Helium Atom Scattering from CF_4, CF_3Cl, CF_2Cl_2 and $CFCl_3$ in Crossed Molecular Beams

Christian Gebauer, Olaf Klein, Ralf Schmidt, and Wolfhart Seidel

Physikalisch-Chemisches Institut, Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Gießen

Z. Naturforsch. **50a**, 468–474 (1995); received August 22, 1994

Herrn Professor Dr. Ewald Wicke zum 80. Geburtstag gewidmet

Differential cross sections have been measured by scattering He atoms from CF_nCl_{4-n} ($1 \leq n \leq 4$) in crossed molecular beams. The damping of the diffraction oscillations was used to extract interaction potentials for these molecules which range from nearly isotropic to rather anisotropic. Macroscopic binary parameters, as second virial coefficients, diffusion coefficients and viscosities were calculated from these potentials.

Key words: Molecular beams, Helium, Chlorofluoromethanes, Interaction potentials, Binary coefficients.

1. Introduction

Rotationally unresolved total differential cross sections (DCS) as measured by He atom scattering can be used to extract intermolecular potentials even for rather anisotropic molecular scatterers [1, 2]. In the present paper this is shown for tetrafluoromethane and its chlorine derivatives. Results from an infinite order sudden approximation (IOSA) [3–6] were fitted to experimental DCS data from crossed molecular beam experiments. Modified Hartree Fock dispersion potentials (HFD) [7] served as model potentials in the computations. Macroscopic binary parameters which are related to molecular interaction (second virial coefficients, diffusivities and viscosities) can be determinated if the respective potentials are known (e.g. [3, 8, 9]).

2. Experimental

The experimental configuration has been described in detail in [1, 2, 10]. Two fixed and well-collimated supersonic nozzle beams, one for He atoms and the other for the respective methane molecules, were crossed rectangularly. Either beam was optimized with respect to its velocity spread by means of time-of-flight (TOF) analysis. The quality of the He beams was repeatedly controlled (and if due re-adjusted) by scattering experiments with Ar atoms. The scattering curve for this system is very well known [7, 11–13]. Scattered He atoms were detected with a quadrupole mass filter (Typ 329-9, Extranuclear, USA). The detector was separately enclosed into a UHV chamber which could be rotated (in plane with respect to the beams) around the scattering center. Some character-

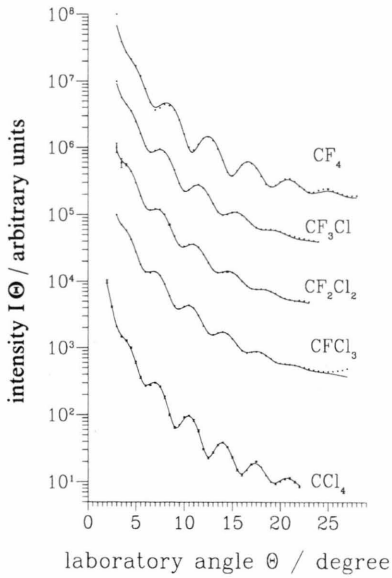

Fig. 1. Laboratory differential cross sections for the scattering of He by CF_xCl_{4-x} ($x = 0 \ldots 4$). The ordinates are shifted arbitrarily. Points with error bars are experimental measurements of the total differential cross section. Solid lines are calculated using best-fit-potentials extracted from measured data.

Reprint requests to Prof. Dr. W. Seidel.

0932-0784 / 95 / 0400-0468 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

Table 1. Beam conditions.

