5 %.

From $T_C - T = 10$ K to T_C the equations of state from literature become very inaccurate. An estimate of the magnitude of the errors is 3 - 5 %. Therefore, if we introduce in Eq. (4) an average value LL_{Dm} given by

$$LL_{Dm} = \frac{1}{2} \left(LL_C + LL_{D_{(at\ T_c - T = 10K)}} \right) \quad (16)$$

then, near T_C, with this equation the liquid vapor density differences $\varrho_l - \varrho_v$ can be calculated more accurately than from the original equations of state.

Combining Eq. (4) and Eq. (15) the actual equation for $\varrho_l - \varrho_v$ becomes

$$\varrho_L - \varrho_v = \varrho_c \cdot B_o \; \tau^{\beta} \quad (17)$$

with $\varrho_c \cdot B_O = B_{on}/LL_{Dm}$

In Table 4 we compile B_{on}, ß and the important dimensionless quantity B_O, where ϱ_c is taken from Table 1.

The estimated uncertainties in B_O combine the uncertainties in ϱ_c and in the temperature variation of the Lorentz-Lorenz function.

The absolute values of the refractive indices are conveniently approximated by a polynomial with exponents i/3. More than

Table 4   Shape of the coexistence curve in temperature range $0.003 < \tau < 0.1$, $\varrho_c B_o = B_{on}/LL_{dm}$ (C Cl_3 F $\tau > 0.028$)

	B_{on}	SD(B_{on})	B_o	β	SD(β)
S F_6	0.2225	0.0004	3.8359 ±0.04	0.3433	0.0004
C Cl_3 F	0.3344	0.001	3.7538 ±0.055	0.3345	0.001
C Cl_2 F_2	0.3055	0.001	3.8728 ±0.04	0.3468	0.001
C Cl F_3	0.2513	0.001	3.8244 ±0.03	0.3451	0.001
C Br F_3	0.2813	0.0005	3.8145 ±0.045	0.3414	0.0005
C H Cl F_2	0.2830	0.0004	3.9090 ±0.04	0.3457	0.0004

5 terms gave no significant improvement. The coefficients are given in Table 5.

Table 5 Refractive index as function of temperature
$$n_L - n_c = \sum_1^5 a_i \cdot (1-T/T_c)^{1/3}, \quad n_c - n_v = \sum_1^5 b_i \cdot (1-T/T_c)^{1/3}$$

	SF_6	CCl_3F	CCl_2F_2	$CClF_3$	$CBrF_3$	$CHClF_2$
n_c	1.08831	1.13792	1.12117	1.10130	1.11407	1.11065
a_1	0.159816	0.313976	0.215331	0.186174	0.211926	0.203528
a_2	0.016277	-0.431007	0.048057	-0.040298	-0.033964	0.007481
a_3	0.195167	1.585269	2.640448	0.405345	0.447844	0.352516
a_4	-0.307545	-1.982831	-0.482539	-0.559194	-0.683392	-0.560331
a_5	0.193775	0.950640	0.323240	0.307527	0.405058	0.338677
SD	0.0001	0.0001	0.00017	0.00014	0.00016	0.000059
SD_r	0.0093	0.0075	0.014	0.012	0.013	0.0045
b_1	0.162728	0.302887	0.220799	0.188934	0.221233	0.206475
b_2	-0.032776	-0.400746	-0.03098	-0.100843	-0.143615	-0.045014
b_3	0.198624	1.216364	0.240774	0.451697	0.538919	0.269038
b_4	-0.536543	-1.852319	-0.708136	-0.900824	-1.015679	-0.727313
b_5	0.298201	0.878711	0.400644	0.464992	0.516123	0.410401
SD	0.00011	0.000073	0.00016	0.00015	0.000053	0.00006
SD_r	0.01	0.0071	0.015	0.015	0.005	0.006

Surface tension

In order to obtain information on the critical parameter of the surface tension σ_o and μ, the one term power laws of a^2 and $\varrho_l - \varrho_v$ are combined in their range of validity

$$\sigma = \frac{1}{2} g a^2 (\varrho_l - \varrho_v) \equiv \sigma_o \; \tau^{\mu} \quad (18)$$

$$\sigma_o = \frac{1}{2} g a_o^2 \varrho_c B_o \quad (19)$$

$$\mu = \phi + \beta \quad (20)$$

The results are given in Table 6 together with equations derived below.

