

Effective collision cross sections for SF₆ from nuclear magnetic relaxation

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The thermal average cross sections for transfer of rotational angular momentum in SF₆ on collision with Ar, Kr, Xe, N₂, CO, HCl, CO₂, CH₄, CF₄, and SF₆ have been determined from pulse measurements of ¹⁹F nuclear spin relaxation times in binary mixtures of gases at 260–400 K.

INTRODUCTION

SF₆ is often used as a heavy “spherical” perturber like Xe in experiments with other molecules, with the expectation that the anisotropy of the SF₆–X potential is mild, and yet SF₆ provides for efficient transfer of vibrational energies over a wide range of frequencies, and rotational energies as well. In the isolated molecule the first nonvanishing electric moment is the hexadecapole and the polarizability tensor is isotropic so the long-range anisotropy of SF₆–X interactions is indeed weak.

Some information on the angle dependence of the SF₆–X intermolecular potential function is available from spectroscopy. Collision-induced absorption provides primarily the long-range anisotropy involving the hexadecapole moment.¹ Depolarized Rayleigh scattering is entirely collision induced in spherical tops. In SF₆, the dipole–quadrupole polarizability A tensor vanishes, as for all centrosymmetric species. The excess of intensity at high frequency assigned to the collision-induced rotational Raman scattering spectrum of SF₆^{2,3} has remained largely unexplained,^{4,5} although following the theory of Buckingham and Tabisz,⁶ a dipole–octopole polarizability $E = 16.7 \pm 4 \text{ \AA}^5$ reproduces well the shape of the experimental profile in the range 40–100 cm⁻¹ if a particular anisotropic pair polarizability function and intermolecular potential are used.² The second Kerr virial coefficient⁷ is dependent on the same pair polarizability.

At short range the anisotropy of the SF₆–X potential is found to be surprisingly large for X = rare gas. The first good intermolecular potentials for SF₆–rare gas interactions have been obtained by Pack *et al.* by simultaneously fitting the total differential cross sections for scattering of Kr, Ar, Ne, and He by SF₆, their viscosities, and virial and diffusion coefficients.^{8,9} Substantial anisotropy is required to fit the observed damping of the rainbow oscillations in the differential cross sections (the damping of the diffraction oscillations for HeSF₆). For KrSF₆, two sets of contradictory virial coefficients led to two potentials each of which fits three properties well. The NMR T_1 data presented here should help to resolve this uncertainty. Nuclear spins are coupled to molecular rotation. Consequently, collisions which change the rotational angular momentum contribute to nuclear spin relaxation. Since ¹⁹F spin relaxation in SF₆ in the gas phase arises entirely from the anisotropy of the SF₆–X potential, relaxation times from NMR experiments provide additional information which can be used to refine such potentials. We

provide cross sections for SF₆ with SF₆, N₂, CO, HCl, CO₂, CF₄, CH₄, and C₂H₆ as collision partners, in addition to Ar, Kr, and Xe. van der Waals C₆ dispersion coefficients have been calculated for SF₆ in these pairs except for HCl, CF₄, CH₄, and C₂H₆.¹⁰

EXPERIMENTAL

¹⁹F nuclear spin relaxation T_1 measurements were made using the inversion recovery method, with a π - τ - $\pi/2$ -pulse sequence at 188 MHz in a Bruker WP-200 4.7 T Fourier transform NMR spectrometer. The sealed samples were pure SF₆ gas at densities 1–30 amagat and mixtures containing 1–3 amagat SF₆ gas and up to 30 amagat of another gas (CH₄, N₂, CO, Ar, HCl, CO₂, Kr, CF₄, and Xe). One amagat is 2.687×10^{19} molecules cm⁻³. The errors in determination of sample densities are the largest errors in these experiments. Gases were frozen out into sample tubes from a calibrated section of the vacuum line. The temperature of the sample was regulated with the standard variable temperature unit which maintains the temperature to $\pm 0.3^\circ$ throughout, and the absolute temperature was determined from the spectrum of a standard sealed sample of methanol or ethylene glycol. The temperature range (260–400 K) for these studies is limited by the condensation of SF₆ at the low end of the range. Data have been obtained with better than 1% standard deviation in the determination of T_1 itself from the slope of the plots of log intensity vs delay time. An example is shown in Fig. 1. Relaxation times range from 0.007 to

TABLE I. Spin relaxation times for ¹⁹F in SF₆ in various buffer gases. The observed temperature dependence is given by $(T_1/\rho)_T = (T_1/\rho)_{300\text{K}} (T/300)^n$.