	He	CF_4	CF_3Cl	CCl_2F_2	$CFCl_3$
Gas purity (%)	99.996	99.95	99.7	99.8	>99
Source pressure (bar)	36	0.15	0.14	0.15	0.13
Nozzle diameter (μm)	25	50	50	50	50
Temperature (K)	298	303	303	303	303
Skimmer diameter (mm)	0.5	0.5	0.5	0.5	0.5
Source-skimmer distance (mm)	8.5	2.5	2.5	2.5	2.5
Distance skimmer-center of collision (mm)	87	34	34	34	34
Collimator diameter (mm)	1.5	–	–	–	–
Most probable velocity (ms^{-1})	1645	420.9	333.6	299.8	280.5
Velocity FWHM $\Delta v/v_{mp}$	0.098	0.713	0.71	0.83	0.79
Angular divergence (degree)	1.3	5.6	5.6	5.6	5.6
Speed ratio S	17	1.4	1.2	0.5	1.05
Collision energy (meV)	–	57.2	56.3	56.1	56.1

Table 2. Experimental total differential cross section measurements.

Θ	$HeCF_4$		$HeCF_3Cl$		$HeCF_2Cl_2$		$HeCFCl_3$	
	$I(\Theta)$	$\Delta I(\Theta)$	$I(\Theta)$	$\Delta I(\Theta)$	$I(\Theta)$	$\Delta I(\Theta)$	$I(\Theta)$	$\Delta I(\Theta)$
2.0			10000.00	436.27				
2.5	10000.00	191.53	4361.80	91.37				
3.0	6012.89	66.84	2568.83	114.11	10000.00	1653.750	10000.00	179.520
3.5	4741.85	35.91	2094.94	75.21	7411.61	1160.785	6696.32	103.595
4.0	3718.97	50.04	1784.69	77.83	6769.15	258.930	5417.39	58.000
4.5	2623.24	45.62	1216.31	35.76	5159.12	77.425	4167.08	32.985
5.0	1668.83	16.42	736.10	26.46	3321.94	24.540	2873.15	38.880
5.5	1121.44	7.29	458.71	20.23	2146.31	43.235	1818.08	27.135
6.0	954.95	7.85	408.19	12.49	1665.40	29.480	1203.38	8.260
6.5	991.60	8.54	454.43	13.96	1675.13	26.575	1083.45	11.485
7.0	976.01	7.24	448.09	11.30	1715.22	26.630	1168.36	9.750
7.5	795.98	5.28	350.60	8.64	1538.03	22.755	1207.51	9.265
8.0	549.23	6.42	208.69	7.56	1191.21	20.700	1027.72	17.050
8.5	370.27	3.18	124.93	4.49	819.01	18.115	773.57	11.865
9.0	286.19	1.79	99.43	2.93	564.39	9.580	520.41	7.070
9.5	282.83	2.09	122.96	1.48	461.56	6.025	337.34	2.885
10.0	308.82	2.14	147.52	2.69	481.24	6.450	286.67	1.600
10.5	306.76	2.99	140.91	3.22	503.76	5.645	306.53	1.785
11.0	262.22	2.57	107.69	2.28	491.02	4.990	351.80	2.400
11.5	189.51	2.29	62.77	1.94	406.30	3.955	353.62	2.265
12.0	137.08	1.96	38.06	1.37	307.63	2.770	303.38	2.750
12.5	114.61	0.99	37.00	0.94	230.92	2.305	236.24	1.655
13.0	114.82	1.31	47.98	1.64	193.32	1.130	172.06	1.630
13.5	122.07	1.77	56.18	1.90	188.71	0.945	134.72	1.045
14.0	123.12	0.74	55.31	2.06	195.04	1.570	126.03	1.430
14.5	109.12	1.13	43.64	1.63	187.33	5.485	134.50	1.975
15.0	90.22	0.74	28.35	1.33	181.83	1.220	141.05	1.470
15.5	71.96	0.71	20.55	0.77	155.76	1.905	136.87	0.945
16.0	62.14	0.86	20.73	0.99	128.52	1.080	120.44	0.820
16.5	60.61	0.82	24.92	1.18	112.81	1.565	104.67	0.905
17.0	62.88	0.63	30.09	1.44	107.65	1.010	90.72	0.600
17.5	62.47	0.45	28.89	1.36	108.66	1.555	80.46	0.615
18.0	58.93	0.33	22.49	0.64	108.19	1.480	78.14	0.620
18.5	53.26	0.45	16.84	0.43	102.89	1.285	78.78	1.105
19.0	47.45	0.46	14.75	0.41	96.50	1.290	78.33	0.940
19.5	43.50	0.38	14.66	0.50	87.64	1.015	75.24	1.015
20.0	41.85	0.42	15.93	0.51	79.93	1.020	71.80	0.750
20.5	41.52	0.47	16.82	0.46	76.28	1.095	66.41	0.775
21.0	40.57	0.48	16.23	0.76	73.38	0.690	62.59	0.760
21.5	39.22	0.39	13.81	0.47	73.34	1.105	60.42	0.615
22.0	37.42	0.42	12.04	0.40	72.47	1.050	58.10	0.740

