State resolved rotational relaxation of CS$_2$ in argon free jet

Shilin Liu, Qing Zhang, Congxiang Chen, Zhiping Zhang, Jinghua Dai, and Xingxiao Ma

Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Rotational relaxation of CS$_2$ in argon free jet was studied using laser-induced fluorescence (LIF). The rotational populations were obtained from LIF detection at 19 different points along the jet axis from 3 to 15 nozzle diameters. On the basis of the energy gap power law, the master equation was solved to fit the experiment results, and the two temperature-independent parameters in the law were determined. The results show that the state-to-state relaxation cross sections vary as the inverse 1.7 power of the energy gap between the initial and the final states. The expressions for the state-to-state relaxation cross sections and the rate constants were written. The relaxation cross sections decrease with increasing temperature over the range of 2–60 K for the CS$_2$+Ar collision. © *1995 American Institute of Physics.*

I. INTRODUCTION

Supersonic jet expansions of gases are the established sources for high intensity molecular beams and, therefore, have attracted extensive experimental and theoretical interests.[1] Moreover, the free jet itself represents an interesting problem that has been subjected to continuous studies by people interested in aerodynamics and its applications.[2]

The study of the rotational relaxation of a polyatomic molecule in the free jet is of interest for two reasons. First, one would like, given the source conditions, to be able to predict the population of individual rotational level once the expansion is terminated. Second, there is a hope that a better understanding of both jets and the mechanism of rotational relaxation may emerge from these studies. For instance, the jet itself represents a unique environment because of the presence of very low energy collision, which can be duplicated only with great difficulty in equilibrium experiments, but are important in unusual physical conditions as those prevailing in interstellar clouds.[3] Several experimental techniques have been employed so far to study rotational relaxation in free jets. The list includes electron beam induced fluorescence,[4] velocity distribution measurement followed by energy balance to get the rotational temperature,[5] molecular beam laser-induced fluorescence,[6] infrared absorption spectroscopy,[7] Raman spectroscopy,[8] and finally Fourier transform emission spectrometry.[9]

The merits and shortcomings of these techniques are too numerous to be discussed here. References 4–9, however, may be divided into two categories. The first contains those involving the measurements averaged over the rotational states such as rotational temperatures, while the second group includes those in which populations of individual rotational level have been measured.

The major theoretical efforts towards an understanding of rotational relaxation in free jets have been made using thermodynamic sudden freeze and numerical integration models.[10,11,12] Since, in these models, a rotational temperature is assumed to exist throughout the expansion and also a constant characteristic rotational relaxation rate constant or cross section is used, such an approach is obviously inadequate for interpretation of experimental results which reveal that deviation from a Boltzmann distribution exists in the population of individual levels, and that the rotational relaxation rate constants and cross sections are temperature dependent.

An alternative to the thermodynamic approach is the use of kinetic model employing state-to-state rate constants. After appropriate modeling of the expansion, the population of the individual rotational level may be calculated out throughout the expansion, by solving the master equation with the state-to-state rate constants. The rate constants, however, must be got from a large amount of computation based on an interaction potential between molecules. This calculation is severely restricted as the lack of knowledge about the interaction potential.

Several empirical expressions of the state-to-state rate constant have been proposed based on experimental results, such as the exponential energy gap law[13,14] and the power law.[15] Appropriately adjusting the parameters in the expressions could yield the best description of the population evolution or the change of the rotational temperature along the jet. This method has been used by Koura[16,17] and Yamazaki *et al.*[18] to explain the dependence of the terminal rotational temperature of N$_2$ on the stagnation pressures, where the rotational temperature was derived from terminal velocity measurement followed by energy balance.