Buffer	$(T_1/\rho)_{300\text{K}}$ (ms amagat ⁻¹)	n	T range (K)
CH ₄	0.678 ± 0.008	-1.49 ± 0.04	300–400
N ₂	0.647 ± 0.010	-1.57 ± 0.03	260–400
CO	0.700 ± 0.023	-1.57 ± 0.09	260–400
Ar	0.815 ± 0.013	-1.47 ± 0.02	260–400
HCl	0.844 ± 0.008	-1.44 ± 0.03	280–400
CO ₂	1.219 ± 0.020	-1.66 ± 0.06	300–400
Kr	1.051 ± 0.016	-1.62 ± 0.03	260–400
CF ₄	1.514 ± 0.032	-1.71 ± 0.04	260–400
Xe	1.188 ± 0.020	-1.73 ± 0.04	290–400
SF ₆	2.132 ± 0.023	-1.75 ± 0.02	290–400

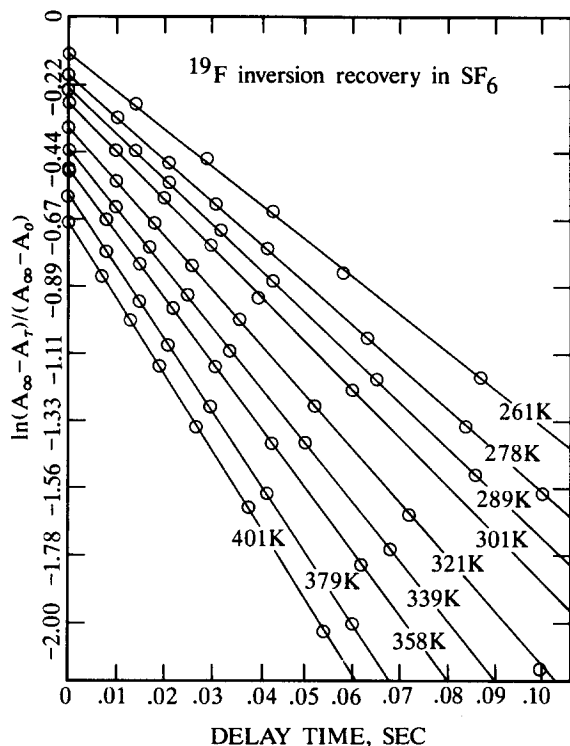


FIG. 1. Typical results of inversion recovery experiments for ¹⁹F spins in SF₆. This example is for SF₆ in CF₄ gas. The ordinates have been displaced from zero for display. The slope of each line is 1/T₁.

0.07 s depending on density, temperature, and buffer gas. Such plots are routinely obtained and examined for possible problems such as systematic curvature due to incorrectly set pulses, partial condensation of the sample, or too long delay times (optimum values are 0–1.5 T₁).¹¹

Relaxation of ¹⁹F in SF₆ in these samples is entirely by the spin rotation mechanism. The spin rotation tensor *C* for ¹⁹F in SF₆ is axially symmetric, $C_{av} = \frac{1}{3}(C_{||} + 2C_{\perp})$ and $\Delta C = C_{||} - C_{\perp}$. In analyzing our data the assumption is made that the correlation times associated with the two types of correlation functions (involving C_{av} and ΔC) are equal, in which case it is possible to write¹²

$$T_1^{-1} = [C_{av}^2 + \frac{4}{45}(\Delta C)^2] 2I_0 kT \{ \tau / [1 + (\omega_I - \omega_J)^2 \tau^2] \}.$$

Here, I_0 is the moment of inertia of the SF₆ molecule, τ is the correlation time, ω_I and ω_J are the Larmor precession frequencies of the nuclear spin and the molecular rotational angular momentum. At room temperature $(\omega_I - \omega_J)^2 \tau^2 = 1$ in SF₆ for $\rho = 0.038$ amagat and $\omega_I/2\pi = 28$ MHz.¹² Our experiments carried out at 188 MHz are in the extreme narrowing limit $(\omega_I - \omega_J)^2 \tau^2 \ll 1$, for all samples at all temperatures (200–400 K).

