Relaxation cross sections for the rotational angular momentum vector in CF_4

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Nuclear spin–lattice relaxation times (T_1) have been measured for ^{19}F in the CF_4 molecule in pure CF_4 gas and in Ar, Kr, Xe, N_2, CO, HCl, CO_2, CH_4, SF_6, and C_2H_6, from which the following relaxation cross sections for the rotational angular momentum vector in CF_4 have been obtained: $\sigma_J/Å^2 = 19.2 \pm 0.7$ (CF_4–Ar), 29.2 ± 0.8 (CF_4–Kr), 34.3 ± 0.8 (CF_4–Xe), 12.7 ± 0.2 (CF_4–N_2), 12.8 ± 0.6 (CF_4–CO), 22.0 ± 0.1 (CF_4–HCl), 29.7 ± 0.7 (CF_4–CO_2), 12.2 ± 0.2 (CF_4–CH_4), 39.4 ± 0.8 (CF_4–CF_4), 58.0 ± 1.2 (CF_4–SF_6), and 20.8 ± 0.7 (CF_4–C_2H_6). The temperature dependence of these cross sections in the range 210–400 K is essentially T^{-1} except for (CF_4–Ar) and (CF_4–CO, N_2) for which it is $T^{-0.5}$ and $T^{-0.7}$, respectively.

INTRODUCTION

The form of the pair potential for tetrahedral molecules has been of some interest partly due to the small anisotropic interactions in highly symmetric molecules. Hardly any molecular beam scattering cross sections are available for them (except for CH_4). No integral or differential scattering cross sections have been reported for CF_4. Therefore, intermolecular potentials have to be obtained largely from the more classical properties such as viscosity, second pressure virial coefficient, and properties of dense phases. Viscosities, diffusion coefficients, and thermal conductivity data provide spherically averaged values of ϵ and r_0 for CF_4 interacting with He, Ne, Ar, Kr, N_2, O_2, CO_2, CH_4, CF_4, SF_6, and C_2H_6,[1] and interaction second virial coefficients for the same pairs have recently been reported.[2]

Additional information is provided by spectroscopy. Spherical tops have been of special interest since the early days of collision-induced absorption spectra and collision-induced scattering because they behave like rare gas molecules in that the polarizability tensors of the independent molecules are spherically symmetric. Collision-induced absorption in the far IR arises due to electric dipole moments produced in CF_4 through a mutual induction process, the most important mechanisms involving polarization by the permanent octopole and hexadecapole moments[3]; the hexadecapole-induced terms contribute 75% to the zeroth and second moments of the far ir absorption spectrum at 110 K.[4,5]

Collision-induced light scattering (CIS), on the other hand, depends on the induced pair polarizabilities. The experimental CIS line shape has been measured in CF_4 gas up to densities of 270 amagat.[6] The high frequency intensities are proportional to the square of the density, indicating binary collision effects whereas the low-frequency scattering has a complex density dependence. The high frequency wing therefore contains information about the pair potential function, in particular the long-range anisotropy arising from the dipole–quadrupole (**A**) and the dipole–octopole (**E**) polarizabilities.[7]

Ab initio calculations of intermolecular potential surfaces are essentially out of the question at this time for the heavier molecules such as CF_4. It is clear that for CF_4 interacting with another molecule, the anisotropic intermolecular potential has to be an empirical one, with parameters determined by fitting to collision-induced properties. Where possible, the most detailed experimental information such as state-to-state cross sections is the best test for comparison with exact close coupling quantum scattering calculations on well-established potential surfaces. For molecules with a small rotational constant, close coupling calculations are not practical, however. These molecules behave nearly classically in the sense that near room temperature many rotational states are occupied and only the vibrational ground state is significantly populated. For such systems a multiproperty-fitted empirical potential surface can be based on thermal average collision cross sections of various types (including those which we report here), together with pressure virial coefficients and molecular beam scattering cross sections, which properties may be treatable at the classical, semiclassical, or IOS level of quantum scattering. Properties which are nonvanishing for isotropic interaction potentials sometimes lead to inaccurate anisotropy information because the anisotropic contribution compensates for the deficiencies of the spherical term. The cross sections reported here have the advantage that they are due entirely to the angle dependence of the interaction potential. Of the thermal average properties which are directly related to or arise solely from the angle-dependent part of the interaction, those which are related to the reorientation of the rotational angular momentum vector from NMR T_1 measurements in the gas phase are the most promising.