Presented in this paper are the experiment results which makes use of laser-induced fluorescence (LIF) excitation spectra to obtain the rotational population of CS$_2$ and its changes in argon free jet in a range of $X/D=3-20$ at a stagnation pressure of one atmosphere (D is the nozzle diameter, X is the axial distance from the nozzle orifice exit). The power law is employed to calculate the evolution of rotational population by the method like Koura's.[17] Fitting of the calculated results with the experiments gives almost all the information about the rotational relaxation of CS$_2$ in Ar free jet.

II. RELAXATION KINETICS IN FREE JET

The relaxation of the rotational distribution $P_I = n_I/n$ of CS$_2$ along the Ar free jet axis is described by the master equation[18]

$$U \frac{dP_I}{dX} = n_a \bar{V} \sum_J (\sigma_{JI} P_J - \sigma_{IJ} P_I), \qquad (1)$$

where the rotation-rotation transition is neglected owing to the diluteness of CS$_2$ in Ar ($n = \sum_I n_I \ll n_a$), n_I and n_a are the number density of CS$_2$ in the ith rotational level and Ar, respectively, U is the flow velocity, $\bar{V}$ is the relative mean velocity between collision partners, σ_{IJ} (or σ_{JI}) is the cross section for the rotational transition $I \rightarrow J$ (or $J \rightarrow I$) of CS$_2$ due to collisions with Ar, and given by the power law[17]

$$\sigma_{IJ} = C(2J+1)|\epsilon_{IJ}| \exp(\epsilon_{IJ}) K_1(|\epsilon_{IJ}|) |\Delta E_{IJ}|^{-\alpha}, \qquad (2)$$

where $\Delta E_{IJ} = E_I - E_J$ is the rotational energy gap, ϵ_{IJ} equals $\Delta E_{IJ}/2kT$, T is the translational temperature, K_1 is the modified Bessel function of the second kind, the parameters C and α are slightly dependent on temperature and can be assumed constant in calculation.

The relation between the total molecular density and the translational temperature in the jet axis is taken from the isentropic flow equation,

$$\frac{n}{n_0} = \left(\frac{T}{T_0} \right)^{1/(\gamma-1)} = \left(1 + \frac{\gamma-1}{2} M^2 \right)^{-1/(\gamma-1)}, \qquad (3)$$

here, n_0 and T_0 are the total molecular density and the temperature in the source gas, respectively, γ is the heat capacity ratio and taken to be 5/3, and M is the Mach number which is a function of X/D. The Mach number distribution along the jet axis is adopted from the work of Anderson[1] and Ashkenas *et al.*[19] If reasonable values of C and α in formula (2) can be chosen, the rotational relaxation kinetic rate constants may be obtained by solving numerically the master equation mentioned earlier above.

III. EXPERIMENT

Our supersonic jet apparatus is similar to those described by other authors in the literature except for the movable nozzle. The supersonic jet was formed by expanding a mixture of 5% CS$_2$ in argon through a 0.5 mm room temperature pulse nozzle (General Valve) into the vacuum chamber pumped by an oil-diffusion pump. The stagnation pressure was 1 atm., the background and working pressure in the chamber were 3×10^{-6} and 2×10^{-5} Torr, respectively, at a repetition rate of 4 Hz.

A dye laser (Lambda Physik FL2002) of a line width of 0.2 cm^{-1} pumped by an XeCl excimer laser with a pulse width of 20 ns irradiated the jet in the direction perpendicular to the jet axis. The total fluorescence of CS$_2$ was detected by a photomultiplier (GDB56, Beijing) through an optical image system which was so arranged that the fluorescence from a small area near the jet axis could only be received. The signal from the photomultiplier was preamplified, and fed to the channel A of a Boxcar integrator (PAR 162/165). The output of a photodiode irradiated by the transmitted dye
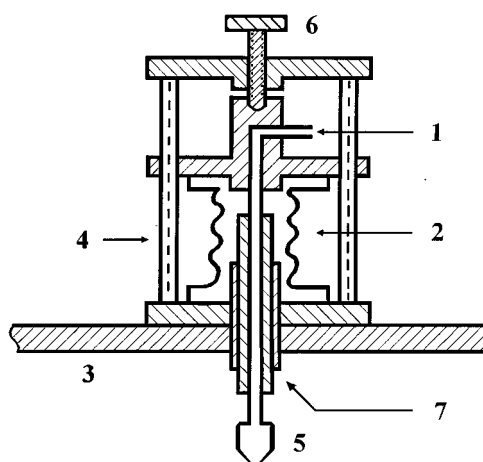