In pure SF₆ gas the relaxation time is directly proportional to the density. The temperature dependence of T₁ is summarized in the following form:

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

which has been shown to be a satisfactory empirical description. Analysis of the data in gas mixtures requires removal of SF₆–SF₆ contributions according to

$$T_1 = (T_1/\rho)_{\text{SF}_6\text{-SF}_6} \rho_{\text{SF}_6} + (T_1/\rho)_{\text{SF}_6\text{-X}} \rho_{\text{X}}$$

in order to extract $(T_1/\rho)_{\text{SF}_6\text{-X}}$. Below about 280 K our higher density pure SF₆ samples begin to condense. Nevertheless, our temperature dependent studies are for a temperature range of 240–400 K for some buffer gases. Using our pure SF₆ data extrapolated below 280 K leads to relatively small errors since the density of SF₆ in the mixtures is very small.

RESULTS

Our T₁ results may be compared with the earlier work in pure SF₆ gas. Courtney and Armstrong reported $(T_1/\rho) = 2.34 \pm 0.08$ ms amagat^{−1} at 293 K, $n = -1.53$ for $T = 238$ –350 K.¹² Ours is 2.22 ± 0.02 ms amagat^{−1} at the same temperature and we obtain $n = -1.75$ for $T = 290$ –400 K. Their values of (T_1/ρ) at 238, 265, 293, 313, and 350 K are included in our Fig. 2 for comparison. It appears that their data are consistent with ours and that the overall fit to $n = -1.75$ is not worse when their data are included. Our measurements are carried out in the density regime in which (T_1/ρ) is a constant at a given temperature. ¹⁹F relaxation times in SF₆ have also been reported at much higher densities up to 2.6 ρ_c, i.e., 140–292 amagat, 253–473 K.¹³ (T_1/ρ) is not a constant in such high density samples, changing from 2.5 to 3.67 ms amagat^{−1} at 296 K in going from 205 to 292 amagat, whereas our values are all 2.2 ms amagat^{−1} at the same temperature.

The temperature dependence of T₁ in various SF₆–X collision pairs are shown in Fig. 3 and Table I. These are the first measurements of T₁ for SF₆ in gas mixtures. Earlier inferences of T₁ from linewidths give incorrect T₁ values due to instrumental line broadening.¹⁴

The spin relaxation in SF₆ at these densities and magnet-

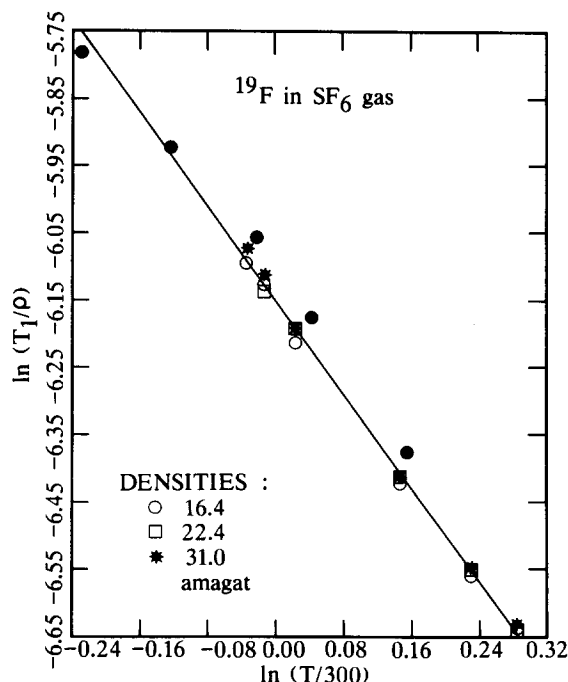


FIG. 2. The temperature dependence of T₁ in pure SF₆ gas. The data of Courtney and Armstrong (Ref. 12) are shown (●).

