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## Low Temperature Rotational Relaxation in Deuterium Nozzle Beams

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During the expansion of deuterium the energy of the rotational degrees of freedom is transferred to directed translational energy. The amount of transferred energy depends on the initial energy content of the rotational modes and on the rotational collision cross section  $Q_{rot}$ . The rotational collision cross section is usually expressed in terms of a temperature dependent rotational collision number  $Z_{rot}(T) = Q_{hs}/Q_{rot}$ , where  $Q_{hs}$  is the collision cross section of hard sphere molecules. Thus,  $Z_{rot}$  may be interpreted as the average number of hard sphere collisions required to relax the gas. Calculations for  $H_2$  and  $D_2$  /1,2/ predict a decrease of  $Z_{rot}$  with increasing stagnation temperature  $T_0$  in the range  $T_0 < 300$  K. We are not aware of any experimental proof of this decrease in free jet expansions. Here, we report results of an investigation of the rotational relaxation in  $D_2$  nozzle beams in the range  $T_0 = 78-473$  K.

The experimental setup is a modification of the molecular beam TOF machine used in this laboratory /3/: a nozzle beam unit with a  $10 \mu m$  free jet source /4/ is now added. The average flow velocity  $\tilde{v}$ ; and the speed ratio  $S$  (i.e. the translational beam temperature  $T_b = \tilde{v}^2 m / 2S^2 k_B$ ) are obtained by pseudorandom TOF measurements as described in detail in ref. 5 (the flight path is increased here to 790 mm).

As in former investigations /6-8/ the rotational energy of the molecules in the beam  $E_{rot}^{beam}$  is evaluated from TOF analysis by means of an energy balance:

$$E_{rot}^{beam} = H_0 - \frac{1}{2} m \tilde{v}^2 - \frac{5}{2} k_B T_b \quad (1)$$

where  $H_0$  is the source enthalpy,  $m$  the molecular mass and  $k_B$  the Boltzmann constant. With the assumption that the rotational states in the beam have a Boltzmann distribution, an effective rotational temperature  $T_{rot}^{beam}$  is derived from the measured  $E_{rot}^{beam}$ . The collision number  $Z_{rot}$  is obtained by integrating a linear relaxation equation with a single, unknown relaxation time for the free jet expansion. Since our approach is similar to the method of Gallagher and Fenn we refer the reader for a detailed description to ref. 6,7.

Figure 1 shows the rotational temperature in  $D_2$  nozzle beams at  $T_0 = 78, 173, 308$  and  $473$  K as a function of the stagnation pressure, determined from eq.1 with experimental TOF data for  $\tilde{v}$  and  $T_b$ . The rotational temperature decreases with increasing  $p_0$ . This is due to the increasing number of collisions suffered by a molecule before entering the free molecular flow region. The solid lines show the best fit numerical solution of the linear relaxation model. The resulting collision numbers  $Z_{rot}$  are shown in fig. 2 as a function of temperature;  $Z_{rot}$  decreases with increasing temperature, reaches a minimum at about 300 K and increases slightly

with further temperature increase. This behaviour may be interpreted following the arguments of Raff /1/ and Rabitz and Lam /2/. At low temperatures  $D_2$  behaves like a two level system. Due to the dominance of short range repulsive forces in the  $D_2$  interaction potential the rotational cross section  $Q_{rot}^{2 \rightarrow 0}$  increases with increasing collision energy, i.e.  $Z_{rot}$  decreases with increasing temperature. Provided that this two level process predominates  $Z_{rot}$  would steadily decrease with increasing temperature. At higher temperatures, however, higher levels become populated. Because of the larger spacings between these levels their corresponding rotational cross section  $Q_{rot}$  is smaller. These levels being increasingly involved in the transitions the temperature dependency is inverted;  $Z_{rot}$  increases with increasing temperature as qualitatively confirmed by the experimental  $Z_{rot}$  value at 473 K.