CROSS SECTIONS FROM SPIN RELAXATION

The nuclear spin angular momenta of ^{19}F nuclei in CF_4 are coupled to the rotational angular momentum by a rather large spin–rotation constant so that the ^{19}F nuclear spin is relaxed predominantly by the rotational magnetic fields (except in the presence of a paramagnetic agent). In the limit that the collision frequency in the gas is large compared to the Larmor precession frequency of the ^{19}F nucleus, the so-called "extreme narrowing" limit (for CF_4, this limit is

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reached at densities greater than 0.1 amagat[8]), the spin–rotation relaxation time T_1 in a mixture is made up of additive contributions from various collision partners:

$$T_1 = (T_1/\rho)_{\mathrm{CF_4\text{-}CF_4}}\rho_{\mathrm{CF_4}} + (T_1/\rho)_{\mathrm{CF_4\text{-}X}}\rho_{\mathrm{X}}. \qquad (1)$$

This allows us to characterize spin relaxation due to CF_4–X interactions precisely by making measurements in mixtures of CF_4 and X with known small densities of CF_4 and various densities of X. The characteristic (T_1/ρ) for the CF_4–X collision pair provides a cross section which has a clearly defined meaning in terms of molecular collision dynamics. At gas pressures low enough such that effects of successive collisions are not correlated, Gordon's theory defines the cross section for a spherical top[9]

$$(T_1/\rho) = \frac{\bar{v}\langle\sigma_J\rangle^T}{2C_{\mathrm{eff}}^2\langle J(J+1)\rangle^T}. \qquad (2)$$

The mean relative velocity $\bar{v}$ and the thermal average $\langle J(J+1)\rangle$ can be determined for any temperature from the reduced mass of the CF_4–X collision pair and the CF_4 moment of inertia. When the effective spin–rotation constant C_{eff} is independently known, then the experimental value of (T_1/ρ) at each temperature provides a thermal average $\langle\sigma_J\rangle^T$ or $\sigma_J(T)$, which is defined as $[\mathbf{d}\cdot(\boldsymbol{\sigma})^{-1}\cdot\mathbf{P}\cdot\mathbf{d}]^{-1}$ in Gordon's semiclassical theory.[10] Populations of the rotational states are in **P**, rotational quantum number weighting elements are in **d**, and $\boldsymbol{\sigma}$ is a particular scattering matrix for the **J** vector, whose elements depend on the probability that a collision induces a change in the rotational angular momentum **J** due to transitions between rotational states, averaged over the relative translational energy and impact parameters. That is,

$$\sigma_{fi} = \frac{1}{\bar{v}}\int_0^\infty 2\pi b\,db\,\langle v[\delta_{fi} - \mathscr{P}_{fi}\cos\alpha]\rangle_{\mathrm{coll}},$$

where $\langle\rangle_{\mathrm{coll}}$ means the average over all types of collisions.[10] Thus, $\sigma_J(T)$ has a precisely defined meaning. Given an anisotropic intermolecular potential function the $\boldsymbol{\sigma}$ matrix elements depend in a particular way on the strong and weak collisions which in turn depend on the anisotropy of the repulsive and attractive parts of the potential. Thus, experimental cross sections at different temperatures can provide independent information on the potential.