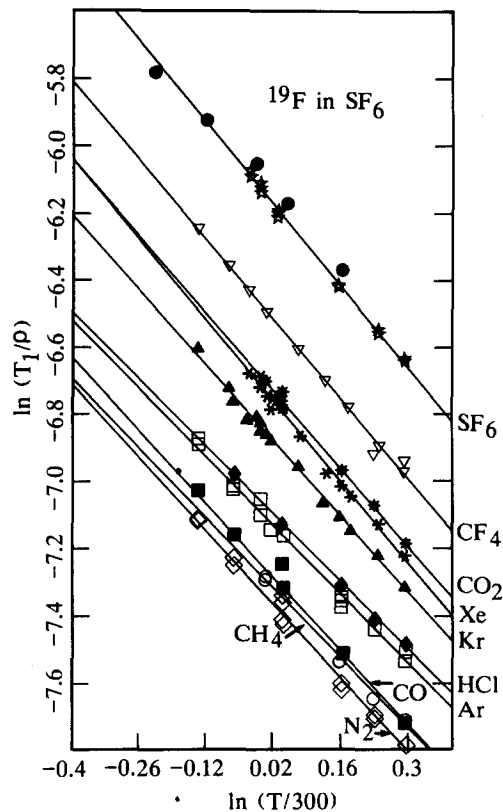


FIG. 3. The temperature dependence of (T_1/ρ) for SF₆ in various buffer gases.

ic fields is so dominated by the spin rotation (SR) mechanism that the observed T_1 can be directly related to a single cross section. Shielding anisotropy and intramolecular dipole-dipole relaxation rates are 7×10^{-3} and 6×10^{-4} times as small as SR relaxation rates. Trace amounts of oxygen do not pose a problem, as shown by the results of a separate study of SF₆ in O₂ as a buffer gas.¹⁵

Whereas molecular beam experiments have yielded up C_{av} for ¹⁹F in SF₆, these were unable to provide ΔC . We use $C_{av} = -4.98 \pm 0.16$ kHz and $\Delta C = 4.21 \pm 0.35$ kHz from NMR shielding tensor analysis.¹⁶ Earlier MBMR spectra gave $C_{av} = 4.7 \pm 0.3$ kHz¹⁷ and 5.27 ± 0.40 kHz¹⁸ which are in good agreement with solid state NMR but with larger error estimates. The effective spin rotation constant is not very sensitive to errors in ΔC in any case, $C_{eff}^2 = C_{av}^2 + \frac{4}{45}(\Delta C)^2$. For SF₆ we use a rotational constant $B_0 = \hbar^2/2I_0$ calculated from the bond length $r_0 = 1.561 \pm 0.002$ Å.¹⁹ Using the impact approximation the correlation time τ can be written in terms of a cross section σ_J for angular momentum transfer²⁰:

$$\tau = (\rho \bar{v} \sigma_J)^{-1},$$

where \bar{v} is the mean relative velocity of the molecules, so that the cross section can be obtained from each T_1 measurement as follows:

$$\sigma_J = (T_1/\rho) \cdot \frac{1}{\bar{v}} \cdot C_{eff}^2 \cdot \frac{kT}{B_0}.$$