izing data for the experimental equipment are given in Table 1.

DCS curves are shown in Figure 1, including that of CCl_4 [2]. In order to achieve sufficient reliability and a proper signal to noise ratio, complete DCS curves were measured repeatedly up to ten times. The damping of the diffraction oscillations in the measured DCS curves – obvious when comparing for instance the curves of CF_4 and CF_2Cl_2 – is due to anisotropic contributions to the respective interaction potential. Experimental DCS results are given in Table 2.

3. Analysis and Procedure

To analyze the experimental results, the IOSA procedure based on a modified HFD potential as used by Aziz et al. [12] was applied to compute differential cross sections (DCS). For the isotropic part of the interaction the potential was as follows in either case.

$$V(R) = \varepsilon_m f(r), \tag{1}$$

$$r = \frac{R}{R_m}, \tag{2}$$

$$f(r) = f_{\text{rep}}(r) + f_{\text{att}}(r)\,\mathrm{d}(r), \tag{3}$$

$$f_{\text{rep}}(r) = a\exp[-b(r-1)], \tag{4}$$

$$f_{\text{att}}(r) = -\left(\frac{c_6}{r^6} + \frac{c_8}{r^8} + \frac{c_{10}}{r^{10}}\right), \tag{5}$$

$$\mathrm{d}(r) = \begin{cases} e^{-\left(\frac{1.28}{r}-1\right)^2} & \text{for } r \le 1.28 \\ 1 & r > 1.28 \end{cases}. \tag{6}$$

The coefficients c_n and a were used in their reduced form $\left(\text{i.e. } c_n = \frac{C_n}{R_m^n \varepsilon_m};\ a = \frac{A}{\varepsilon_m}\right)$. According to a combination rule of Douketis [14], $c_{10} \approx 1.225\frac{c_8^2}{c_6}$. The parameters a and b can be calculated from the minimum conditions $\left(\frac{\mathrm{d}f(r)}{\mathrm{d}r} = 0;\ f(1) = -1\right)$ of the respective potential. Anisotropy of the scattering molecules was taken into account (corresponding to their symmetry) by expanding the energy and range parameters, ε_m and R_m, into Legendre polynomials or spherical harmonics [2].

4. Analysis and Data Fitting

By means of partial wave analysis using phase shifts, calculable from Langer's modified semiclassical Jeffrey-Wentzel-Kramer-Brillouin approximation [15], DCS were computed in the center of mass system (CMS) for various orientations of collision. These are characterized by the angles θ and ϕ as in the IOS formula [3, 16]. Averaging with respect to θ and ϕ was computed as described in [2] by means of a 16 point Gauss-Legendre quadrature. After transformation to the laboratory system using the elastic Jacobian, the transformed results had to be averaged with respect to the angular and velocity distribution of the two beams and to the finite aperture of the quadrupole detector [10]. Potential parameters (Table 3) were determined by least squares fitting of the calculated DCS to the

Table 3. Best-fit potential parameters. Detailed explanation for T_i, y_{jk} is given in [2].

