Low temperature measurements of the rotational relaxation in D₂ free jets

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The rotational relaxation of molecular deuterium in a free jet expansion has been studied between 78 and 473 K by pseudorandom time-of-flight technique. In the temperature range 78–308 K a decrease of the rotational collision number Z_{rot} with increasing temperature is observed as predicted theoretically by Raff and by Rabitz and Lam. Also reported are room temperature data of Z_{rot} for H₂ and HD expansions. The number of collisions required to relax H₂, D₂, and HD at room temperature is in the ratio 10:5:1.

I. INTRODUCTION

The rapid translational cooling in free jet expansions of gases causes a nonequilibrium between the translational and the internal degrees of freedom. In the early stage of expansion the internal degrees of freedom relax by collisional energy transfer into the translational mode. With progressing rarefaction (decreasing collision frequency) the relaxation slows down and eventually becomes frozen. The relaxation processes can be studied by measuring the characteristic parameters of the "frozen" jet as a function of the stagnation conditions.[1-5,9]

According to enthalpy conservation in the adiabatic expansion of a gas, the average flow velocity of thermal nozzle beams is given by:

$$\tilde{v} = [2c_p(T_0 - T_b)/m]^{1/2},\qquad(1)$$

where c_p is the specific heat, T_0 the stagnation temperature, T_b the translational beam temperature, and m the molecular mass. In the zero enthalpy limit of infinite expansion ($T_b \to 0$) this corresponds to $(5/3)^{1/2}v_{mp}$ for monatomic and $(7/3)^{1/2}v_{mp}$ for diatomic gases on which we are focusing here; $v_{mp} = (3k_B T_0/m)^{1/2}$ is the most probable velocity in a Maxwellian flux, where k_B is the Boltzmann constant. In the derivation of the diatomic gas value it is implied in addition that (a) prior expansion the mean rotational energy of diatomic molecules is $k_B T$, i.e., $c_p = \tfrac{7}{2}k_B$ and that (b) during the expansion this energy is fully transferred into translational energy, i.e., the rotational energy is fully relaxed.

However, hydrogen and deuterium are in some way unusual diatomic molecules because of their large characteristic rotational temperatures $\theta_{rot} = \hbar^2/2k_B I = 85.4$ and 43 K, respectively (i.e., large rotational level spacings), where I is the moment of inertia of the molecule. The fractional rotational level populations of a gas in equilibrium are given by:

$$N_J = -k_B T \cdot \frac{1}{\zeta_{rot}} \cdot \frac{d\zeta_{rot}}{dE_J},\qquad(2)$$

$$\zeta_{rot} = \sum_{J=0}^{\infty} (2J+1)\exp[-E_J/k_B T],$$

with

$$E_J = k_B \theta_{rot} J(J+1).$$

Due to the large level spacings only a few rotational levels are populated at moderate temperatures, say $T < 500\,K$ (vi-

brational excitation is anyhow negligible); for $T \lesssim \theta_{rot}$ practically only the lowest one is populated. For instance, the population of the rotational levels $J = 0$ and 2 of para-H₂ at 78 K (ortho-D₂ at 39 K) are 99.3% and 0.7%, respectively; likewise for $J = 1$ and 3, i.e., for ortho-H₂ at 78 K (para-D₂ at 39 K), the corresponding figures are 99.996% and 0.004%. As a consequence the average rotational energy E_{rot} of the molecules

$$E_{rot} = \sum_{J=0}^{\infty} E_J N_J = \frac{\sum_0^{\infty} E_J(2J+1)\exp[-E_J/k_B T]}{\sum_0^{\infty}(2J+1)\exp[-E_J/k_b T]}\qquad(3)$$

is for normal -H₂ at 78 K 0.08 meV and for normal-D₂ at 39 K 0.11 meV, in contrast to the classical value $k_B T$ which is 6.7 and 3.4 meV, respectively.

Obviously, the average rotational energy of hydrogen and deuterium in the usual stagnation temperature range is substantially less than $k_B T$. Accordingly, $c_p = \tfrac{7}{2}k_B$ cannot hold for H₂ and D₂ in this temperature range simply because the stored average rotational energy prior expansion is less than $k_B T$. Thus, at low temperatures, say $T \lesssim 78$ K (for H₂) and $T \lesssim 39$ K (for D₂), these molecules show monatomic like behavior, i.e., $\tilde{v}_{H_2, D_2} \approx 1.29\, v_{mp}$.