The temperature dependence of σ_J is shown in Fig. 4 and

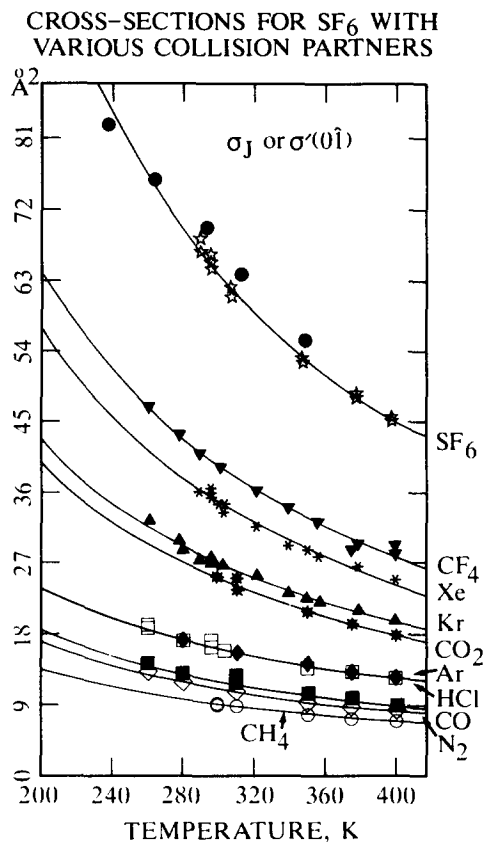


FIG. 4. The relaxation cross section $\sigma_J(T)$ for the rotational angular momentum vector of SF₆ molecule in collision with various molecules. The data of Courtney and Armstrong (Ref. 12) for pure SF₆ have been included (●) and are seen to be consistent with our results.

summarized in Table II for various collision pairs involving SF₆. The expected temperature dependence of σ_J is T^{-1} so the plots in Fig. 5 of $(T/300)\sigma_J(T)$ illustrate any deviation from the expected behavior as systematic deviations from horizontal lines. The data of Courtney and Armstrong for pure SF₆ have been included in Figs. 4 and 5 for comparison, using our value of $C_{eff}^2 = 26.376$ kHz² rather than theirs. The data are consistent with ours.

TABLE II. Relaxation cross sections for the rotational angular momentum vector in SF₆ with various collision partners. The observed temperature dependence is given as either $\sigma_J(T) = \sigma_J(300 \text{ K})(T/300)^m$ or $\sigma_J(T) = \sigma_J(300 \text{ K})(300/T)[1 + a_1(T - 300)]$.

Collision partner	$\sigma_J(300 \text{ K})$ (Å ²)	m	$a_1 \times 10^2$ (deg ⁻¹)
CH ₄	9.1 ± 0.3	-0.99	Nil
N ₂	11.0 ± 0.2	-1.07	Nil
CO	12.0 ± 0.4	-1.07	Nil
Ar	16.1 ± 0.3	-0.97	Nil
HCl	16.1 ± 0.1	-0.95	Nil
CO ₂	25.0 ± 0.4	-1.17	-1.2 ± 0.4
Kr	27.0 ± 0.4	-1.12	-1.0 ± 0.3
CF ₄	39.6 ± 0.8	-1.21	-2.4 ± 0.5
Xe	34.8 ± 0.6	-1.23	-2.3 ± 0.5
SF ₆	64.1 ± 0.7	-1.25	-4.5 ± 0.4

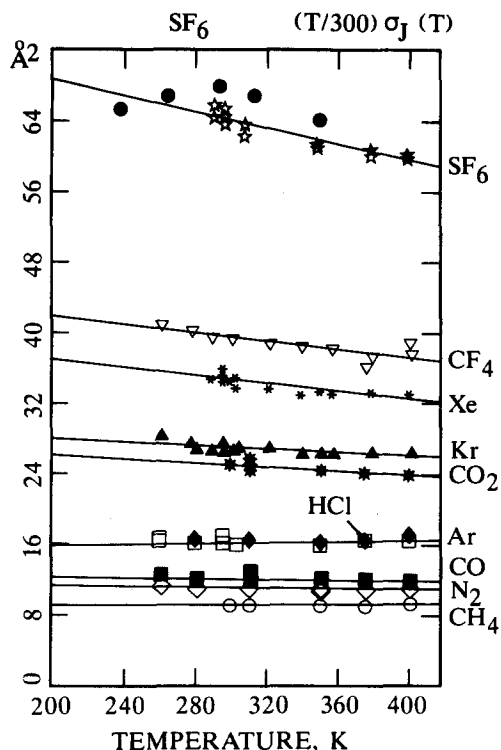


FIG. 5. $(T/300)\sigma_J(T)$ shows the temperature dependence of $\int_0^\infty \langle \Delta J^2 \rangle 2\pi b db$.