Parameter	$HeCF_4$	([2])	$HeCF_3Cl$	([2])	$HeCF_2Cl_2$	([2])	$HeCFCl_3$	([2])
ε_0 (meV)	4.05		3.89		3.88		3.98	
ε_1 (meV)	−2.12	(T_3)	−0.09	(y_{10})	−1.49	(y_{10})	0.11	(y_{10})
ε_2 (meV)	0.23	(T_4)	−0.57	(y_{20})	−1.00	(y_{20})	−0.94	(y_{20})
ε_3 (meV)			−1.40	(y_{30})	−1.24	(y_{30})	−2.61	(y_{30})
ε_4 (meV)			0.34	(y_{33})	0	(y_{22})	0.15	(y_{33})
ε_5 (meV)					1.13	(y_{32})		
R_0 (pm)	396		433		471		487	
R_1 (pm)	24	(T_3)	44	(y_{10})	60	(y_{10})	55	(y_{10})
R_2 (pm)	−3	(T_4)	12	(y_{20})	26	(y_{20})	30	(y_{20})
R_3 (pm)			16	(y_{30})	27	(y_{30})	28	(y_{30})
R_4 (pm)			6	(y_{33})	0	(y_{22})	2	(y_{33})
R_5 (pm)					−62	(y_{32})		
a	0.26		0.36		0.62		0.32	
b	30.76		25.39		17.93		27.67	
c_6	0.82		0.73		0.80		0.72	
c_8	0.36		0.43		0.53		0.41	
c_{10}	0.19		0.31		0.43		0.29	

experimental data. A more detailed description of the procedure is given in [1, 2, 10].

5. Macroscopic Parameters

Binary macroscopic coefficients, i.e. second virial coefficients B_{ij}, diffusion coefficients D_{ij} and viscosities η_{ij} may be calculated if the interaction potentials, $V(r, \theta, \phi)$, are known.

B_{ij} follows from [17]

$$B_{ij}(T) = \int_{r=0}^{\infty} \frac{1}{2} \int_{\phi=0}^{2\pi} \int_{\cos\theta=-1}^{+1} (1 - e^{V_{ij}(r,\theta,\phi)/kT}) * N_L \cdot r^2 \, d(\cos\theta) \, d\phi \, dr, \quad (7)$$

with $B_{ij}(T)$ in cm^3/mol. Equation (7) is equivalent to (22) in [17], but extended with respect to averaging over the additional angle ϕ.

Central to the calculation of binary transport coefficients are the respective collision integrals $\bar{\Omega}_{ij}^{(l,s)}$ [18]. For isotropic interaction Maitland et al. [19] used Ω integrals which differ somewhat from those defined in [20]. Following Mason and Monchick [21], an anisotropic interactional shape can be taken into account (under the same conditions as for IOSA) by averaging over all spatial orientations:

$$\langle \bar{\Omega}_{ij}^{(l,s)}(T) \rangle = \frac{1}{4\pi} \int_{-1}^{1} \int_{0}^{2\pi} \pi \sigma_{ij}^2(\theta, \phi) \bar{\Omega}_{ij}^{(l,s)*}(T_{ij}^*) \, d\phi \, d(\cos\theta) \quad (8)$$

with l, s: Quantum numbers, θ, ϕ: angle parameters of the potential function, σ_{ij}: zeropoint of the potential function, T_{ij}^*: reduced temperature, $= \frac{T}{k \varepsilon_{ij}(\theta, \phi)}$.

Equation (8) includes the reduced (isotropic) collision integral $\bar{\Omega}_{ij}^{(l,s)*}(T_{ij}^*)$, which was calculated by means of a computer program of Maitland et al. [19a], slightly modified in order to join our HFD model. Values of the collision integrals are given in Tables 4 and 5 as a function of the temperature.

The transport coefficients were computed to first order by [19b].

$$[D_{ij}]_1 = 8.3679 \cdot 10^{-3} \frac{\sqrt{\frac{T^3}{2\mu}}}{p \langle \bar{\Omega}_{ij}^{(1,1)}(T) \rangle}, \quad (9)$$

$[D_{ij}]_1$ in cm^2/s, with p: pressure in bar, μ: reduced mass in g/mol, and

$$[\eta_{ij}]_1 = 83.868 \frac{\sqrt{2\mu T}}{\langle \bar{\Omega}_{ij}^{(2,2)}(T) \rangle} \quad (10)$$

with $[\eta_{mix}]_1$ in μPoise.

