Gas Phase Molecular Relaxation at very low Temperatures. A comparative Study of N₂ and of its Mixtures with He and Ne

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Abstract

The low temperature (< 100 K) relaxation of N₂ in self-collisions and in collisions with He and Ne has been experimentally studied with resonance-enhanced-multiphoton-ionization and time-of-flight techniques. The following average values of the rotational relaxation cross sections, σ_r , have been derived from the measurements: $\sigma_r^{N_2-N_2}$ (T=5-60 K) $\approx 35 \text{ \AA}^2$; $\sigma_r^{N_2-He}$ (T=5-80 K) $\approx 15 \text{ \AA}^2$ and $\sigma_r^{N_2-Ne}$ (T=5-60 K) $\approx 40 \text{ \AA}^2$. The cross section trend $\sigma_r^{N_2-N_2} \approx \sigma_r^{N_2-Ne} > \sigma_r^{N_2-He}$ reported in the literature for T= 300 K is confirmed below 100 K, but the absolute values are larger in the low temperature range.

1. Introduction

The rotational relaxation of nitrogen in free jets has been investigated by various research groups over the last decades (see [1,2] and references therein). Pioneering studies [3,4] used time-of-flight (TOF) measurements and energy balance in order to determine the rotational temperatures, T_r . This procedure however is inaccurate due to the fact that small errors in the measured flow velocities lead to large errors in T_r . In the eighties and nineties rotational temperatures of N₂ were measured with different spectroscopic methods [1,5] but these measurements were usually dedicated to the

demonstration of spectroscopic techniques rather than to a systematic study of relaxation. Most studies of N_2 relaxation in free jets have been performed with the electron-induced-fluorescence (EIF) technique (see [6] and references therein). This method is very sensitive, but the data obtained are indirect and their interpretation is not straightforward (see for instance [5,7]). More recently the resonance enhanced multiphoton ionisation (REMPI) technique which has a high sensitivity and selectivity has been used for the study of relaxation in N_2 jets [2,8]. In previous articles, we reported rotational relaxation cross-sections derived from stimulated Raman spectroscopy [1] and from REMPI measurements [2]. In the present work we extend our previous studies and compare the different efficiency of collisions with N_2 , He and Ne for the relaxation of molecular nitrogen at low temperatures.

2. Experimental Section

The experimental arrangement used for the present measurements is described elsewhere [1,2,9] and only the relevant details are given here. Free jets of pure nitrogen and of N_2 diluted in He and Ne (with a 0.1 mole fraction in N_2) were generated by expanding the gases from both pulsed and continuous sources at room temperature. For the pulsed expansions a commercial solenoid-driven valve with an effective opening diameter, $d_{\text{eff}} = 0.4 \text{ mm}$ ($\pm 10\%$), a pulse frequency of approximately 10 Hz and a pulse length of 0.5-1 ms was used. The source of the continuous jets was a circular pinhole with a diameter of 0.195 mm ($\pm 5\%$) perforated in a 0.1 mm stainless steel foil. The source pressures, p_0 , were varied between ≈ 15 and 2500 mbar and the relevant $p_0 d_{\text{eff}}$ parameter, which is proportional to the total number of binary collisions during the expansion, ranged between 0.5 and 100 mbar cm. The gases were expanded into a 50 l chamber pumped by a 2000 $l \text{ s}^{-1}$ oil diffusion pump. The background pressure of the expansion chamber was always in the 10^{-4} - 10^{-5} mbar interval. Molecular beams were extracted by collimating the central part of the free jets with a skimmer placed at ≈ 3 -5 cm distance from the nozzle. These beams travelled along an arrangement of interconnected vacuum chambers towards the analysers. Beyond the skimmer, the pressure was always lower than 5×10^{-6} mbar, and in the detection chambers, pumped with turbomolecular pumps, the pressure was in the 10^{-7} mbar range. A quadrupole mass spectrometer was used for the detection of the nitrogen molecules and rare-gas

