

PRESSURE BROADENING OF THE GROUND VIBRATIONAL STATE $J = 31 \rightarrow J = 32$ TRANSITION OF CH_3F BY COINCIDENCE LASER SPECTROSCOPY

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Abstract—We have studied self-broadening and foreign gas broadening of the ground state $J = 31 \rightarrow J = 32$ transition of CH_3F using a coincidence with the $184.3 \mu\text{m}$ emission from an optically pumped CH_2F_2 laser. Experiments have been carried out with polar and non-polar species as well as the noble gases.

This transition is in the region where the classical rotation period is of the same order as the duration of a collision. The measurements indicate an anomalously low value of 7.0 MHz/Torr for the self-broadening coefficient of CH_3F and an unusually large value for the CH_3OH broadening coefficient. The latter is believed to be due to the presence of a low energy OH torsional model in CH_3OH .

1. INTRODUCTION

The study of gaseous spectral lineshapes and linewidths has been an active area of research for several decades. Theoretical and experimental investigations have spanned the various regions of molecular interactions as well as photon energies from the microwave to the ultraviolet.

To date, most of the experimental work on molecular linewidths for pure rotational transitions has utilized high resolution microwave spectroscopic techniques.⁽¹⁾ The microwave region offers tunable sources but is unfortunately restricted to lower frequencies. This constraint has led to the study of primarily low angular momentum states. Most recently, elegant frequency mixing techniques using an optically pumped far-infrared laser and microwave sources, as well as CO_2 laser lines, have extended the upper limit on the angular momentum states accessible.⁽²⁾ In addition, the accidental coincidence between molecular laser lines (CO_2 , N_2O) has led to pure rotational lasing in excited vibrational states and accurate rotational spectroscopic parameters. Unfortunately, these experiments cannot yield pressure broadening information since these pure rotational lasers rarely operate beyond a few hundred millitorr of pressure. These systems, however, have been used to observe Doppler regime linewidth effects such as Dicke narrowing.^(3,4)

In this paper we report on linewidth measurements which were performed using a spectroscopic coincidence between an optically pumped CH_2F_2 laser and CH_3F . Similar measurements have been performed by Duxbury and collaborators by exploiting the near coincidence of the $337 \mu\text{m}$ line of the HCN laser with the $6_{15} \rightarrow 6_{24}$ pure rotational line of D_2O .^(5,6) The $184.3 \mu\text{m}$ line of the CH_2F_2 laser is near resonant with the ground vibrational state $(31, K) \rightarrow (32, K)$ manifold. The motivation for these measurements is that for such a high angular momentum state, the classical rotation period, $\tau_R = 1/2BJ$ is of the same order as the duration of a collision $\tau_c = \langle R \rangle / \langle V \rangle$, where B is the rotational constant, $\langle R \rangle$ is the collision distance, and $\langle V \rangle$ is the collision velocity. This regime of line broadening is difficult to treat theoretically since neither phase shift nor diabatic collision theories are completely appropriate.

2. EXPERIMENTAL DESCRIPTION

The absorption experiments were carried out using an optically pumped CH_2F_2 FIR laser. The CH_2F_2 laser excitation source was an actively frequency-stabilized CO_2 laser operating on its 9R32 line which vibrationally excites the ν_3 mode of CH_2F_2 on the $(18_{17,2})$ to $(18_{17,1})$ transition.

The FIR cavity consists of an 81 cm long, 2.54 cm in diameter quartz tube with plane reflectors at each end. A central coupling hole of 1.5 mm in diameter in one mirror allows the CO_2 pump

beam to be injected using a 30.0 cm focal length lens. The output coupler is a gold coated plane mirror having an 8.0 mm diameter hole. The output of the quartz waveguide laser is linearly polarized and was found to be in a ratio of 130 to 1 for the two orthogonal polarization orientations. For some of the experiments, a metal waveguide with identical dimensions was used, but because the polarization of the metal waveguide laser is very poor (measured to be 2/1 for parallel vs perpendicular polarizations), a polarizing grid was used to insure linearly polarized light.