To calculate the surface tension in the entire temperature range the required densities are determined in the following way:

- at high temperatures by means of refractive index measurements using Eq. (17), the parameter of which are given in Table 4,

- at medium temperatures from equations of state,
- at very low temperatures, beyond the range of validity of the equations of state the refractive indices could again be used. The improvement on using the refractive indices are not very significant. Therefore the details of the procedure is not discussed here.

The experimental data of σ are then fitted to the following equation.

$$\sigma = \sigma_0 T^\mu (1 + b_1 T^\delta) \qquad (21)$$

After extensive preliminary investigations on possible forms of functions, Eq. (21) turned out to be the most simple and effective form to describe the surface tension of simple fluids as well as the unusual behaviour of the surface tension of the highly polar and associating substance H_2O. There may be a physical reason for adding only one second term to describe σ in the polar fluids. One may imagine the surface tension to be composed of two contributions, one due to dispersive and one due to polar intermolecular forces.

Similar corrections terms to asymptotic power laws were recently proposed by Wegner (17). They are very likely to be valid especially near T_C. In the present case the simple power law for σ holds in a wide temperature range. It is still interesting to see what value the second exponent δ will have. According to Wegner's asymptotic expansion near T_C the exponent of the correction terms should also be universal.

The results of the nonlinear fit procedure are compiled in Table 6. For each substance three analysis were carried out. In the first row the simple power law derived above was used, in the second row the most accurate approximation in the whole temperature range was used and in the third row the simple power law fitted again with equal weights to the entire temperature range. In this large range the simple power law is a satisfactory approximation to the data for simple non-polar or weakly polar and non-associating substances. The errors of this third equation are about $1 - 2$ % for $T_C - T > 20$ K, except for the highly polar substance $CHClF_2$. In the latter case the two term equation leads to a significantly better approximation

DISCUSSION OF RESULTS AND CONCLUSION

In this work we have determined the temperature dependence of the capillary constant and the surface tension. It has been shown that for substances with either zero or a small permanent dipole momemt a simple power law is a representation within experimental error of the capillary constant data from triple point to critical point. The surface tension of these substances can only approximately be described by a one term power law, with deviations of about $1 - 2$ % outside the critical region. For many technical calculations this might be sufficient.

Table 6 Temperature dependence of surface tension, parameter of the equations
$\sigma = \sigma_0 T^\mu$ and $\sigma = \sigma_0 T^\mu (1 + b_1 T^\delta)$

Subst.	T_C °C	$(T_C - T)/T_C$ min.	max.	σ_0 10^{-3} N/m	μ	b_1	δ
$S F_6$	45.48	0.0025	0.1	54.28	1.286	-	-
		0.0025	0.29	54.88	1.289	-0.0296	0.51
		"	"	54.44	1.289	-	-
$C Cl_3 F$	198.0	0.028	0.1	63.24	1.263	-	-
		0.028	0.65	(67,06)	(1.271)	(-0.091)	(0.51)
		"	0.65	62.07	1.252	-	-
$C Cl_2 F_2$	111.78	0.0021	0.1	59.63	1.283	-	-
		"	0.67	61.20	1.285	-0.094	0.584
		"	"	56.98	1.268	-	-
$C Cl F_3$	28.778	0.0026	0.1	52.53	1.283	-	-
		"	0.69	53.95	1.287	-0.093	0.664
		"	"	50.56	1.274	-	-
$C BrF_3$	67.035	0.005	0.1	54.05	1.279	-	-
		"	0.68	54.74	1.282	-0.069	1.09
		"	"	52.63	1.270	-	-
$CH Cl F_2$	96.12	0.0027	0.1	69.03	1.283	-	-
		"	0.68	69.93	1.285	-0.154	0.87
		"	"	64.23	1.270	-	-
H_2O [1]	374.00	0.02	0.58	247.73	1.272	-0.640	0.92

[1] in (20) are given smoothed values, which have been reevaluated by our computer program.