atoms of the various molecular beams investigated. Terminal flow velocities, u_∞ , and translational temperatures, $T_{t,\infty}$, were derived through a deconvolution of the time-of-arrival distributions of the molecular pulses generated by the narrow slits of a mechanical chopper placed in the chamber behind the skimmer as indicated in refs 1,2. The terminal rotational temperatures of the nitrogen molecules were obtained from REMPI spectra performed on the molecular beams [2]. A (2+2) REMPI scheme based on the two-photon resonant excitation to the (1,0) vibrational band of the $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ transition was used. Tuneable radiation in the 283-285 nm range was generated by frequency doubling the output of a Nd: YAG pumped dye laser operated with a mixture of rhodamine 590 and 610. The resulting laser pulses were linearly polarized and had time and frequency widths of 6 ns and 0.1 cm^{-1} respectively. The experiments were performed with a power of 2 mJ/pulse, which guaranteed a quadratic dependence of the signal on the photon energy, and the formed N_2^+ ions were detected by means of a time-of-flight mass spectrometer of the Wiley McLaren type provided with a microchannel plate.

3. Results and Discussion

Fig. 1 shows characteristic REMPI spectra of molecular nitrogen together with their theoretical simulations. The three spectra were recorded for a $p_0 d_{\text{eff}} \approx 0.9\text{ mbar cm}$. The upper panel corresponds to pure nitrogen, the middle panel to N_2 diluted in He and the lower panel to N_2 diluted in Ne. In all the cases studied, the measured spectra could be approximately reproduced with a Boltzmann distribution of rotational states characterized by T_r . As can be seen, the degree of rotational cooling attained in each expansion is different; the lowest T_r is obtained in the N_2/Ne expansion, whereas the highest T_r corresponds to the N_2/He mixture. The expansion of pure nitrogen leads to a value of T_r between the other two. This qualitative trend for the terminal rotational temperatures is observed only for the lower source pressures. The decrease of $T_{r,\infty}$ as a function of $p_0 d_{\text{eff}}$ is much more pronounced in the expansions of nitrogen diluted in noble gases than in those of pure nitrogen, as shown in Figs 2 and 3.

The terminal rotational and translational temperatures for the three cases considered, are displayed in Fig. 2. The breakdown of equilibrium between translation and rotation at the end of all the expansions is made patent by these measurements. In

order to get quantitative information about the probability of rotational relaxation, we have resorted to the same simple model described in our previous works [1,2]. In a typical free jet, the internal energy of the particles in the source is transformed into directional kinetic energy of the flow during the supersonic expansion. The model takes into account a possible lack of equilibrium in the jet between the various energetic modes (vibration, rotation and translation) of the gas, but imposes thermal equilibrium within each mode. For the conditions of the present work, with the jet source kept at room temperature, the vibrational mode needs not to be taken into account [2]. The evolution of the translational temperature is considered to be isentropic, which implies that it is solely determined by the heat capacity ratio, γ , of the expanded gas [10]; furthermore, the expansion is supposed to cease abruptly (“sudden freeze”) at the point where the measured terminal translational temperature $T_{t,\infty}$ is reached. In the course of the expansion, the rotational temperature is assumed to be coupled to the “translational thermal bath” provided by the jet, through a linear equation:

$$\frac{dT_r}{dt} = -\frac{1}{\tau_r}(T_r - T_t) \quad (1)$$

where τ_r is the rotational relaxation time and T_t is the (isentropic) local translational temperature. The inverse of the rotational relaxation time gives the collision frequency for rotational relaxation and can be expressed as a function of the effective rotational cross section σ_r . For a pure gas we have:

$$(\tau_r)^{-1} = 4n(kT_t / \pi m)^{\frac{1}{2}} \sigma_r \quad (2)$$

where m is the molecular mass, k the Boltzmann constant and n the jet local density. By using the isentropic relationships available in the literature [10], one can easily compute the local flow velocity, temperature or density. For a binary mixture, the mole fractions of the two components and reduced masses of the colliding pairs must be taken into account [10]. For the binary mixtures we have assumed an effective adiabatic coefficient, $\gamma_{\text{eff}}=1.64$, obtained by weighting the heat capacity ratio of N_2 ($\gamma=7/5$) and of the noble gases ($\gamma=5/3$) with their respective mole fractions. The evolution of T_t during these expansions will be thus close to that of a monoatomic gas.