EXPERIMENTAL

^{19}F spin–relaxation measurements were made at 188 MHz at 4.7 T on an IBM WP-200SY NMR spectrometer, using the inversion recovery pulse sequence, in sealed gas samples containing either pure CF_4 or mixtures of CF_4 and another gas. Buffer gases used were Ar, Kr, Xe, N_2, CO, HCl, CO_2, CH_4, SF_6, and C_2H_6. Some earlier data had been acquired on a Bruker WP-80 spectrometer at 75 MHz. The dependence on the density shown in Eq. (1) was verified experimentally for several CF_4-buffer pairs in the density range 1–40 amagat. The temperature of the sample was regulated by the spectrometer's variable temperature controller unit and was determined at each temperature from the NMR spectra of calibration standards (methanol or ethylene glycol). Further experimental details have been discussed earlier.[11]

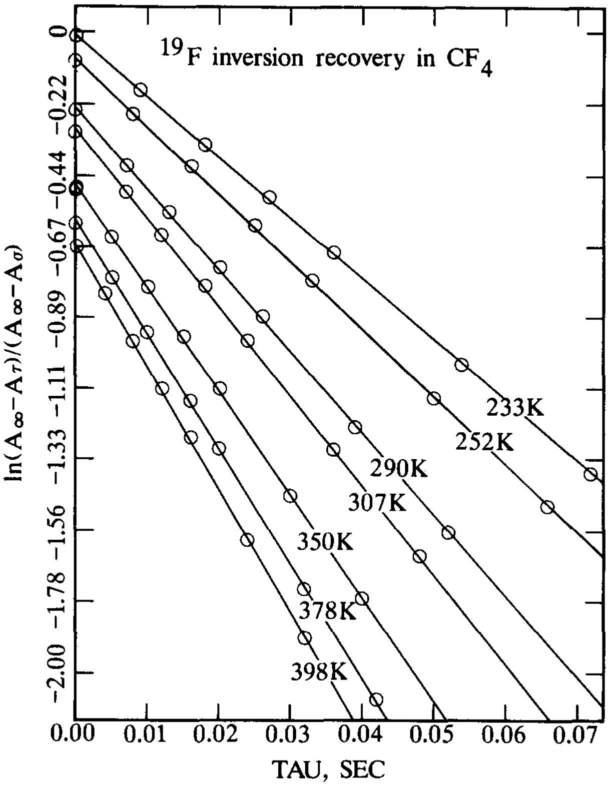

FIG. 1. Typical inversion recovery data for ^{19}F in CF_4. This example is for CF_4 in N_2 gas. The ordinate of each line has been displaced for display purposes. The slope of each line is $-1/T_1$.

RESULTS

The typical precision of the data is shown in Fig. 1. We routinely obtain T_1 values from such plots with standard deviations less than 0.5%. The 2–4% standard deviation in (T_1/ρ) is largely due to errors associated with measurement of density in our samples. It has been shown empirically that (T_1/ρ) obeys a power law in temperature[11,12] so that we report the temperature dependence of the spin relaxation in the form

$$(T_1/\rho) = (T_1/\rho)_{300\,\mathrm{K}}(T/300)^n, \qquad (3)$$

where n is found to be -1.0 to -1.5 in CF_4 in various mixtures. These results are shown in Table I and Fig. 2. The

TABLE I. Spin-relaxation times for ^{19}F in CF_4 in various buffer gases. The observed temperature dependence is described by $(T_1/\rho)_T = (T_1/\rho)_{300\mathrm{K}}(T/300)^n$.