The data of σ are plotted in Fig. 6. The solid line represents the one term power law fit in the entire temperature range. The larger deviations for $CHClF_2$ are clearly to be seen.
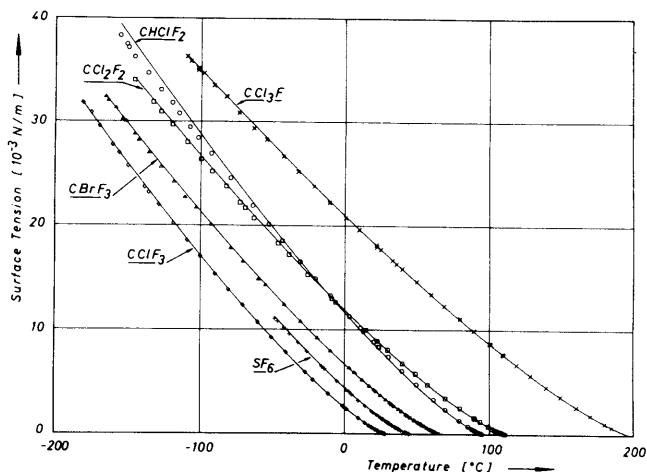

Fig. 6 surface tension

As expected from theoretical insight into phenomena occuring in interfacial regions (18), a permanent diple moment significantly contributes to the temperature dependence of σ. On the basis of our results and the data of water we may conclude that a sole additional term $(b_1 T^\delta)$ is sufficient to take

this contribution into account. The coefficient b_1 increases with increasing dipole moment and the exponent δ is found to be in a small range of $0.5 < \delta < 1.1$.

But it is not clear whether this second term can be identified with Wegner's corrections to asymptotic power laws (17). Following Wegner, δ should be a universal exponent and nearly 0.5; we found higher values. Until now, it is not known, how close to the critical point the measurements have to be carried out in order to answer this question.

Furthermore, it is of interest to see that δ_o and μ of the two term function are nearly the same as δ_o and μ obtained by approximizing δ only near T_c. Hence, in their range of experimental uncertainties, they may be identified as critical parameter.

Our results concerning the exponent $\emptyset$ of the capillary constant a^2 are to be compared with results of Gielen for Ar, O_2, N_2, CH_4 and CO_2 (19). He obtained: $0.927 < \emptyset < 0.936$ which is in good agreement with $0.928 < \emptyset < 0.943$ measured in this work.

The critical exponent μ we found to be $1.279 < \mu < 1.29$. The differences between the highest and lowest values of these exponents are not unsignificant and probably outside their experimental uncertainty. On the other hand no trend due to the molecular structure becomes evident.

In view of the fact that these simple power laws are valid in such a large temperature range we may state that both $\emptyset$ and μ are the true critical exponents and are probably universal.

Furtheron we have shown that the value $\mu = 1.22$ proposed by Guggenheim is too low. In order to predict the surface tension on the basis of the principle of corresponding states for nonpolar substances μ should assumed to be 1.28 as a compromise.

ACKNOWLEDGEMENTS

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APPENDIX

Table 7 Experimental values of the capillary constant a^2 (T in K, a^2 in mm^2)

SF_6

T	a^2	T	a^2
224.640	1.24050	303.346	0.22612
226.656	1.21787	304.048	0.21775
231.220	1.16589	304.514	0.21067
235.236	1.11095	305.363	0.19893
241.080	1.04091	306.165	0.18652
247.306	0.96361	306.206	0.18532
257.534	0.82729	307.627	0.16139
259.383	0.80665	308.411	0.15194
267.838	0.69018	309.059	0.14601
274.489	0.60600	310.095	0.13201
276.695	0.58457	310.269	0.12592
278.302	0.55673	310.727	0.11694
282.802	0.49408	311.930	0.10391
287.649	0.43424	314.658	0.06186
291.860	0.37576	315.039	0.05719
292.971	0.36237	315.780	0.04506
294.938	0.33915	316.082	0.04075
296.756	0.31818	316.157	0.03881
298.260	0.29392	317.181	0.02287
299.148	0.27924	317.679	0.01622
299.892	0.27452	317.693	0.01558
301.228	0.25500	317.817	0.01470
302.539	0.23671	318.63	0