Table 4. Collision integral $\langle \bar{\Omega}_{ij}^{(1,1)}(T) \rangle$ in $Å^2$.

T [K]	$HeCF_4$	$HeCF_3Cl$	$HeCF_2Cl_2$	$HeCFCl_3$
200	28.6414	37.5162	43.7366	45.6627
250	27.7036	36.2463	42.0375	44.2913
300	27.0727	35.3844	40.6638	43.3392
350	26.6052	34.7229	39.5523	42.5571
400	26.2399	34.1971	38.6661	41.9301
450	25.9327	33.7618	37.9389	41.3867
500	25.6804	33.3989	37.3379	40.8767
550	25.4916	33.0944	36.8083	40.4780
600	25.2758	32.8106	36.3799	40.0988
650	25.1146	32.5159	35.8849	39.7254
700	24.9398	32.2828	35.5426	39.4015
750	24.8015	32.0673	34.9882	39.1257
800	24.6493	31.8381	34.6787	38.8379

Table 5. Collision integral $\langle \bar{\Omega}_{ij}^{(2,2)}(T) \rangle$ in $Å^2$.

T [K]	$HeCF_4$	$HeCF_3Cl$	$HeCF_2Cl_2$	$HeCFCl_3$
200	30.2185	39.8900	47.4460	48.3977
250	29.2348	38.5818	45.6521	46.9763
300	28.5871	37.7095	44.1771	45.9982
350	28.1114	37.0482	42.9752	45.1920
400	27.7429	36.5264	42.0391	44.5490
450	27.4356	36.0957	41.2898	43.9629
500	27.1829	35.7359	40.6908	43.4000
550	26.9937	35.4310	40.1695	42.9499
600	26.7763	35.1479	39.7585	42.5540
650	26.6137	34.8453	39.2714	42.1374
700	26.4368	34.6075	38.9474	41.7885
750	26.2887	34.3844	38.5004	41.5076
800	26.1277	34.1270	38.1982	41.2070

Table 6. Viscosity of the pure compounds at $T = 298$ K and $p = 1.013$ bar.

	η in μPoise	Ref.
He	198.59	[26]
CF_4	173.6_8	[26]
CF_3Cl	114.5	[31]
CF_2Cl_2	113	[32]
$CFCl_3$	110	[32]

Viscosities of the respective mixtures were calculated by [19c]

$$[\eta_{mix}]_1 = \frac{1 + Z_\eta}{X_\eta + Y_\eta}, \quad (11)$$

where X_η, Y_η, and Z_η are terms containing $\bar{\Omega}_{ij}^{(1,1)*}$, $\bar{\Omega}_{ij}^{(2,2)*}$ and $[\eta_{ij}]_1$. Viscosities of the pure components were used as given in Table 6.

Results for the different coefficients are shown in Figs. 2, 3, and 4. Solid or dashed lines in these figures have been computed from our potentials. Points represent results from "macroscopic" measurements of