Buffer	$(T_1/\rho)_{300\,\mathrm{K}}$ (ms amagat^{-1})	n	T range (K)
CH_4	1.081 ± .015	− 1.45 ± 0.02	210–400
N_2	0.905 ± .014	− 1.27 ± 0.02	230–400
CO	0.910 ± .038	− 1.24 ± 0.05	210–400
Ar	1.207 ± .045	− 1.01 ± 0.04	210–400
HCl	1.419 ± 0.008	− 1.38 ± 0.02	280–400
CO_2	1.795 ± 0.040	− 1.56 ± 0.04	260–400
Kr	1.460 ± 0.039	− 1.43 ± 0.03	260–400
CF_4	1.948 ± 0.039	− 1.41 ± 0.02	210–400
Xe	1.548 ± 0.031	− 1.47 ± 0.04	280–400
SF_6	2.557 ± 0.055	− 1.42 ± 0.05	290–400
Ethane	1.439 ± 0.047	− 1.36 ± 0.06	260–400

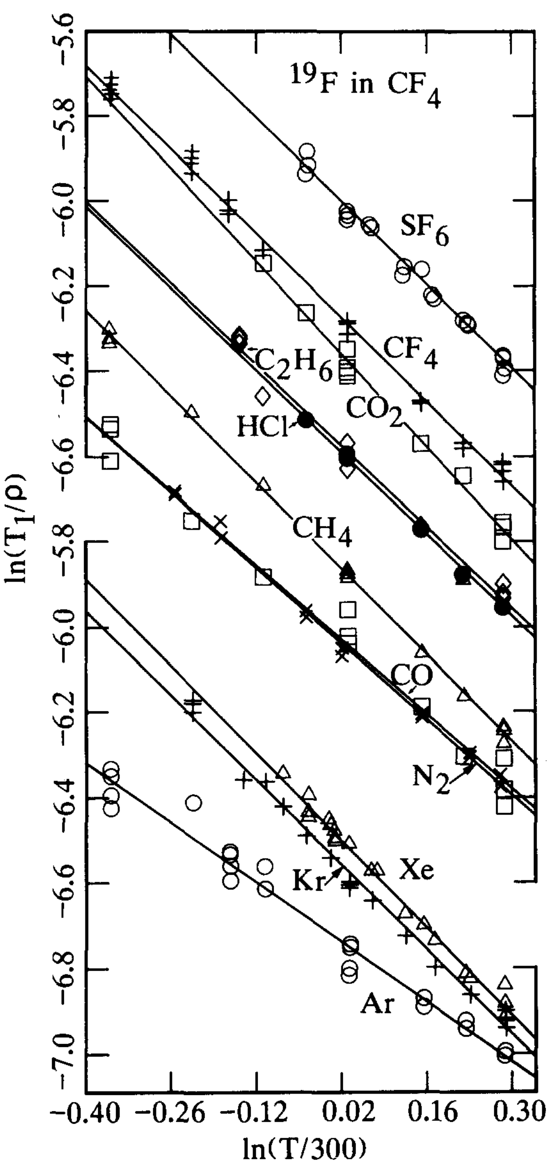

FIG. 2. The temperature dependence of T_1 due to CF$_4$–X collisions in the gas phase.

quoted uncertainties in Table I are standard deviations obtained from fitting of all data to Eq. (3). The $C_{\rm eff}^2$ required in Eq. (2) is known for spherical tops:

$$C_{\rm eff}^2 = C_{\rm av}^2 + (4/45)(\Delta C)^2. \qquad (4)$$

For ^{19}F in CF$_4$ we use $C_{\rm av} = -6.8 \pm 0.3$ kHz and $\Delta C = C_\parallel - C_\perp = 3.62 \pm 0.15$ kHz[13] which are in good agreement with the molecular beam results $C_{\rm av} = -6.78 \pm 0.06$ kHz and $\Delta C \leqslant 5$ kHz.[14] With these values of the spin–rotation constants, the cross sections $\sigma_J(T)$ are calculated from the measured (T_1/ρ) values using Eq. (2), and are shown in Table II. The temperature dependence of these cross sections shown in Fig. 3, can be expressed as a power law,

$$\sigma_J(T) = \sigma_J(300\ {\rm K})(T/300)^m, \qquad (5)$$

where m is around -1. The temperature dependence is significantly different from T^{-1} for CF$_4$ with N$_2$, CO, and Ar. These collision pairs have the smallest absolute cross sections and also the smallest cross sections compared to the gas kinetic cross section (See Table II).