CCl_3F (R 11)

T	a^2	T	a^2
163.615	4.20189	306.235	2.34815
166.245	4.16142	308.844	2.31083
171.124	4.10050	313.049	2.26568
171.363	4.08090	323.127	2.12986
175.258	4.06690	333.269	1.99654
182.258	3.95940	342.129	1.86683
191.196	3.87139	353.159	1.73333
190.479	3.87220	362.981	1.59372
199.794	3.72260	373.926	1.44228
210.108	3.58680	374.765	1.43963
218.729	3.48970	382.917	1.31618
230.451	3.34744	383.423	1.29994
240.664	3.20226	392.323	1.17947
251.808	3.06755	402.140	1.04571
262.690	2.91290	412.941	0.88736
273.891	2.76822	422.824	0.75737
283.322	2.65489	433.639	0.59773
295.257	2.50545	443.316	0.45013
295.646	2.48286	453.112	0.30393
298.149	2.45713	457.807	0.22707
		471.15	0

CCl_2F_2 (R 12)

T	a^2	T	a^2
127.630	3.86644	313.269	1.15292
140.554	3.68891	322.435	1.02456
145.901	3.60551	330.617	0.88792
153.625	3.49903	343.002	0.69926
164.121	3.35253	353.048	0.54707
173.675	3.20591	362.755	0.38912
181.234	3.09453	363.461	0.37752
191.160	2.96923	367.129	0.32648
200.556	2.81777	372.680	0.23328
204.259	2.76988	375.287	0.18009
210.404	2.67451	377.213	0.14475
227.066	2.43846	378.490	0.12114
234.681	2.33021	380.317	0.08800
247.595	2.12454	380.497	0.08423
264.341	1.87956	380.969	0.07705
266.761	1.84189	381.730	0.06175
288.095	1.54350	383.305	0.03319
295.859	1.41907	384.101	0.01854
303.229	1.31407	384.93	0

$CClF_3$ (R 13)

T	a^2	T	a^2
92.126	3.47807	246.089	0.98508
97.922	3.40832	251.402	0.89188
103.685	3.29649	261.961	0.71806
112.877	3.15069	271.934	0.54551
117.435	3.08359	272.606	0.53913
123.504	2.97502	274.717	0.50823
134.878	2.79813	282.897	0.36513
137.632	2.75161	287.376	0.28127
144.570	2.64707	289.996	0.23048
154.571	2.48050	292.096	0.19377
164.049	2.32657	294.440	0.14562
173.054	2.18497	296.187	0.11659
183.323	2.01635	298.785	0.06676
192.654	1.86097	299.745	0.04800
202.528	1.71225	300.540	0.03146
213.041	1.53804	300.607	0.02912
222.752	1.37565	300.788	0.02681
232.575	1.21699	301.141	0.01883
		301.928	0

CBrF₃ (R 13B1) and CHClF₂ (R 22):