The FIR laser emission wavelength which results is $184.3\ \mu\text{m}$. The frequency of this transition has been measured using heterodyne techniques by Peterson *et al.*⁽⁷⁾ and is given as $1626602.6\ \text{MHz} \pm 0.80\ \text{MHz}$. With 10 W of injected pump power, the FIR laser was typically able to produce 15.0 mW of output power. Using measurements of nearby ground state rotational transitions of CH_2F_2 ,⁽⁸⁾ one can calculate the linewidth of the lasing transition based on a pressure broadening coefficient of $\approx 22\ \text{MHz/Torr}$. At the typically low operating pressures of this laser (150 mT), we find the homogeneous linewidth to be $\approx 3.3\ \text{MHz}$. The Doppler width of the transition is 3.0 MHz, resulting in a total oscillation bandwidth of the order of 4.3 MHz.

The absorption cell was 52.0 cm in length and consisted of two quartz windows 50.8 mm in diameter for injection and extraction of the FIR radiation. Pressure was measured using a capacitance pressure gauge and temperature was measured using a bayonet thermocouple. Finally, the FIR radiation was measured using a pyroelectric radiometer whose sensitivity extended down to nW of power. For the temperature data, a second radiometer head was included whose function was to measure a part of the FIR beam which was split off before entering the cell to properly normalize any laser fluctuations over the course of the experiments. This technique improved our long-term stability and increased the sensitivity. The apparatus used for our absorption measurements is shown in Fig. 1.

3. EXPERIMENTAL RESULTS

The raw experimental data obtained was in the form of a transmittance as a function of pressure or temperature and was converted to absolute absorption coefficient (m^{-1}). The buffer gas experiments were all performed with an initial charge of 3 Torr of CH_3F at 298 K. The absorption coefficient vs temperature measurements were performed with the same initial charge but only

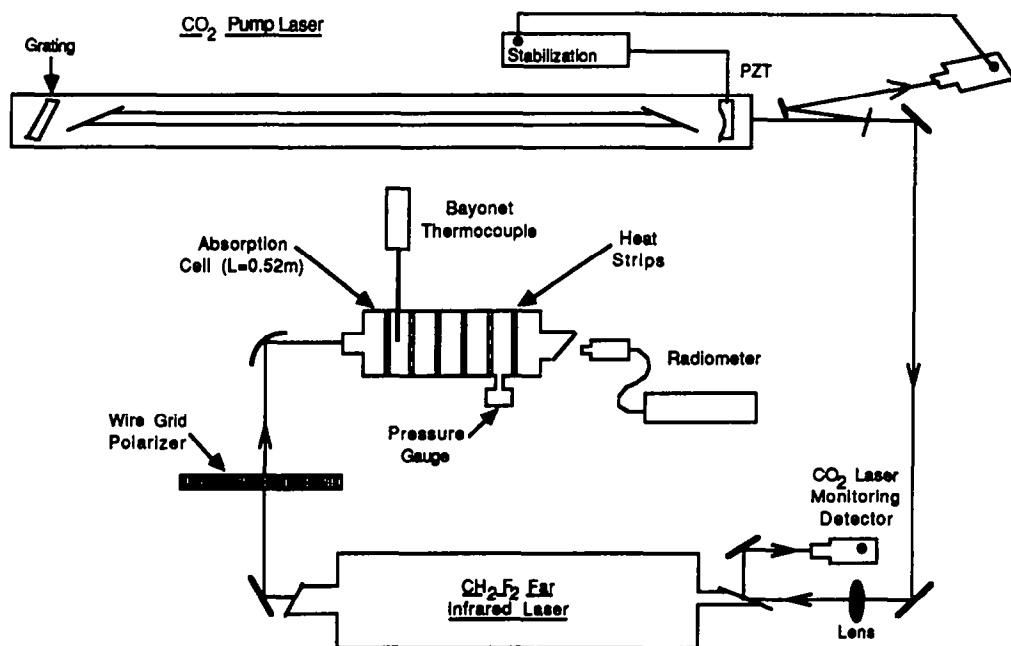


Fig. 1. Experimental setup.