DISCUSSION

Our results for pure CF$_4$, $(T_1/\rho) = (1.948 \pm 0.03)(T/300)^{-1.412 \pm .015}$ ms amagat^{-1} are in good agreement with earlier published results for the pure gas, $(T_1/\rho) = (2.03 \pm 0.08)(T/300)^{-1.58}$,[15] and 2.1 ± 0.05 ms amagat^{-1} at 297 K up to 40 amagat.[16] (One amagat is 2.687×10^{19} molecules cm^{-3}.) At densities considerably greater than our samples, (T_1/ρ) is no longer constant, increasing from 2.0 to 4.4 ms/amagat with increasing density of CF$_4$ in the range 50–405 amagat in pure CF$_4$ at room temperature.[17] Similar observations have been reported in the dense fluid up to four times the critical density in CF$_4$ mixtures in Ar or Ne.[18]

An attempt to extract the octopole moment of CF$_4$ from T_1 using Bloom and Oppenheim theory has been reported.[19] The result depends on the parameters of the assumed spheri-

TABLE II. Relaxation cross sections for the rotational angular momentum vector in CF$_4$ with various collision partners. The observed temperature dependence can be described by either $\sigma_J(T) = \sigma_J(300\ {\rm K})(T/300)^m$ or $\sigma_J(T) = \sigma_J(300\ {\rm K})(300/T)[1 + a_1(T - 300)]$.

Collision partner	$\sigma_J(300\ {\rm K})^{\rm a}$ (Å^2)	m	$a_1 \times 10^2$	r_0(Å)	$\sigma_{\rm geom}$ (Å^2)	$\sigma_J/\sigma_{\rm geom}$$^{\rm c}$
CH$_4$	12.2 ± 0.2	-0.95	NIL	4.196	55.31	0.22
N$_2$	12.7 ± 0.2	-0.77	1.0 ± 0.1	4.103	52.89	0.24
CO	12.8 ± 0.6	-0.74	1.1 ± 0.2	4.0855$^{\rm b}$	52.44	0.24
Ar	19.2 ± 0.7	-0.51	3.2 ± 0.2	3.968	49.46	0.39
HCl	22.0 ± 0.1	-0.88	0.8 ± 0.1	3.959$^{\rm b}$	49.24	0.45
CO$_2$	29.7 ± 0.7	-1.06	NIL	4.167	54.55	0.55
Kr	29.2 ± 0.8	-0.93	NIL	4.094	52.66	0.55
CF$_4$	39.4 ± 0.8	-0.91	1.2 ± 0.2	4.579	65.87	0.60
Xe	34.3 ± 0.7	-0.97	NIL	4.248$^{\rm b}$	56.69	0.61
SF$_6$	58.0 ± 1.2	-0.90	1.3 ± 1.0	4.841	73.62	0.79
Ethane	20.8 ± 0.7	-0.86	0.9 ± 0.3	4.499	63.59	0.33

[a] Quoted error reflects only the standard deviation of (T_1/ρ), not including the uncertainties in the magnitude of the spin–rotation constant for ^{19}F in CF$_4$ molecule.

[b] These r_0 values were calculated from arithmetic mean of like pairs, using 3.339 Å for HCl–HCl. All other values of r_0 are from Table A 3.2 of Ref. 1, based on corresponding states universal curve.

[c] Collision efficiencies at 300 K.