Translational relaxation, i.e. the conversion of the random translational energy of the atoms and molecules in the jet, into directed kinetic energy of the flow, leads to the low translational temperatures displayed in Fig. 2. For the strongest expansions of the N₂-rare gas mixtures, temperatures lower than 1 K are reached. The degree of translational relaxation is usually expressed in terms of the speed ratio, which is defined as the quotient: $S = u / (2kT_t/m)^{1/2}$, where u is the local flow velocity. The speed ratio is a measure of the amount of translational energy remaining as thermal motion at a given point of the expansion. The terminal speed ratio, S_∞ , will be a function of the total number of binary collisions taking place in the expansion and of the collision cross section. A simple expression of the type:

$$S_\infty = A(Kn_0^{-1})^B \quad (3)$$

where Kn_0 is the source Knudsen number and A and B are constants, was obtained by Beijerinck and Verster [11] with a model which also assumed isentropic behaviour and a sudden freeze of the expansion. In this model the A and B constants depend only on γ and their values are [10] $A = 0.527$; $B = 0.545$ for $\gamma = 5/3$ and $A = 0.783$; $B = 0.353$ for $\gamma = 7/5$ respectively. The S_∞ corresponding to the experimental $T_{t,\infty}$ represented in Fig. 2, have been fitted with equation 3. Following Miller [10] we have used the expression:

$Kn_0^{-1} = \sqrt{2}n_0d(53C_6/kT_0)^{1/3}$ where d is the nozzle diameter and C_6 is the attractive term of a Lennard-Jones 6-12 potential. In the mixtures, we have assumed for simplicity, that translational relaxation is essentially caused by the major component and have used the noble gas C_6 coefficient. The C_6/k values used were [12]: 6.2×10^{-43} K.cm⁶ for N₂, 0.154×10^{-43} K.cm⁶ for He, and 0.8×10^{-43} K.cm⁶ for Ne. The results of the fit, represented in terms of $T_{r,\infty}$ as lines in figure 2, yielded $A = 1.02$ and $B = 0.31$ for pure N₂ [2]; $A = 0.34$ and $B = 0.62$ for the N₂/He mixture and $A = 0.70$ and $B = 0.47$ for the N₂/Ne mixture. The main dependence of S_∞ on Kn_0^{-1} (i.e. on p_0d for a fixed T_0) is carried by the B exponent and, as can be seen, the B constants for the mixtures with $\gamma_{\text{eff}} = 1.64$ are relatively close to the predictions of the model for $\gamma = 5/3$ whereas the smaller B value obtained for the expansions of pure N₂ is much closer to the prediction for $\gamma = 7/5$. The differences in the translational relaxation obtained in the expansions of monoatomic and diatomic gases is clearly seen in the lower panel of Fig. 3. It should be noted that the picture presented thus far is too simplistic and does not account for the

separation in the T_t of the two components of the N_2/He mixture observed for the weaker expansions (see Fig. 2).