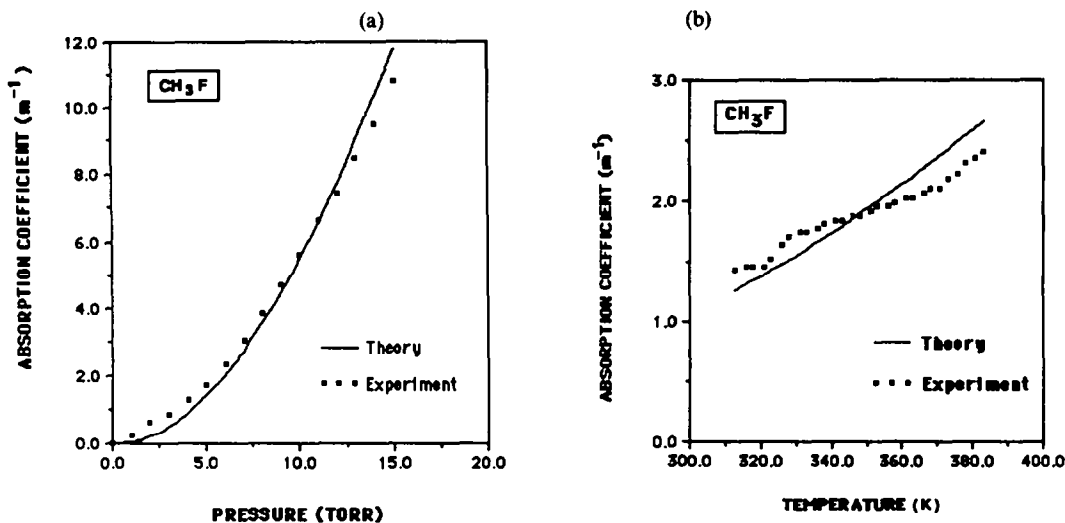


Fig. 2(a). Absorption coefficient vs pressure for CH₃F self-pressure broadening at a temperature of 298 K. (b) Absorption coefficient vs temperature for CH₃F self-pressure broadening. Measurements were performed with an initial charge of 3 torr of CH₃F, but only the portion of the data which exhibited an ideal gas law behavior was used in the experiments.

the portion of the data which exhibited an ideal gas law behavior was used in the experiments. This procedure was used in order to exclude wall desorption effects.

The first data runs obtained were for pure CH₃F and are shown in Fig. 2(a). This particular case is of paramount importance as the broadening and pressure shift parameters obtained are utilized to determine values for the buffer gas experiments. The data from experiments on the absorption coefficient as a function of temperature for pure CH₃F are shown in Fig. 2(b).

Buffer gas experiments were performed with a variety of molecules representative of the various interaction potential classes, as well as C¹³H₃F, in order to test for rotational resonance effects. We examined noble gases, linear polar and nonpolar molecules, spherical tops, symmetric tops, and asymmetric tops.

Figures 3(a)–(d) serve to illustrate the data and theoretical curve fits for the noble gases (He), linear molecules (CS₂), symmetric tops (NH₃), and spherical rotor (SF₆). These figures also show that the data can be reasonably fit by the theoretical expressions using only the linewidth and pressure shift parameters as variables. Table 1 summarizes the results of our data analysis for all the molecules we studied. The theoretical expression used and its limitations are discussed in the section that follows.

4. DATA ANALYSIS

The absorption coefficients as a function of pressure and temperature were fitted to an absolute absorption coefficient for a symmetric top interacting with linearly polarized light. The spectroscopy of C¹²H₃F performed by Winton and Gordy⁽⁹⁾ and the heterodyne frequency measurements of the 184.6 μm line of the CH₂F₂ laser were used to determine the coincidence with the 31, K → 32, K transitions. The values from these works show that the laser line is 150 ± 26 MHz from the 31, 0 → 32, 0 absorption line. From the rotational Hamiltonian for a symmetric top given by Townes and Schawlow and the rotational constants, we are able to determine the offset between the laser line and the other remaining 31 ΔK = 0 transitions.

Using the detunings for each ΔK = 0 transition and the appropriate fractional occupations, we are able to formulate an expression for the absorption coefficient with only the pressure broadening and shift as free parameters. Previous work on a variety of symmetric tops has revealed that the linewidth and shift may depend on the K quantum number.^(10,11) This is particularly true for resonance line broadening. Unfortunately, we are not able to observe such a variation with a fixed frequency FIR laser source. However, the results using isotope broadening results show that resonance effects do not play a significant role at these high angular momentum states and that