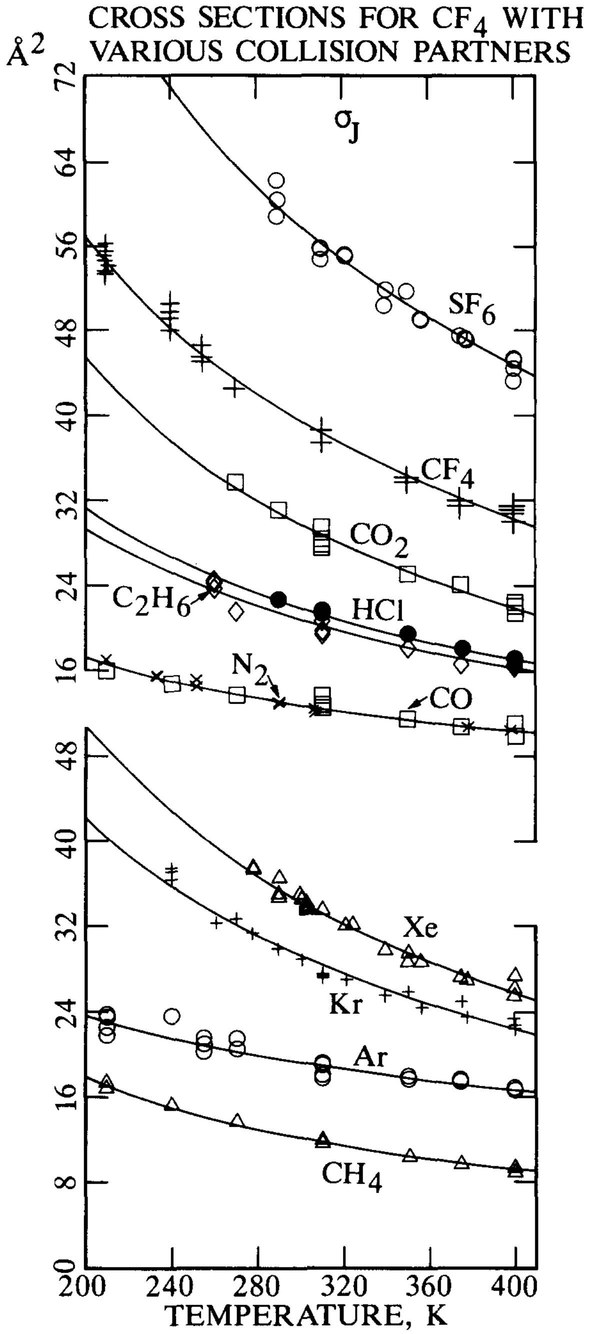

FIG. 3. The temperature dependence of the cross section $\sigma_J(T)$ for CF_4 with various collision partners.

TABLE III. Various cross sections for CF_4 at 300 K.

Experiment	Cross section	Å²	Reference
NMR T_1	σ_J or $\sigma'(0\hat{1})$	39	This work
Shear viscosity	$\sigma(20)$	63	23
Viscomagnetic effect	$\sigma(02\pi)$	60	21,22
Magnetic eff. on thermal conductivity	$\sigma(12q)$	84	20
Thermal transpiration	$\sigma(0001)$	7.1	30
(rotational relaxation)	$\sigma_{\rm rot}(0001)$	23.1	

cal potential, but the value obtained is comparable to the values derived from CIA spectra, i.e., 3.33×10^{-34} esu cm^3 compared to $4.4–4.6\times10^{-37}$ esu cm^3. In their calculation, all of the anisotropy in the potential is taken to be in the attractive part and restricted to the term in the permanent octopole moment which goes as R^{-7}. However, the dispersion term containing the dipole–quadrupole polarizability also goes as R^{-7} and could be much more important for CF_4 than it is for CH_4. It has not been established that spin relaxation in CF_4 is dominated by long range anisotropy due to the octopole moment.