FIG. 1. Schematic framework of the movable nozzle: (1) sample gas; (2) stainless-steel bellows; (3) flange; (4) supporting frame; (5) pulsed nozzle; (6) adjusting handle; (7) guide body.

laser beam from the exit arm of the chamber was sent to the channel B. The Boxcar was working on A/B mode. Scanning the dye laser frequency, the averaged laser-induced fluorescence (LIF) spectrum of CS$_2$ by Boxcar was monitored and recorded by a chart recorder. The operation of the nozzle and the laser was controlled sequentially by a homemade pulse generator. The pulse width opening the nozzle was 2 ms.

The main difference between our apparatus and others is that the nozzle position can be changed relative to the intersection point between the jet axis and the dye laser beam, as can be seen in Fig. 1. By turning the adjusting handle, the nozzle which was connected to a stainless-steel bellow, could be moved within a range of 0–40 mm.

IV. RESULTS AND DISCUSSION

In order to get the evolution of the CS$_2$ rotational distribution along the expansion, we had obtained nineteen LIF spectra of CS$_2$ corresponding to $\tilde{A}\ ^1B_2(150) - X\ ^1\Sigma_g^+(000)$ transition (352.5–352.6 nm) for different positions in the jet within a range of $X/D = 3-15$. For illustration, Figs. 2 and 3 are the LIF spectra of CS$_2$ at $X/D = 3$ and 15, respectively. It can be seen from these spectra that considerable cooling has taken place as the spectrum in Fig. 3 is much simpler than that in Fig. 2. The corresponding simulated spectra are also given in each graph according to the known spectroscopic constants, the Honl–London factor, and an assumed population. From these simulated spectra, the rotational distribution and its evolution along the jet axis were obtained.

Now we are in a position to calculate the rotational distribution and its evolution through the expansion, and to fit the calculated results with those of the experiments. In the early stages of the expansion (usually negative X/D), the translational temperature changes rather slowly and the collision rate is very high, the translational and rotational degrees of freedom are in a equilibrium. However, with the expansion proceeding, and as a result of the decrease both in the number density and the translational temperature, the col-
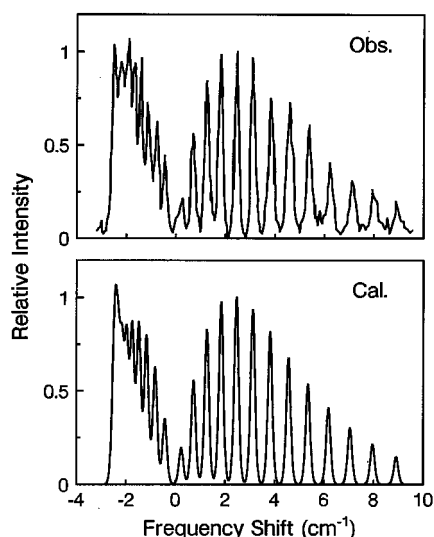
FIG. 2. A comparison of the experimental (upper panel) and simulated (lower panel) laser-induced fluorescence excitation spectra of CS$_2$ centered at 28 362.9 cm^{-1} in the Ar free jet for $X/D = 3$.

lision rate begins to fall, the equilibrium between the translational and rotational degrees of freedom as well as that between the individual rotational states will no longer exist, the master equations have to be solved.