CBrF₃ (R 13B1)				CHClF₂ (R 22)			
T	a^2	T	a^2	T	a^2	T	a^2
107.776	2.72076	298.163	0.54280	117.713	4.57388	293.494	1.53785
109.671	2.70019	301.808	0.49880	122.255	4.50016	296.691	1.47331
114.726	2.66059	304.502	0.46520	123.335	4.46963	297.145	1.46928
119.634	2.59290	305.691	0.45100	127.694	4.39077	303.744	1.35041
121.820	2.58073	306.124	0.44760	136.792	4.25802	313.031	1.15929
127.952	2.50345	307.652	0.42870	145.675	4.11589	322.915	0.97228
130.579	2.45878	307.795	0.42510	153.386	4.00298	334.775	0.74750
137.743	2.38354	310.679	0.39240	158.288	3.90352	342.854	0.58107
145.868	2.29071	312.689	0.36890	165.661	3.77760	352.479	0.37790
154.728	2.19612	315.671	0.32950	171.396	3.67999	358.538	0.24979
162.608	2.08933	316.945	0.31280	180.649	3.53839	361.046	0.19415
170.347	2.02694	318.646	0.29120	193.958	3.30181	362.510	0.16189
180.688	1.91096	321.257	0.26100	209.486	3.02902	363.706	0.13466
194.557	1.74898	322.060	0.25000	220.566	2.84007	365.143	0.10157
202.667	1.64895	324.077	0.22390	230.098	2.67330	366.152	0.07852
213.460	1.51769	325.490	0.20510	242.382	2.45434	366.860	0.05831
218.476	1.47711	327.004	0.18630	252.948	2.26964	367.226	0.05348
231.415	1.32752	328.540	0.16690	263.409	2.07797	367.512	0.04577
242.893	1.19425	330.295	0.14330	276.492	1.84211	367.751	0.03968
254.417	1.06120	332.074	0.11760	276.548	1.83721	368.081	0.02924
263.682	0.94886	332.999	0.10240	284.355	1.70396	368.279	0.02481
276.668	0.80160	333.983	0.08900	286.263	1.66292	369.27	0
280.387	0.76350	334.977	0.07690				
285.716	0.69050	335.516	0.07020				
290.720	0.63540	336.597	0.05620				
293.712	0.59920	338.389	0.02820				
295.075	0.58100	340.185	0				

Table 8   Experimental values of the refractive index (T in K)

SF₆

T	n_L	n_v	T	n_L	n_v	T	n_L	n_v
224.640	1.22440	1.00232	299.148	1.16014	1.02724	317.619	1.11268	1.06457
226.656	1.22315	1.00252	306.165	1.14886	1.03485	317.679	1.11208	1.06526
231.220	1.22020	1.00302	310.269	1.14045	1.04112	317.692	1.11191	1.06542
235.236	1.21754	1.00351	311.930	1.13632	1.04436	317.693	1.11198	1.06535
241.080	1.21358	1.00436	313.270	1.13245	1.04742	317.699	1.11200	1.06530
247.306	1.20920	1.00540	314.658	1.12790	1.05123	317.705	1.11195	1.06525
257.533	1.20168	1.00759	315.039	1.12653	1.05238	317.742	1.11138	1.06581
259.383	1.20015	1.00808	315.780	1.12346	1.05500	317.817	1.11107	1.06609
267.838	1.19332	1.01050	316.083	1.12198	1.05621	317.836	1.11050	1.06669
274.489	1.18776	1.01274	316.157	1.12175	1.05654	317.844	1.11064	1.06640
276.695	1.18544	1.01365	316.339	1.12069	1.05738	317.889	1.11020	1.06698
278.302	1.18401	1.01433	316.748	1.11848	1.05937	317.897	1.11023	1.06683
282.802	1.17954	1.01633	317.019	1.11727	1.06080	317.960	1.10943	1.06772
287.649	1.17438	1.01900	317.181	1.11581	1.06178	317.980	1.10898	1.06815
291.860	1.16961	1.02156	317.532	1.11329	1.06419	318.112	1.10747	1.06957
293.032	1.16824	1.02234	317.570	1.11301	1.06434	318.118	1.10741	1.06961
						318.134	1.10750	1.06935

CCl₂F₂ (R 11)

T	n_L	n_v	T	n_L	n_v	T	n_L	n_v
163.615	1.46483	1.00000	230.451	1.42391	1.00006	353.159	1.34318	1.00659
166.245	1.46314	1.00000	240.664	1.41762	1.00012	362.981	1.33562	1.00825
166.818	1.46306	1.00000	251.808	1.41074	1.00022	373.926	1.32677	1.01045
171.124	1.46043	1.00000	262.690	1.40394	1.00038	382.917	1.31918	1.01265
171.363	1.46007	1.00001	273.891	1.39705	1.00059	392.323	1.31073	1.01538
173.443	1.45901	1.00000	283.322	1.39111	1.00087	402.140	1.30162	1.01869
175.258	1.45771	1.00000	295.257	1.38337	1.00128	412.941	1.29032	1.02325
182.568	1.45329	1.00000	298.149	1.38155	1.00145	422.824	1.27912	1.02841
190.479	1.44836	1.00000	306.235	1.37607	1.00192	433.639	1.26552	1.03541
191.196	1.44797	1000001	308.844	1.37451	1.00205	443.316	1.25135	1.04363
199.794	1.44267	1.00010	313.049	1.37151	1.00236	453.112	1.23431	1.05470
210.108	1.43633	1.00036	323.127	1.36484	1.00309	457.806	1.22368	1.06221
218.729	1.43114	1.00010	342.129	1.35136	1.00503			