DISCUSSION

The end result of our measurements are the cross sections σ_J which contain information about the angle-dependent parts of the intermolecular potential. At a given temperature, σ_J represents a weighted average which in semiclassical terms can be described as²¹

$$\sigma_J = [\mathbf{d} \cdot (\boldsymbol{\sigma})^{-1} \cdot \mathbf{P} \cdot \mathbf{d}]^{-1}.$$

The weighting factors are determined by the populations of the rotational states in \mathbf{P} and the initial rotational quantum numbers J_i (before collision) in \mathbf{d} whose elements d_i are given by

$$d_i = [J_i(J_i + 1) / \langle J(J + 1) \rangle]^{1/2}.$$

TABLE III. Geometric cross sections and collision efficiencies at 300 K for SF₆ with various collision partners.

	$r_0(\text{\AA})$	$\sigma_{\text{geom}}(\text{\AA}^2)$	$\sigma_J(\text{\AA}^2)$	$\sigma_J/\sigma_{\text{geom}}$
CH ₄	4.561	65.35	9.1	0.14
N ₂	4.3436	59.27	11.0	0.19
CO	4.422*	61.43	12.0	0.19
Ar	4.251	56.77	16.1	0.28
HCl	4.2955*	57.97	16.1	0.28
CO ₂	4.426	61.54	25.0	0.41
Kr	4.390	60.54	27.0	0.45
CF ₄	4.841	73.67	39.6	0.54
Xe	4.584*	66.02	34.8	0.53
SF ₆	5.252	86.66	64.1	0.74

* This r_0 calculated from arithmetic mean of like pairs, using 3.339 Å for HCl-HCl (Ref. 33). All other values are directly from Maitland Table A3.2 based on the corresponding states universal curve (Ref. 34).

$\langle J(J + 1) \rangle$ is the equilibrium thermal average square of the rotational angular momentum. $\boldsymbol{\sigma}$ is the scattering matrix for the J vector, with elements

$$\sigma_{fi} = \frac{1}{v} \int_0^\infty 2\pi b db \langle v(\delta_{fi} - \mathcal{P}_{fi} \cos \alpha) \rangle$$

involving \mathcal{P}_{fi} , the probability that a collision changes the energy from the quantum level i to f , α the angle between \mathbf{J}_i and \mathbf{J}_f . These collision-induced transitions arise only from the angle-dependent terms in the intermolecular potential energy. In the classical limit,²⁰

$$\sigma_J = \frac{1}{2\langle J^2 \rangle} \int_0^\infty 2\pi b db \langle [\mathbf{J}(1) - \mathbf{J}(0)]^2 \rangle,$$

where $\mathbf{J}(0)$ and $\mathbf{J}(1)$ are the rotational angular momentum vectors before and after a collision, the average $\langle \rangle$ being over the distribution of internal molecular states before the collisions.

The cross sections in Table III are small. Except for SF₆-SF₆ the cross sections for changes in the rotational angular momentum vector in SF₆ at 300 K are two to seven times smaller than the geometric cross sections; i.e., only one in every two to seven "hard sphere collisions" at 300 K result in reorientation of the SF₆ molecule or in rotational energy transfer.

Several other cross sections for SF₆ can be obtained. That which can be calculated from the shear viscosity coefficient η is $\sigma(20) = 92 \pm 1 \text{ \AA}^2$.²² Furthermore, Senftleben-Beenakker effects (magnetic field effects on transport properties) have been measured for SF₆. The magnetic field effect on the viscosity (decrease) is well described by an excellent fit to experiment by the field/pressure dependence (B/p) associated with $\mathbf{J}\mathbf{J}$ reorientation.²² The cross section $\sigma(02\pi)$ (as defined by Ref. 23) can be obtained from that value of (B/p) for which the viscomagnetic effect reaches half its saturation value ($25.5 \pm 1 \text{ kOe/Torr}$).²² Using the molecular g value for SF₆ from the MBMR experiment of Ozier *et al.*¹⁸ we obtain $\sigma(02\pi) = 96 \text{ \AA}^2$. This cross section is related to the cross section $\sigma(0\hat{2})$ which is obtained from depolarized Rayleigh line broadening²³ or the cross section $\sigma'(0\hat{2})$ from quadrupolar relaxation in NMR (if ¹⁹F had been a quadrupolar nucleus). The thermal conductivity of SF₆ gas in a magnetic field has also been measured. From the reported $(B/p)_{1/2}^{\lambda} = 42.5 \text{ kOe/Torr}$ at 300 K,²⁴ we calculate the cross section $\sigma(12q) = 126 \text{ \AA}^2$. A cross section for collision-induced relaxation from individual rotational levels in SF₆ was derived from the measured rate constants obtained by infrared double resonance laser spectroscopy, $\sigma_{\text{rot}} \sim 170 \text{ \AA}^2$.²⁵