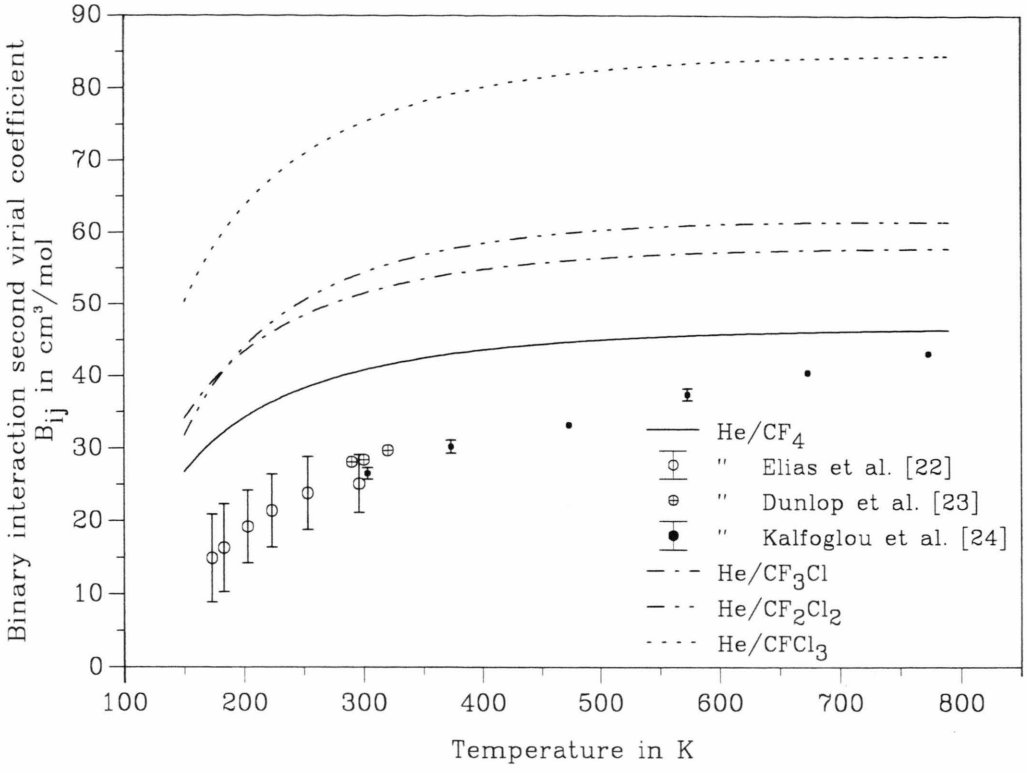

Fig. 2. Second virial coefficient for CF_nCl_{4-n} ($0 \leq n \leq 3$) at $p = 1.013$ bar.

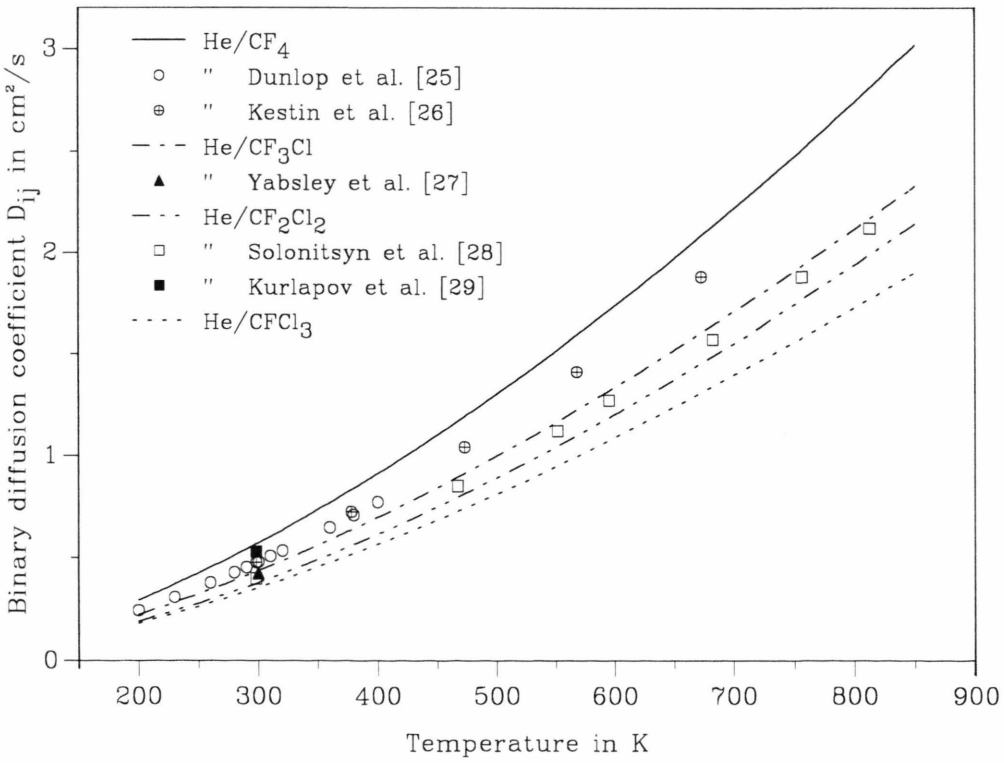

Fig. 3. Diffusion coefficient for CF_nCl_{4-n} ($0 \leq n \leq 3$) at $p = 1.013$ bar.