For solving the master equation (1), we must consider the coupling effect of vibration-rotation relaxation on the evolution of rotational distribution, because the vibration-rotation relaxation process enriches the rotational population. Fortunately, from the analysis of the vibrational structures of the LIF spectra of CS$_2$ at room temperature and in the supersonic jet, we can conclude that there appears to be no change
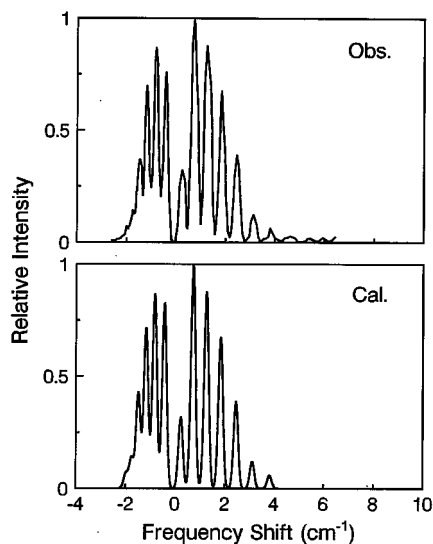

FIG. 3. A comparison of the experimental (upper panel) and simulated (lower panel) laser-induced fluorescence excitation spectra of CS$_2$ centered at 28 362.9 cm^{-1} in the Ar free jet for $X/D = 15$.
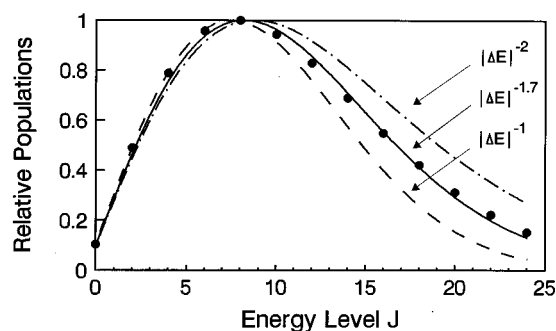

FIG. 4. Rotational population of CS$_2$ at $X/D = 3$ in free expansion. The lines show calculated results based on a power law dependence of transition probabilities on the energy gap. The points are experimental values.

of CS$_2$ vibrational population even though the rotational temperature is cooled significantly as the jet proceeds, which implies that the vibration-rotation coupling effect could be neglected in our experiment. Of course, this is obviously reasonable because the vibrational relaxation takes much more collisions than the rotational relaxation.

The rotational population at the starting point (X_0/D) of calculation can be obtained from the Boltzmann equation with the rotational temperature setting equal to the translational temperature. In practice, the starting point was varied in order to check the stability of the calculated results. Typical value of $X_0/D = -1$ was used in the calculation. The calculated results of rotational population are illustrated in Figs. 4 and 5 for $X/D = 3$ and 15, respectively. It emerges from the fit of the calculated populations and the experimental results that if the rotational transition probability decreases with the 1.7 power of the difference between the initial and the final rotational states, the theoretical predictions agree well with the experimental results from $X/D = 3 - 15$ throughout the expansion. To our knowledge, this is probably the first experiment to detect the evolution of the molecular rotational populations point-by-point along the jet axis, not only for CS$_2$, and to check the theoretical results with experiments. Now, some information about the rotational relaxation can be obtained from the calculation.
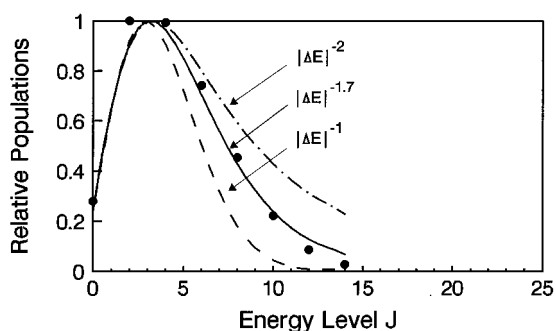