In figure 2 also shown are room temperature collision numbers for HD and  $H_2$  expansions. HD relaxes after undergoing only one fifth of the number of collisions required to relax  $D_2$ . This is because the level spacings in HD are smaller and because HD rotates about a center of mass displaced from the geometrical center of the molecule. On the other hand, due to the larger level spacings,  $H_2$  is found to require two times the number of collisions required to relax  $D_2$ . The  $H_2$  value is in good agreement with the value of Gallagher and Fenn /7/ obtained at the same temperature.

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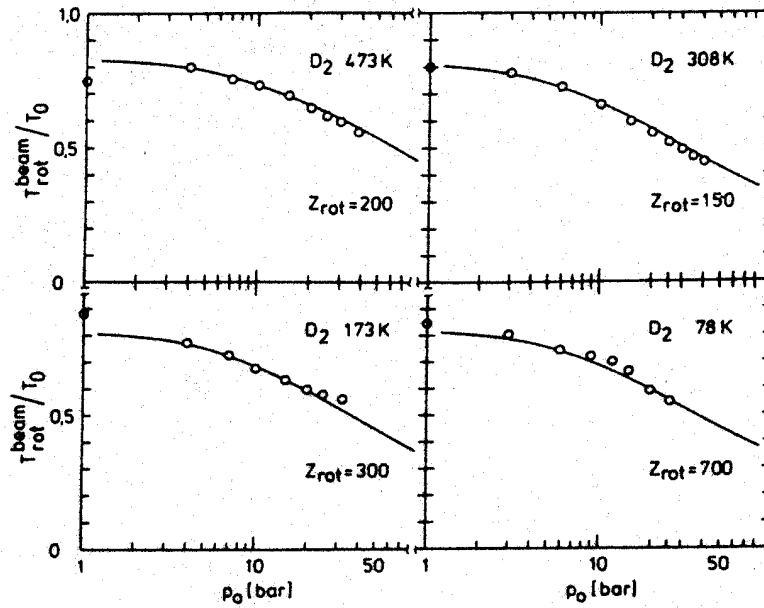


Fig. 1 The measured rotational temperature  $T_{rot}^{beam}$  in  $D_2$ -expansions as a function of the stagnation pressure  $p_0$  at four stagnation temperatures  $T_0 = 78, 173, 308$  and  $473$  K. The solid lines show the best fit numerical solution of the linear relaxation model.

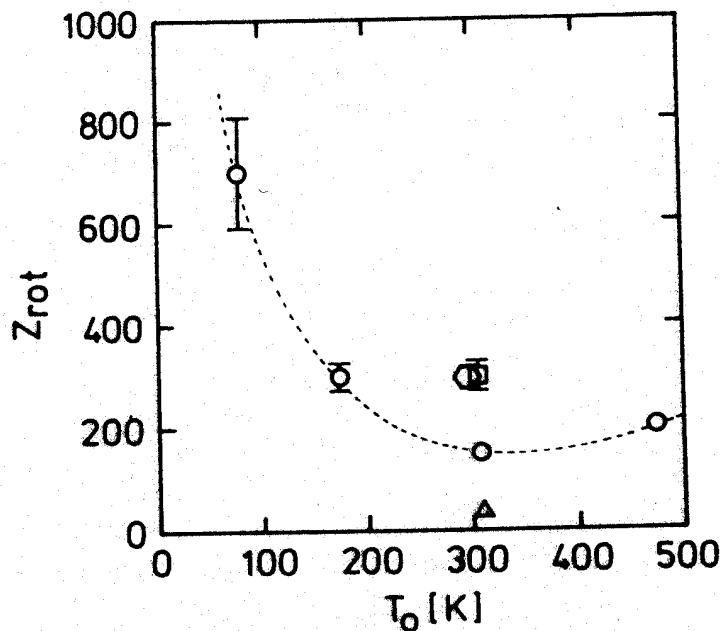


Fig. 2 The temperature dependency of the rotational collision number  $Z_{rot}$  of  $D_2$  ( $\circ$ );  $Z_{rot}$  values for  $H_2$  ( $\square$ ) and  $HD$  ( $\triangle$ ) at  $308$  K, as well as for  $H_2$  ( $\odot$ ) at  $300$  K from ref. 7 are added for comparison. (The dashed line is only to guide the eye.)