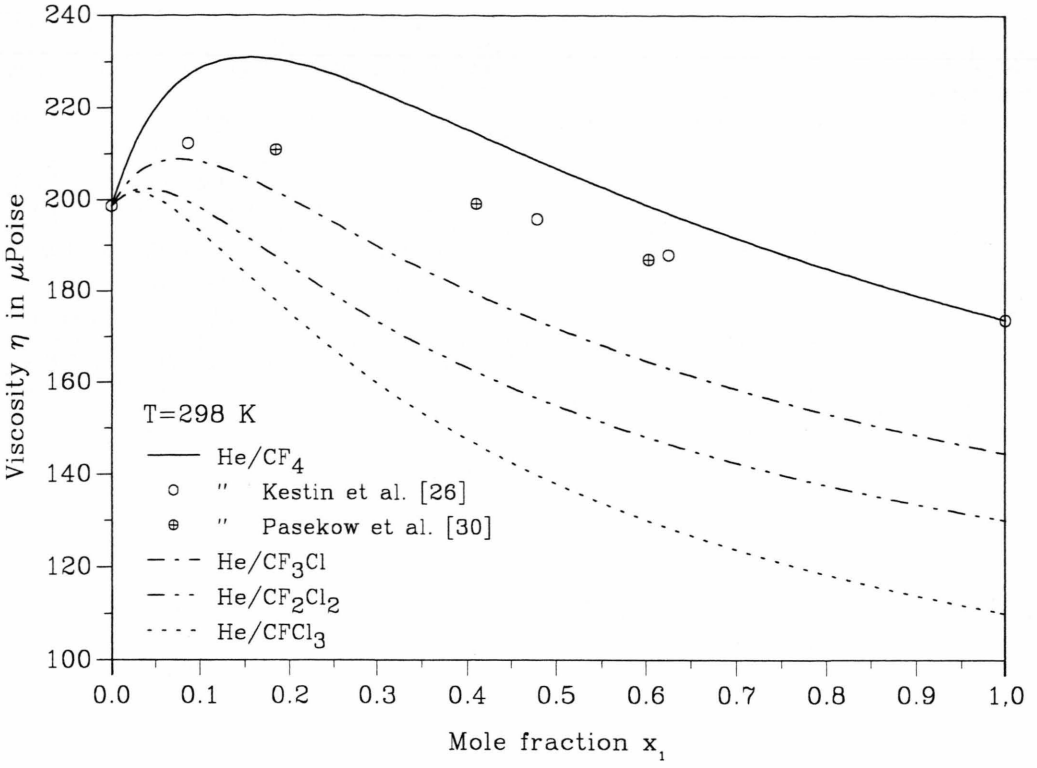

Fig. 4. Viscosity for CF_nCl_{4-n} ($0 \leq n \leq 3$) at $T = 298$ K.

other authors. Apparently the trends are mainly the same. But regarding the large scale differences in experimental conditions, deviations as shown in the figures are not unusual. Also, the procedure to calculate the binary coefficients does not appear to be very sensitive to the anisotropy of the molecules under investigation.

Acknowledgement

Support by the "Fond der Chemischen Industrie", the "Cassella AG" and the "Deutsche Forschungsgemeinschaft" is gratefully acknowledged. We also have to thank Dr. Scheibitz, Hoechst AG, for information on CF_nCl_{4-n} data.