FIG. 5. Rotational population of CS$_2$ at $X/D = 15$ in free expansion. The lines show calculated results based on a power law dependence of transition probabilities on the energy gap. The points are experimental values.
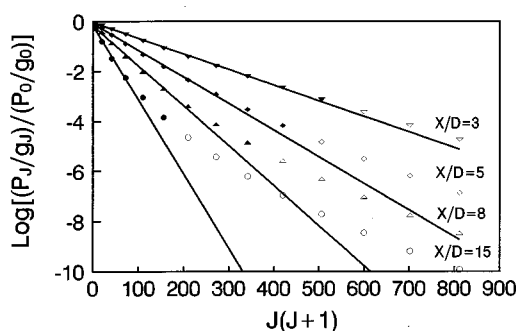
FIG. 6. Rotational distributions in free expansion where the closed signs represent the experimental values, and the open signs represent the values from calculation. The solid linear lines are fitted to linear patterns for each distribution at lower J.

FIG. 7. The temperature dependences of the cross section (solid) and rate constant (dashed) for the transition $CS_2(J=2)+Ar \rightarrow CS_2(J=0)+Ar$.

The rotational distributions in the free jet are one of our concerns. Figure 6 shows the relative rotational distributions of CS_2 at $X/D=3$, 5, 8, and 15, respectively, where the closed signs show the experimental results and the open signs represent the theoretical prediction. It can be seen in Fig. 6 that the population becomes more and more non-Boltzmannian as the free jet proceeds. This is in agreement with the results of diatomic molecules reported by other authors.[20,21]

The state-to-state transition cross sections are the fundamental result, which can be written as the following formula based on our calculation:

$$\sigma_{IJ} = 5.94 \times 10^{-43}(2J+1)$$

$$\times \left| \frac{\Delta E_{IJ}}{2kT} \right| \exp\left(\frac{\Delta E_{IJ}}{2kT} \right) K_I \left(\frac{\Delta E_{IJ}}{2kT} \right) |\Delta E_{IJ}|^{-1.7}(\text{cm}^{-2}),$$

(4)

where $\Delta E_{IJ} = E_I - E_J$ is the energy gap between the initial state I and the final state J. The relaxation rate constant

$$k_{IJ} = \bar{V}\sigma_{IJ} = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \sigma_{IJ},$$

where μ is the reduced mass of CS_2 and Ar. From this formula, the relaxation cross section and the rate constant for any couple states could be obtained. Taking the lowest transition $2\rightarrow0$ as an example, shown in Fig. 7, the order of σ_{2-0} is 10^{-16} cm² which is close to the hard sphere collision cross section, meaning that the rotational relaxation is very effective in collision. The temperature dependence of σ_{2-0} and k_{2-0} in the range of 2–60 K proves the assumption for the relaxation of the diatomic molecules.

The rotational temperature T_R which is used in thermodynamic models can be defined as

$$T_R = \sum_I \frac{P_I E_I}{k} = \sum_I I(I+1)P_I B,$$

where B is the rotational constant. Figure 8 shows T_R and translational temperature T as a function of X/D. The result can be compared with the sudden freeze model which has been used to describe a variety of rotational relaxation pro-
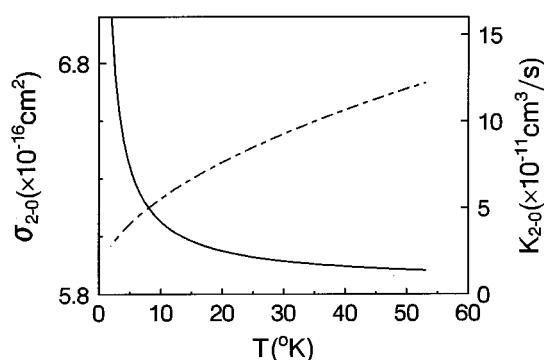
cesses, and where it was assumed that during the early stages of expansion, the translational and rotational degrees of freedom remain in thermodynamic equilibrium (i.e., $T_R = T$). This situation persists until a certain critical point, where the collision frequency becomes sufficiently low, and T_R freezes, giving the terminal rotational temperature T_R^∞. Figure 8 shows quite clearly that considerable deviation from this type of behavior occurs. Of course, the primary limitation of the sudden freeze model stems from the fact that the rotational relaxation is described in terms of Boltzmannian temperature, and hence contains no information concerning the non-Boltzmann behavior of the rotational distributions.