Other experiments provide cross sections which have different sensitivity to the weaker and stronger collisions and thus given complementary information about the anisotropic potential. The notation for these cross sections is defined in Ref. 24. σ_J or $\sigma'(0\hat{1})$ is the cross section describing the decay of the J vector polarization which occurs both by reorientation ($\Delta J = 0, \Delta M_J \neq 0$) and by inelastic ($\Delta J \neq 0$) collisions.[9] On the other hand, $\sigma_{\rm rot}(0001)$, which describes the decay of rotational energy, is affected by inelastic collisions only. Since molecules tend to reorient more readily than they transfer internal energy, $\sigma_J > \sigma_{\rm rot}(0001)$. The large difference between these two values confirm the dominant contribution of molecular reorientation to σ_J in CF_4 in the temperature range 210–400 K. Our cross section for CF_4 at 300 K $\sigma_J = \sigma'(0\hat{1}) = 39$ Å^2 is 0.45 times that of $\sigma(12q) = 84$ Å^2 (at 300 K) for magnetic effects on heat conductivity.[20] This is similar to the finding for CH_4 $[\sigma'(0\hat{1})/\sigma(12q) = 0.32]$ and for N_2 $[\sigma'(0\hat{1})/\sigma(12q) = 0.35]$.[11,12] Other cross sections for CF_4 are: (a) the reorientation cross section for tensorial polarization of the rotational angular momentum $\sigma(02\pi) = 60$ Å^2.[21,22] This is obtained from the viscomagnetic effect and is closely related to the cross sections obtained from quadrupolar NMR relaxation. (b) $\sigma(20) = 63$ Å^2 [23] obtained from viscosity at room temperature. $\sigma(20)$ and $\sigma(12q)$ contain a contribution from the center of mass scattering effect and do not vanish in the case of an isotropic intermolecular potential, whereas $\sigma(02\pi)$ and $\sigma'(0\hat{1})$ arise entirely from the anisotropic part of the potential. While the concept of effective cross sections appears to be very useful in that it allows a comparison of the results obtained from all the phenomena that can be described in terms of the matrix elements of the scattering operator, no exact relations exist between various effective cross sections without going to the sophistication of the intermolecular potential function.[24]

The chemical shift virial coefficient,[25] the second Kerr virial coefficient B_K,[26] and the collision-induced rotational scattering (CIRS)[6,27–29] have been measured in CF_4 as a function of temperature and density. Unfortunately, unlike spin–rotation relaxation, the connections of these quantities with the anisotropic potential function are not simple. In each of these quantities another electronic function of intermolecular separation has to be averaged over the intermolecular potential functions. These are, respectively, the pair shielding function for the first and the pair polarizability functions $\langle\alpha_{ZZ}^2\rangle$ and $\langle\alpha_{XZ}^2\rangle$ for the CIRS and B_K.[7] The experiments yield a convolution of these pair polarizability functions (or pair shielding functions) with the distribution function and it is difficult to separate the two.

CONCLUSIONS

In this paper we reported our experimental results in the form of cross sections $\sigma_J(T)$ for changes in the rotational angular momentum vector of CF_4 in collisions. We are able to report CF_4–X cross sections just as precisely as the CF_4–CF_4 cross sections, for X = Ar, Kr, Xe, N_2, CO, HCl, CO_2, CH_4, CF_4, SF_6, and C_2H_6. We believe that spin–rotation relaxation data can have a unique and important contribution to determination of anisotropic potentials. A precise $\sigma_J(T)$ can be calculated from a known anisotropic potential function by semiclassical or IOS methods and compared directly with experimental values. No other observable has quite the same dependence on the repulsive and attractive anisotropic potentials as $\sigma_J(T)$ does.

Note added in proof: New absolute measurements of the thermal conductivity of CF_4 have been reported [J. Millat, M. Ross, W. A. Wakeham, and M. Zalaf, Physica A **148**, 124 (1988)]. The thermal conductivity has been used with other transport property data to deduce a set of effective cross sections for CF_4 in the range 308–428 K, including $\sigma(1001)$, $\sigma(1010)$, $\sigma(20)$, and $\sigma(10E)$, which are 51.75, 59.91, 61.63, and 46.70 $Å^2$ at 308 K.

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