Even at moderate stagnation temperatures but low $p_0 d$ values (p_0-stagnation pressure and d-effective nozzle diameter) H₂ and D₂ have apparently monatomic like behavior. Indeed, due again to the large level spacings and to the small anisotropy of the potential, rotational relaxation in H₂ and D₂ is in general inefficient and only a small amount of stored rotational energy is transferred into translational energy. The degree of energy transfer increases with $p_0 d$, because this product determines the total number of collisions suffered by a molecule during the expansion. The rotational collision number Z_{rot}, i.e., the number of hard sphere collisions necessary for an effective rotational-translational energy transfer, and its dependency on stagnation temperature has to be known for predicting the actual behavior of H₂ and D₂.

Numerous attempts have been made to predict theoretically the temperature dependency of the rotational translational relaxation, expressed in terms of the rotational collision number Z_{rot} (T).[6] Calculations for H₂[7] and D₂[8] predict a decrease of Z_{rot} with increasing stagnation temperature in the region $T_0 < 300$ K. We are not aware of any experimental

proof of this prediction in free jet expansions. Here we report the results of an investigation of the rotational relaxation in D_2 free jets in the range $T_0 = 78$–473 K. The rotational temperature T_{rot}^{beam} in the frozen jet is evaluated as in former investigations, performed at higher temperatures, from TOF analysis by means of an energy balance. Using these experimental T_{rot}^{beam} data, the collision number Z_{rot} is obtained from the integrated linear relaxation equation, with a single unknown relaxation time for the free jet expansion; the procedure is similar to the method of Gallagher and Fenn[1,2] (see also Refs. 4 and 5).

II. EXPERIMENTAL AND PROCEDURE

The experimental arrangement (Fig. 1) is a modification of the TOF machine used in this laboratory[10,11]: a nozzle beam unit with a sonic orifice nominally $10 \mu m$ in diameter is the free jet source.[12] The effective nozzle diameter was determined by total flow rate measurements of helium expansions, yielding a value of $d_{eff} = 7.6 \mu m$. The TOF measurements are performed by means of pseudorandom chopping with $10 \mu s$ time resolution. The TOF distribution is obtained by cross correlation deconvolution carried out by means of an online computer. Here, only the average flow velocity $\bar{v}$ and the speed ratio S (related to the translational beam temperature $T_b = \bar{v}^2 m/2S^2 k_B$) deduced from the deconvoluted distribution are used.

The first step is the evaluation of E_{rot}^{beam}, the rotational energy of the molecules in the frozen beam. Assuming that no vibrational modes are excited conservation of energy yields:

$$E_{rot}^{beam} = \tfrac{3}{2} k_B T_0 + E_{rot}^{source} - \tfrac{1}{2} m \bar{v}^2 - \tfrac{3}{2} k_B T_b . \qquad (4)$$

The rotational energy of the molecules in the source E_{rot}^{source}, in which thermal equilibrium is assumed, can be evaluated by means of Eq. (3) in which E_{rot}^{source} and T_0 are substituted for E_{rot} and T. E_{rot}^{beam} is thus obtained through Eq. (4) from the measured $\bar{v}$ and S values.

The next step is the evaluation of a rotational temperature T_{rot}^{beam} of the molecules in the "frozen beam" as a function of T_0 and p_0. This "temperature" is only an approximation because the rotational state distribution in the beam is in general not Boltzmann like.[13,14] However, Raman scattering measurements by Godfried et al.[15] for H_2 and D_2 expansions indicate that these deviations are small for high stagnation pressures and low stagnation temperatures. Accordingly, the rotational temperature T_{rot}^{beam} is obtained again from Eq. (3) in which now E_{rot}^{beam} and T_{rot}^{beam} are substituted for E_{rot} and

T, respectively. The experimental T_{rot}^{beam} values obtained in this way are analyzed in terms of a linear relaxation model[1,2]:

$$\bar{v} \frac{dT_{rot}^{beam}}{dz} = - \frac{1}{\tau_{rot}} (T_{trans}^{beam} - T_{rot}^{beam}) , \qquad (5)$$

where τ_{rot} is the relaxation time and T_{trans}^{beam} the translational temperature in the isentropic approximation. The collision number for rotational translational energy transfer Z_{rot} is defined as:

$$Z_{rot} = \tau_{rot}/\tau_{hs} = Q_{hs}/Q_{rot}, \qquad (6)$$

where τ_{hs} is the average time between collisions for hard sphere molecules (cross section Q_{hs}) and Q_{rot} the rotational collision cross section. Here we use the value $Q_{hs} = \pi \cdot 2.93^2$ $\mathring{A}^2$.[16] Obviously Z_{rot} may be seen as the average number of hard sphere collisions required to transfer one rotational energy quantum into the translational mode. The procedure to obtain Z_{rot} from the just derived T_{rot}^{beam} data is as follows. By numerical integration of Eq. (5) the dependency T_{rot}^{beam}/T_0 vs p_0, with Z_{rot} as parameter is obtained. For a given stagnation temperature T_0, the corresponding Z_{rot} value is obtained by fitting the calculated dependency to the experimental one using Z_{rot} as fitting parameter. Since our approach is similar[17] to former methods we refer the reader for a detailed description to Refs. 1, 2, 4, and 5.