The rotational collision number Z_R defined by

$$Z_R = \tau_R \sigma_t \left(\frac{8kT}{\pi\mu} \right)^{1/2} n_a$$

is an interesting physical quantity, where τ_R is the rotational relaxation time and σ_t is the CS_2+Ar hard sphere collision cross section taken to be 40 Å².[22] The rotational relaxation time is defined by
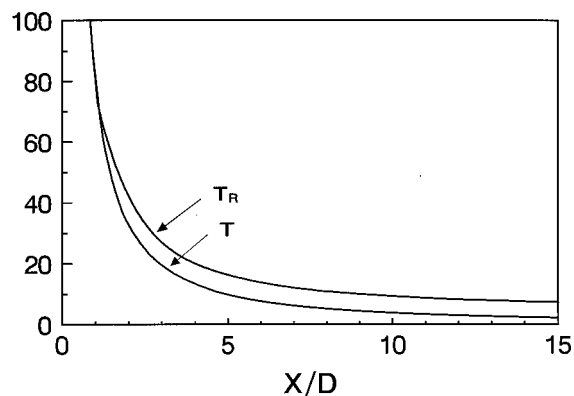

FIG. 8. Rotational temperature along the free jet axis in comparison with the translational temperature. The rotational temperature was calculated according to the expression $T_R = \sum_J J(J+1)P_J B$, where θ_R is the characteristic rotational temperature, and P_J is the population at level J.
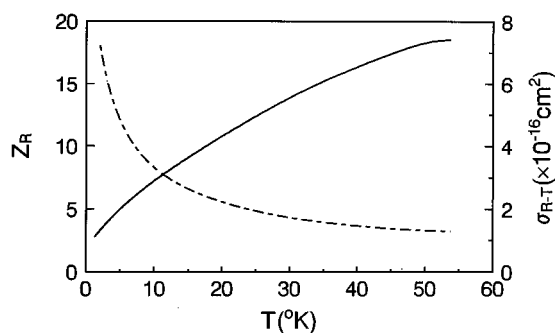
FIG. 9. The temperature dependencies of the collision number Z_R (solid) and the effective overall relaxation cross section σ_{R-T} (dashed) for the CS$_2$+Ar collision.

$$\tau_R = (T - T_R) \; / \; [U(dT_R/dX)],$$

where

$$U \frac{dT_R}{dX} = \sum_I \; U \; \frac{dP_I}{dX} \frac{E_I}{k},$$

and $U(dP_I/dX)$ is given by Eq. (1).

Z_R for our experiment presented in Fig. 9 is an increasing function of T which is consistent with the usual assumption. The overall rotational relaxation cross section $\sigma_{R-T} = \sigma_t / Z_R$ is also given in Fig. 9, which increases with the decrease of temperature, implying that, in the low temperature region, the attractive forces between collision partners may take a more important role than the repulsive forces.

In conclusion, the present work provides a direct measurement of the CS$_2$ rotational population and its change along the Ar free jet. Using the energy gap power law, the master equations were solved with fitting to the experimental measurements. The results show that the state-to-state relaxation cross sections are proportional to the inverse 1.7 power of the energy gap between the initial and the final states. The formula expressing the state-to-state relaxation cross sections and rate constants are presented which provide almost all the information about the rotational relaxation of CS$_2$ in Ar free jet.

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[22] Here, σ_t is approximately calculated from the diameter of the Ar atom and the band length of CS$_2$ at its ground state. Although the value of σ_t is not correct, the relation of collision number Z_R with temperature is still right.