[1] R. Brandt, M. Henkel, B. Pfeil, and W. Seidel, J. Chem. Phys. **95,** 135 (1991).
[2] M. Henkel, B. Pfeil, and W. Seidel, J. Chem. Phys. **96,** 5054 (1992).
[3] G. A. Parker and R. T. Pack, J. Chem. Phys. **68,** 1585 (1978).
[4] U. Buck, V. Khure, and M. Kick, Mol. Phys. **35,** 65 (1978).
[5] R. T. Pack, Chem. Phys. Lett. **55,** 197 (1979).
[6] G. Rotzoll and A. Lübbert, J. Chem. Phys. **71,** 2275 (1979).
[7] K. M. Smith, A. M. Rulis, G. Scoles, R. A. Aziz, and V. Nain, J. Chem. Phys. **67,** 152 (1977).
[8] L. Beneveti, P. Casavecchia, F. Vecchiocattivi, and G. G. Volpi, U. Buck, Ch. Lauenstein, and R. Schinke, J. Chem. Phys. **89,** 4671 (1988).
[9] R. D. Trengove, H. L. Robjohns, and P. D. Dunlop, Ber. Bunsenges. Phys. Chem. **80,** 3725 (1984).
[10] M. Henkel, Dissertation, Justus-Liebig-Universität Gießen 1991.
[11] C. H. Chen, P. E. Siska, and Y. T. Lee, J. Chem. Phys. **59,** 601 (1973).
[12] R. A. Aziz, P. W. Riley, U. Buck, G. Maneke, J. Schleusener, G. Scoles, and U. Valbusa, J. Chem. Phys. **71,** 2637 (1979).
[13] L. J. Danielson and M. Keil, J. Chem. Phys. **88,** 851 (1988).
[14] C. Douketis, G. Scoles, S. Marchetti, M. Zen, and A. J. Thakkar, J. Chem. Phys. **76,** 3057 (1982).
[15] R. E. Langer, Phys. Rev. **51,** 669 (1937).
[16] R. T. Pack, J. Chem. Phys. **60,** 633 (1974).
[17] R. T. Pack, J. Chem. Phys. **78,** 7217 (1983).

[18] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, New York 1964, p. 484.
[19] G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, Intermolecular Forces, Clarendon Press, Oxford 1981, p. 299.
[19a] "App. 12.
[19b] "p. 342.
[19c] "p. 327.
[20] S. Chapman and T. G. Cowling, The Mathematical Theory of Nonuniform gases, Cambridge University Press 1939.
[21] L. Monchick and E. A. Mason, J. Chem. Phys. **35,** 1676 (1961).
[22] E. Elias, N. Hoang, J. Sommer, and B. Schramm, Ber. Bunsenges. Phys. Chem. **90,** 342 (1986).
[23] P. J. Dunlop, C. M. Bignell, and H. L. Robjohns, Ber. Bunsenges. Phys. Chem. **90,** 351 (1986).
[24] N. K. Kalfoglou and J. G. Miller, J. Phys. Chem. **71,** 1256 (1967).
[25] P. J. Dunlop, H. L. Robjohns, and C. M. Bignell, Ber. Bunsenges. Phys. Chem. **91,** 156 (1987).
[26] J. Kestin, H. E. Khalifa, S. T. Ro, and W. A. Wakeham, Physica **88A,** 242 (1977).
[27] M. A. Yabsley, P. J. Carson, and P. J. Dunlop, J. Phys. Chem. **77,** 1256 (1973).
[28] B. P. Solonitsyn, v sb., Obshch. i Prikl. Fizika, (7), 244 (1974); From: Ref. Zh., Khim. 1976, Abstr. No. 12I121.
[29] L. I. Kurlapov and K. K. Musenov, Russ. J. Phys. Chem. **61,** 1024 (1987).
[30] M. F. Pasekov, D. L. Timrot, and B. F. Reutov, Thermal Engineering **36,** 583 (1989).
[31] Die dynamische Zähigkeit von Frigen Kältemitteln, Informationsschrift der Hoechst AG; W. Scholten, Die Kälte- und Klimatechnik **35,** 266 (1982).
[32] CRC Handbook of Chemistry and Physics, CRC Press, Inc., Boca Raton, Florida, 1st Stud. Ed. 1988, p. E-25.