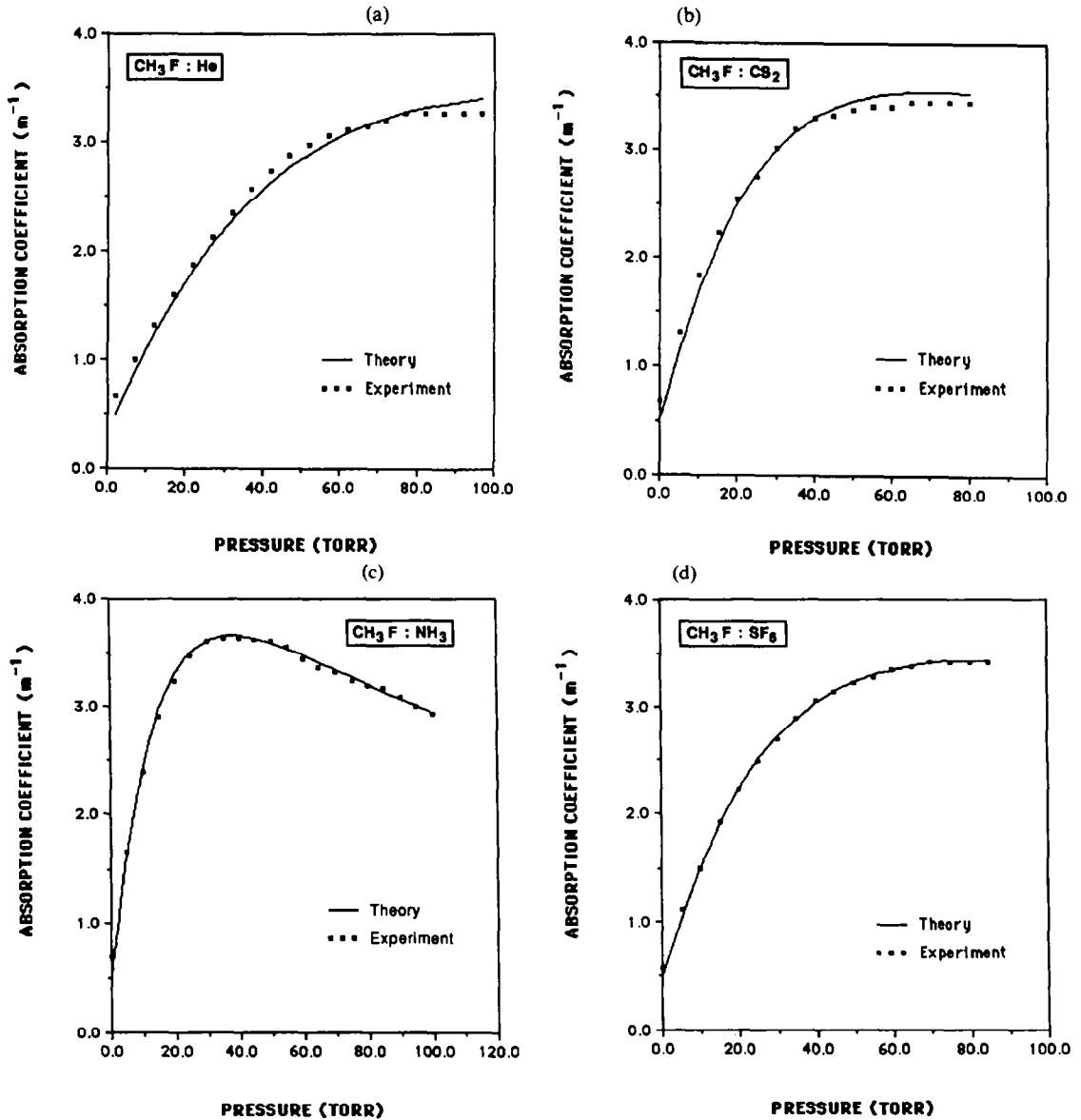


Fig. 3. (a)–(d) Absorption coefficient vs pressure for $[\text{CH}_3\text{F} : \text{A}]$ where A denotes He, CS_2 , NH_3 and SF_6 , respectively. The measurements were taken with an initial charge of 3.0 torr of CH_3F at 298 K. The $\text{CH}_3\text{F}:\text{NH}_3$ curve is noteworthy in that it shows the effect of the pressure shift. We find the transition is initially shifted into resonance, and then shifted out of resonance beyond a NH_3 pressure of 40.0 torr.