III. RESULTS AND DISCUSSION

Clustering, which may occur during free jet expansions, complicates the energy balance. The released condensation energy heats the expanding gas and should be accounted for in Eq. (4). An exact assessment of the released condensation energy requires the knowledge of the fraction of clustered molecules under the specific conditions of each relaxation measurements. An accurate determination of the clustered fraction can hardly be performed because, as shown recently by Buck and Meyer,[20] the mass spectrometric determination is strongly biased by electron impact induced fragmentation. We will confine ourselves here to a crude estimation of an upper limit of the clustered fraction. To this end we compare the "mass pattern" of a heavily clustered H_2 beam with the mass patterns of the D_2 beams obtained under the specific conditions of the relaxation measurements. (The isotope effect can be certainly neglected in the frame of this crude estimation.) By assuming that in the heavily clustered H_2 beam all molecules are clustered (i.e., 100% polymers), the comparison of the mass patterns gives a rough estimate of the upper limit of the clustered fraction in the various D_2 beams.

The heavy clustered beam is produced by expansions of H_2 with the source cooled to 25 K. In Fig. 2 the measured cluster ion intensities are plotted vs stagnation pressure p_0. The various odd masses reach intensities up to 5% of the H_2^+ signal, in contrast to the even masses with intensities about two orders of magnitude lower. This is because of the fragmentation reaction $H_{2n} + e \rightarrow H_{2n-1}^+ + H + e$. The observation is in good agreement with former experimental results[18] and theoretical calculations of cluster ion stability.[19] The observed slight decrease of the cluster ion intensities with increasing stagnation pressure is yet unclear; it might
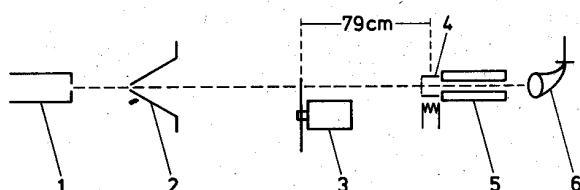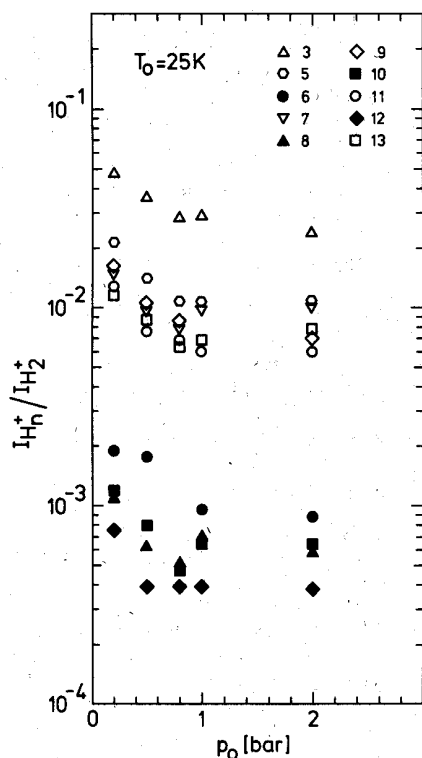
FIG. 2. Relative intensity of the different cluster ions in hydrogen expansions at $T_0 = 25$ K as a function of stagnation pressure.
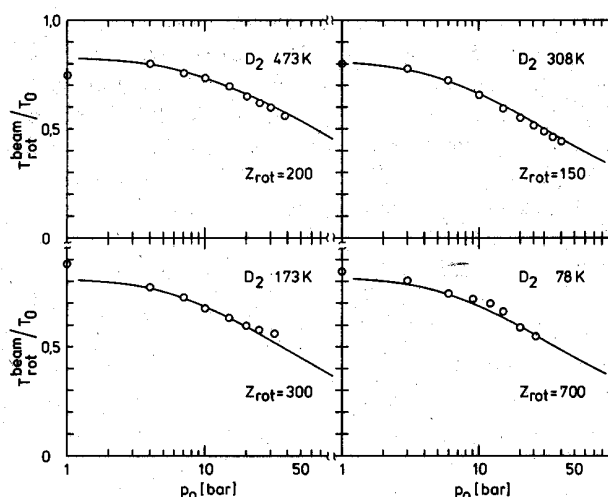

FIG. 3. Rotational relaxation of deuterium in free jet expansions at stagnation temperatures of 78, 173, 308, and 473 K as a function of the stagnation pressure. The solid lines show the best fit numerical solution of the relaxation equation.

be due to scattering effects in the nozzle exhaust chamber upstream of the skimmer.