These cross sections (summarized in Table IV) are considerably larger than our σ_J [or $\sigma'(0\hat{1})$ in standard notation, as in Ref. 26] shown in Table II. In particular, $\sigma_J = 64 \text{ \AA}^2$ is drastically different from the cross section 170 \AA^2 obtained by IRDR in vibrationally excited SF₆. The theoretical interpretation of the latter²⁷ is related to that of pressure-broadening cross sections, which are typically much larger than NMR relaxation cross sections. For example, the total inelasticity cross section for the $J = 11$ state of CO (obtained by IRDR) is 63 \AA^2 ,²⁸ which is nearly a factor of 3 larger than $\sigma_J = 22 \text{ \AA}^2$ at 300 K from NMR relaxation.²⁹ A small part of

TABLE IV. Various cross sections for SF₆ at 300 K.

Expt.	Cross section	Å ²	Reference
NMR T ₁	σ _J or σ'(01̂)	64	This work
Viscosity	σ(20)	92	22
Viscomagnetic effect	σ(02π)	96	See the text ^a
Magnetic effect	σ(12q)	126	See the text ^b
on thermal conductivity			
IR double resonance	σ _{rot}	170	25

^a Calculated from the measured magnetic field/pressure coefficient at half saturation at 300 K using (Ref. 23) $\sigma(02\pi) = 2g(\mu_N kT/\hbar\omega)(B/p)_{1/2}$, where $(B/p)_{1/2} = 25.5 \pm 1$ kOe/Torr (Ref. 22) and $g = g_J = -0.03732(5)$ (Ref. 18).

^b Calculated from the magnetic field/pressure coefficient at 300 K using (Ref. 24) $\sigma(12q) = (g\mu_N kT/0.6248\hbar\omega)(B/p)_{1/2}^2$, where $(B/p)_{1/2}^2 = 42.5$ kOe/Torr.

the difference between cross sections obtained from NMR relaxation measurements and pressure-broadening cross sections is that only the self-contributions are included in nuclear magnetic relaxation. The "self" part corresponds to the result obtained for monatomic collision partners, the "non-self" part contains the effects of collisional changes in the internal states of the collision partner and corresponds to an exchange of tensor polarization between the molecule of interest and its collision partner.³⁰ It is assumed that there is no exchange of nuclear spin polarization between collision partners in our experiments. The rest of the difference, then, must arise from the different averages contained in σ_J and the other cross sections on the intermolecular potential surface.³¹

CONCLUSIONS

The cross sections obtained in these experiments σ_J are associated with changes in the rotational angular momentum vector which include molecular reorientation (M_J changes) as well as rotational inelasticity (J changes). The rotational constant of SF₆ is very small, hence the rotational energy levels are very close together even for large J , so that these NMR relaxation cross sections and those from the Senftleben-Beenakker effects can be treated by classical scattering theory^{20,32} or by semiclassical calculations³¹ on a given interaction potential surface. The quantum approach at the infinite order sudden (IOS) level of approximation has been formulated for A–XY₆ scattering by Pack⁸ and has been shown to be particularly suitable to do the scattering dynamics in SF₆–X interactions. The IOS approximation is most accurate when the internal energy level spacing is small compared to the kinetic energy of the collision.

Of the data which have been used to determine the anisotropic SF₆–rare gas potentials, the differential scattering cross sections are mostly sensitive to the attractive well (except for HeSF₆), viscosity and diffusion coefficients are mostly sensitive to the repulsive wall, and the second pres-

sure virial coefficient has some sensitivity to both. Our cross sections for changes in the rotational angular momentum vector are expected to be sensitive to the anisotropy in both the attractive and repulsive parts and so provide useful information which is different from and complementary to that of other observables.

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