CCl_2F_2 (R 12)

T	n_L	n_v	T	n_L	n_v	T	n_L	n_v
119.947	1.41064	1.00000	173.675	1.37667	1.00000	322.435	1.26864	1.01436
120.525	1.41032	1.00000	177.435	1.37416	1.00000	330.617	1.26038	1.01754
120.753	1.41032	1.00000	181.234	1.37187	1.00001	343.002	1.24646	1.02369
121.222	1.41006	1.00000	182.101	1.37124	1.00000	353.048	1.23348	1.03068
122.614	1.40923	1.00000	191.160	1.36544	1.00001	362.755	1.21857	1.03922
123.438	1.40853	1.00000	200.556	1.35949	1.00002	363.461	1.21742	1.03983
127.630	1.40603	1.00000	204.259	1.35712	1.00003	367.129	1.21078	1.04406
131.735	1.40304	1.00000	209.749	1.35359	1.00018	372.680	1.19894	1.05218
133.658	1.40191	1.00000	210.404	1.35316	1.00002	375.287	1.19204	1.05755
138.724	1.39892	1.00000	227.066	1.34217	1.00048	377.213	1.18664	1.06157
140.554	1.39775	1.00000	234.681	1.33709	1.00082	378.490	1.18223	1.06525
141.835	1.39665	1.00000	247.595	1.32821	1.00143	380.317	1.17468	1.07103
145.901	1.39437	1.00000	264.341	1.31647	1.00268	380.497	1.17449	1.07166
152.338	1.39005	1.00000	266.761	1.31463	1.00296	380.969	1.17238	1.07349
153.625	1.38938	1.00000	288.095	1.29863	1.00569	381.730	1.16880	1.07662
164.121	1.38274	1.00000	295.859	1.29233	1.00724	382.699	1.16219	1.08182
164.590	1.38231	1.00005	303.229	1.28615	1.00881	383.305	1.15773	1.08580
171.694	1.37785	1.00002	313.269	1.27736	1.01137	384.101	1.14999	1.09318
171.820	1.37784	1.00000	315.820	1.27489	1.01209	384.328	1.14708	1.09595

$CClF_3$ (R 13)

T	n_L	n_v	T	n_L	n_v	T	n_L	n_v
92.126	1.33967	1.00005	202.528	1.26524	1.00189	294.440	1.15871	1.04912
97.922	1.33601	1.00004	213.041	1.25732	1.00291	296.187	1.15334	1.05341
103.685	1.33226	1.00006	222.752	1.24949	1.00430	298.785	1.14329	1.06186
112.877	1.32628	1.00008	232.575	1.24123	1.00626	299.745	1.13787	1.06645
117.435	1.32330	1.00010	246.089	1.22849	1.00992	300.540	1.13236	1.07142
123.504	1.31933	1.00012	251.402	1.22350	1.01191	300.607	1.13189	1.07185
134.878	1.31190	1.00016	261.961	1.21215	1.01634	300.788	1.13042	1.07322
137.632	1.31009	1.00017	271.934	1.19982	1.02232	300.953	1.12911	1.07444
144.570	1.30553	1.00020	272.606	1.19893	1.02278	301.141	1.12706	1.07631
154.571	1.29889	1.00019	274.717	1.19632	1.02416	301.366	1.12423	1.07895
164.049	1.29253	1.00020	282.897	1.18403	1.03133	301.558	1.12147	1.08162
173.054	1.28631	1.00033	287.376	1.17546	1.03689	301.644	1.11964	1.08323
183.323	1.27921	1.00065	289.996	1.16996	1.04070	301.825	1.11439	1.08837
192.654	1.27251	1.00110	292.096	1.16510	1.04402	301.865	1.11221	1.09034