the pressure broadening is likely to be approximately constant for different K states. Based on this reasoning, we have formulated the expression for curve fitting the data using a K independent pressure broadening and line shift. The resulting expression for the absorption coefficient as a function of pressure is given by:

$$\gamma(\nu) = \frac{\beta P^2}{c} \left[\frac{[(J+1)^2]}{\left\{ 4 \left[\frac{(\delta - acP)^2}{c^2} \right] + P^2 \right\}} \right] + 2U_2\beta, \quad (1)$$

with

$$U_2 = \sum_{K=1}^{31} \frac{[(J+1)^2 - K^2] \exp(-6.1 K^2/T)}{4/c^2(\delta - acP + 28.4 K)^2 + P^2}, \quad (2)$$

$$\beta = \frac{4N_0\pi\nu\mu_0^2}{3c_0Ch(J+1)T^{3/2}} \left(\frac{S(I, K)}{4I^2 + 4I + 1} \right) \left(\frac{B^2Ah^3}{\pi(kT)^3} \right)^{1/2} \left[\exp\left\{ \frac{-BJ(J+1)h}{kT} \right\} - \exp\left\{ \frac{-BJ(J-1)h}{kT} \right\} \right], \quad (3)$$

Table 1. Line broadening collision number and pressure shift parameter for each of the buffer gases used

Gas	$\Delta\nu/P$ (MHz/Torr)	ν_c (MHz/Torr)	Z_c	a
He	3.5	13.12	0.27	+0.20
Ne	2.5	7.52	0.33	+0.20
Ar	2.25	7.47	0.30	+0.40
Kr	3.3	6.82	0.48	+0.23
Xe	3.8	7.19	0.53	+0.22
CH ₄	5.5	9.04	0.61	+0.18
SF ₆ *	5.0	10.15	0.49	+0.20
N ₂	5.5	8.82	0.62	+0.22
CO ₂	6.0	8.49	0.71	+0.27
CS ₂	6.0	8.58	0.70	+0.18
I ₂	6.5	8.65	0.75	+0.00
CH ₃ F	7.0	8.43	0.83	0.00
C ¹³ H ₃ F	7.0	8.31	0.84	0.00
NH ₃	11.0	7.70	1.42	+0.16
NH ₃ *	11.0	6.52	1.69	+0.16
CH ₃ OH	20.0	5.74	1.72	+0.15
CH ₃ OH*	20.0	4.03	2.45	+0.15
CH ₃ Br	7.5	7.86	0.95	+0.22
CH ₃ I	8.0	7.97	0.99	+0.20

All collision diameters were taken from viscosity data except where noted by * in which case the collision diameter was taken from virial coefficient data.

N_0 is 3.16×10^{16} molecules/cm³ at 1 torr of pressure, C is the speed of light, μ_0 is the dipole moment of CH₃F in $v = 0$ (1.8 D), A and B are the rotational constants, J is the upper state quantum number (32), ν is the transition frequency, P is the pressure in torr, and T is the temperature. In addition, h is Planck's constant, k is the Boltzmann constant, δ is detuning of the laser emission line from line center of the 31, 0 → 32, 0 absorption line, I is the nuclear spin, and $S(I, K)$ is a statistical weighting factor which is a function of the molecules nuclear spin (I) and the K quantum number. The quantity $S(I, K)/4I^2 + 4I + 1$ was taken to be 2 for a symmetric-top molecule.⁽¹⁾ The transition frequency ν , is given by:

$$\nu = 2(J + 1)(B - D_{JK}K^2) - 4D_J(J + 1)^3, \quad (4)$$

and the following parameters were utilized: $B = 25536.1466 \pm 0.0015$ MHz⁽⁹⁾; $A = 154 \times 10^3$ MHz⁽¹⁾; $D_J = 0.05987 \pm 0.002$ MHz⁽⁹⁾; $D_{JK} = 0.44027 \pm 0.0004$ MHz⁽¹⁾; $\mu_0 = 6.3 \times 10^{-30}$ C-M⁽¹⁾. Expressions (1)–(3) have only the pressure broadening coefficient (c in MHz/torr) and the pressure shift parameter (a) as adjustable parameters. This expression was utilized to fit all the gases, and the results are summarized in Table 1. The quantity Z_c is the ratio of the measured linewidth to the gas kinetic collision frequency at one torr and $T = 297$ K.

5. DISCUSSION

We have measured the self-broadening coefficient of the ground state $J = 31 \rightarrow J = 32$ transition of CH₃F and found an anomalously low value of 7.0 MHz/Torr. In addition, we have examined the foreign gas broadening coefficients of noble gases, linear molecules, symmetric tops, and spherical rotors. Using the expressions in Section 4 [Equations (1)–(3)], we fitted our experimental results to theory, and we were able to back out values for the foreign gas broadening coefficients shown in Table 1. From these measured values, we calculated a collision number $Z_c = \Delta\nu/\nu_c$ and have expressed this value versus mass number in Fig. 4.