For D_2 expansions in the high temperature range $T_0 = 120$–500 K and for stagnation pressures up to 40 bar, only D_3^+ cluster ions are formed. Their relative intensity with respect to the D_2^+ intensity is about a factor 50 smaller than in the 25 K H_2 expansion; we conclude that the D_2-polymer concentration is less than 2%. This leads to a beam heating of not more than 0.5 K. This heating can be neglected compared with the nearly two orders of magnitude larger amount of transferred rotational energy. In the intermediate case, $T_0 = 78$ K, a small amount of D_5^+ cluster ions is also observed. Even in this case the concentration of the clusters is still a factor five smaller than in the 25 K H_2 expansion; the corresponding upper limit of the condensation energy is a few K. The error resulting from not considering the condensation heating lies, even in the 78 K case, within the error bar in Fig. 4.

We return now to the determination of Z_{rot} (T). First we show in Fig. 3 the experimentally determined rotational temperature T_{rot}^{beam} in D_2 free jets at $T_0 = 78$, 173, 308, and 473 K as a function of p_0. In all cases the rotational temperature decreases with increasing stagnation pressure. With increasing pressure the total number of hard sphere collisions suffered by a molecule during the hydrodynamic expansion increases. Thus, the probability for a molecule to participate in an effective rotational-translational energy transfer during the expansion increases, and a larger amount of rotational energy is transferred into translational energy. The solid lines show the numerical solutions of the relaxation equation which produce the best fit to the experimental data

with Z_{rot} as fitting parameter. Figure 4 summarizes the results for the collision number Z_{rot} for deuterium as a function of the stagnation temperature; Z_{rot} decreases with increasing temperature, reaches a minimum around 300 K and increases slightly with further temperature increase. The results may be interpreted following the arguments of Raff and of Rabitz and Lam. At low temperatures, $T < 300$ K, D_2 behaves like a two level system, and we can concentrate only on the 2↔0 transition. Since the rotational relaxation cross section is governed by inelastic collisions only, which are dominated by short range repulsive forces for deuterium in the energy range being significant here, the rotational cross section $Q_{rot}^{2↔0}$ of D_2 increases with increasing collision energy.[21,22] This leads to an increase of the transition probability of the 2↔0 transition, causing a drop of the collision number Z_{rot}. At higher temperatures higher rotational levels become populated. Due to the even larger spacing between the higher levels now involved in the transitions, the temperature dependency is inverted: the still increasing rotational cross section of each level with collision energy cannot completely
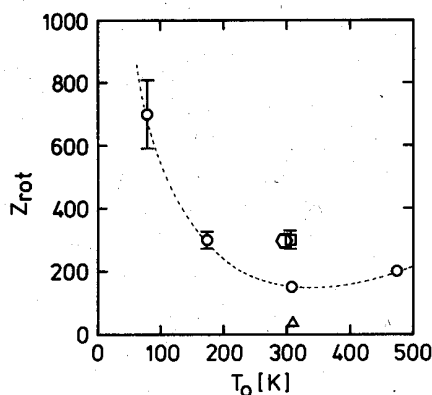

FIG. 4. Rotational collision number Z_{rot} for D_2 (O) as a function of the stagnation temperature; plotted are also Z_{rot} values for H_2 (□) and HD (△) at 308 K, as well as from Ref. 2 for H_2 (O) at 300 K. (The dashed line is only to guide the eye.)

compensate the slower transition rates between the increasingly populated higher levels; Z_{rot} increases with increasing temperature. As a result the rotational collision number has a minimum as observed in Fig. 4 around 300 K. The smooth rise of the Z_{rot} function between 308 and 473 K as indicated by $\Delta Z_{rot}^{D_2}/\Delta T = 0.3 \pm 0.17$ K^{-1} illustrates the same trend as observed for hydrogen by Gallagher and Fenn, $\Delta Z_{rot}^{H_2}/\Delta T = 0.16$ K^{-1}.[2]

Also shown in Fig. 4 are experimentally determined room temperature collision numbers Z_{rot} for H$_2$ and HD expansions at 308 K. H$_2$ is found to require two times more collisions then deuterium for an effective rotational-translational energy transfer, $Z_{rot}^{H_2} \approx 2 \cdot Z_{rot}^{D_2}$. This is due to the larger level spacings with respect to D$_2$. The $Z_{rot}^{H_2}$ value is in good agreement with the value of Gallagher and Fenn[2] at the same temperature (see Fig. 4). HD relaxes after undergoing only one-fifth of the number of collisions required to relax D$_2$. Besides the smaller level spacings due to transitions between even and odd levels the relaxation of HD is favored by the rotation about a center of mass which is displaced from the geometrical center of the molecule.

ACKNOWLEDGMENTS

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