$CBrF_3$ (R 13B1)

T	n_L	n_v	T	n_L	n_v	T	n_L	n_v
107.776	1.38398	1.00007	242.893	1.28830	1.00375	315.671	1.21314	1.03203
109.671	1.38247	1.00000	254.417	1.27883	1.00552	316.945	1.21105	1.03326
114.726	1.37901	1.00006	263.682	1.27085	1.00742	318.646	1.20824	1.03500
119.634	1.37554	1.00001	276.668	1.25966	1.01085	321.257	1.20374	1.03792
121.819	1.37420	1.00002	280.387	1.25614	1.01208	322.060	1.20222	1.03890
127.952	1.36965	1.00000	285.716	1.25074	1.01394	324.077	1.19830	1.04146
130.579	1.36809	1.00003	290.577	1.24556	1.01597	325.489	1.19543	1.04344
137.743	1.36325	1.00000	290.720	1.24540	1.01604	327.004	1.19190	1.04580
145.868	1.35778	1.00001	293.712	1.24211	1.01740	330.295	1.18403	1.05156
154.728	1.35175	1.00000	295.075	1.24064	1.01808	332.074	1.17906	1.05537
162.608	1.34639	1.00003	298.163	1.23690	1.01964	332.999	1.17617	1.05759
170.347	1.34108	1.00008	301.808	1.23248	1.02171	333.984	1.17296	1.06017
180.688	1.33403	1.00018	304.503	1.22906	1.02340	334.977	1.16941	1.06308
194.557	1.32439	1.00042	305.691	1.22763	1.02416	335.516	1.16694	1.06491
202.667	1.31872	1.00064	306.124	1.22695	1.02447	336.052	1.16501	1.06676
212.942	1.31124	1.00110	307.652	1.22500	1.02554	336.597	1.16204	1.06893
213.460	1.31070	1.00115	307.795	1.22471	1.02560	337.179	1.15903	1.07155
218.476	1.30703	1.00143	310.679	1.22066	1.02777	338.143	1.15379	1.07629
231.415	1.29728	1.00244	312.689	1.21775	1.02938			

CHClF$_2$ (R 22)

T	n_L	n_V	T	n_L	n_V	T	n_L	n_V
117.713	1.37843	1.00001	220.566	1.31477	1.00054	334.775	1.22023	1.02413
122.255	1.37580	1.00003	230.098	1.30850	1.00084	342.854	1.20919	1.03006
123.335	1.37501	1.00000	242.382	1.30023	1.00147	352.479	1.19313	1.03989
127.694	1.37236	1.00004	252.948	1.29287	1.00221	358.538	1.18010	1.04892
136.792	1.36669	1.00000	263.409	1.28532	1.00327	361.046	1.17351	1.05383
137.364	1.36630	1.00008	276.492	1.27573	1.00486	362.510	1.16904	1.05731
145.675	1.36140	1.00000	276.548	1.27569	1.00490	363.706	1.16500	1.06062
153.386	1.35667	1.00000	284.355	1.26957	1.00619	365.143	1.15923	1.06532
158.288	1.35369	1.00000	286.263	1.26802	1.00652	366.152	1.15448	1.06937
165.661	1.34916	1.00000	293.494	1.26201	1.00804	366.860	1.15060	1.07271
171.396	1.34565	1.00000	296.691	1.25929	1.00879	367.226	1.14830	1.07472
180.649	1.33997	1.00003	297.145	1.25890	1.00893	367.512	1.14636	1.07647
184.049	1.33789	1.00002	303.744	1.25306	1.01067	367.751	1.14460	1.07803
193.958	1.33167	1.00009	313.031	1.24427	1.01366	368.081	1.14177	1.08063
209.486	1.32186	1.00029	322.915	1.23403	1.01773	368.279	1.13988	1.08243