It is worth noting a number of the interesting features in Fig. 4 and the possible energy transfer mechanisms associated with these features. First, the solid line shown through points a through e indicates a linear relationship between collision number and mass number for the inert gases. In an attempt to explain this behavior, we have employed Widom's⁽¹²⁾ classical rough sphere model for rotational relaxation of a spherical top molecule in collision with an inert gas molecule. The collision number for such an interaction is given by:

$$Z_R = \frac{3}{8}(1 + b)^2/b,$$

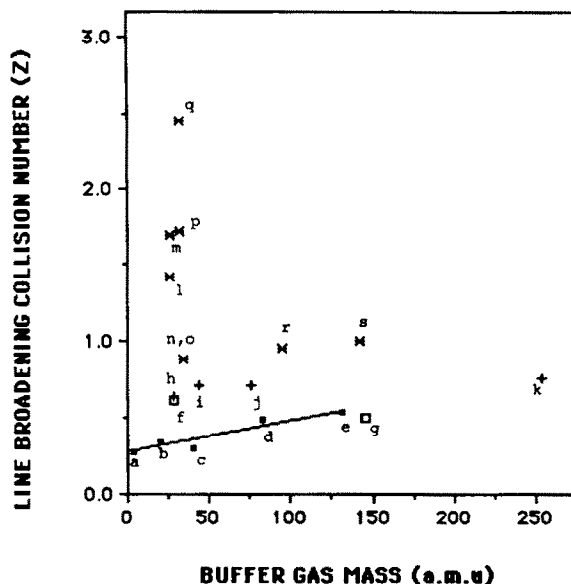


Fig. 4. Line broadening collision number (Z) vs buffer gas mass. a, He; b, Ne; c, Ar; d, Kr; e, Xe; f, CH_4 ; *g, SF_6 ; h, N_2 ; i, CO_2 ; j, CS_2 ; k, I_2 ; l, NH_3 ; *m, NH_3 ; n, CH_3F ; o, $\text{C}^{13}\text{H}_3\text{F}$; *p, CH_3OH ; q, CH_3OH ; r, CH_3Br ; s, CH_3I . All collision diameters were taken from viscosity data except where noted by *, in which case the collision diameter was taken from virial coefficient data.

where $b = I/\mu a^2$, I being the moment of inertia, μ the reduced mass of the collision, and a the molecular diameter. Using an averaged moment of inertia for CH_3F , one finds an approximately linear relationship for Z_R vs mass number, where the magnitude of the result is higher than our experimentally measured values, but the slope of the curve gives a good fit to the data.

We have also found that the measured line broadening collision numbers for the two spherical top buffer gases (CH_4 and SF_6) were comparable to those found for the noble gases. These low values would indicate that SF_6 and CH_4 behave like hard spheres during a collision with CH_3F , and that none of the molecules low vibrational modes are contributing to the interaction.

Finally, one notes the anomalously high collision number measured for CH_3OH , which is insensitive to either of the gas kinetic collision diameters used. Sather and Dahler⁽¹³⁾ have derived an expression for the relaxation of smooth, solid, prolate spherocylinders in self-collision, and find that the efficiency of the energy transfer depends mainly on a parameter given by:

$$\alpha = mL^2/8(I_a I_b I_c)^{1/2},$$

where m is the mass of the molecule, L the length of the cylinder, and I_a , I_b , I_c the three moments of inertia. In an attempt to understand our anomalous result, we have calculated the efficiency of CH_3F in self-collision and of CH_3OH in self-collision where the cylinder is assumed to be along the C-F bond and the C-O bond, respectively. The calculations show in fact that the CH_3OH energy transfer efficiency is lower by a factor of 2 than that of CH_3F . Based on this result, it seems plausible that the high efficiency can be attributed to a low energy torsional mode of CH_3OH interacting with the highly excited CH_3F . A more complete theory will be required to fully explain this interaction.

Future work will involve shifting the frequency of our FIR laser by optically inducing a moving refractive index grating in an Si wafer.⁽¹⁴⁾ This technique has been applied to the beam of a $119\ \mu\text{m}$ CH_3OH FIR laser, where frequency shifts of up to 80 MHz were observed. Using this technique, we plan to examine the low pressure K structure of the $J = 31 \rightarrow J = 32$ transition and possibly to determine more accurately the rotational constants associated with this rotational state.

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