For the derivation of the rotational relaxation cross sections, equation (1) has been integrated numerically for each $p_0 d_{eff}$ along the jet axis until the translational temperature reaches $T_{t,\infty}$. At this point, the calculated rotational temperature is compared to the measured $T_{r,\infty}$ and σ_r varied until a good fit to the experimental data is obtained. A single effective, i.e. temperature independent σ_r has been used for the fit of the set of data corresponding to the different expansions of N_2 and of each of the binary mixtures. The values obtained from the fits were: $\sigma_r^{N_2-N_2}(T_t=5-60 \text{ K}) \approx 35 \text{ \AA}^2$; $\sigma_r^{N_2-He}(T_t=5-80 \text{ K}) \approx 15 \text{ \AA}^2$ and $\sigma_r^{N_2-Ne}(T_t=5-60 \text{ K}) \approx 40 \text{ \AA}^2$, and the curves calculated with these cross sections are represented in Fig. 2. The use of a temperature independent σ_r is an approximation, but is useful for comparative purposes. Our results show that in this low temperature region, collisions with Ne atoms have roughly the same efficiency (or slightly more) than self-collisions for the relaxation of the rotational energy of N_2 . The likelihood of rotational relaxation through collisions with He is significantly smaller.

Experimental σ_r values for pure N_2 have been reported by a number of groups over a wide temperature interval (see [1,2] and the references therein). In ref. [2] we presented the result of a detailed study of the rotational relaxation of N_2 , derived a temperature dependent cross section $\sigma_r(T_t)$ with a maximum of $50-60 \text{ \AA}^2$ corresponding to $T_t \approx 20-30 \text{ K}$ and attributed the decline of $\sigma_r(T_t)$ with decreasing T_t below that maximum to the reaching of the adiabatic regime for rotational energy transfer. We also noted the discrepancy with the very high σ_r from a recent EIF experiment [6]. In this work, we have just taken the average $\sigma_r^{N_2-N_2}$ for consistency with the lower resolution analysis performed on the present preliminary data corresponding to N_2-He and N_2-Ne .

Experimental values for the σ_r of the gas mixtures studied here are scarce. Kistemaker and de Vries [13] have reported room temperature rotational relaxation times in nitrogen-noble gas mixtures derived from acoustical absorption measurements. From their results, the following cross sections are inferred: $\sigma_r^{N_2-He} \approx 3-6.5 \text{ \AA}^2$ and $\sigma_r^{N_2-Ne} \approx 10-16 \text{ \AA}^2$ reflecting the lower efficiency of He for the rotational relaxation of nitrogen. Most experimental studies of the rotational relaxation of nitrogen at room temperature (see [1] and references therein) lead to $\sigma_r^{N_2-N_2}$ in the $8-12 \text{ \AA}^2$ range, comparable or somewhat lower than the cross section for relaxation with Ne. This trend

is the same as the one observed in our low T experiments, but the room temperature cross sections are smaller.

The rotational relaxation of N₂ mixtures with noble gases in free jets was studied by Poulsen and Miller [14] and by Faubel and Weiner [7]. They both used the EIF technique for the determination of N₂ rotational temperatures, which, as mentioned above, is subject to uncertainties in the interpretation of the data [2,5]. From these measurements, Poulsen and Miller derived a $\sigma_r^{N_2-He} = 3 \text{ \AA}^2$, much lower than the value of the present work. Faubel and Weiner did not provide σ_r values and their measurements have been performed with different N₂ mole fractions which renders a comparison of $T_{r,\infty}$ or $T_{t,\infty}$ difficult.

In a more recent work, Belikov and Sharafutdinov [15] used also the EIF method for the study of rotational relaxation in a free jet of N₂ diluted in He. They extrapolated below 70 K the rotational relaxation times obtained from transport collision integrals available for three N₂-He potentials termed respectively HFD1 [16], BTT [17] and M3SV [18] and from a comparison with their measured T_r concluded that the HFD1 potential was too anisotropic and lead to an overestimation of the rotational relaxation, whereas the other two potentials lead to a good agreement with the measurements. The corresponding σ_r show a monotonic increase with decreasing temperature. In the 5-70 K range they vary between ≈ 15 and $40 \text{ \AA}^2$ for the HFD1 potential, between 7 and $20 \text{ \AA}^2$ for the BTT and between 7 and $30 \text{ \AA}^2$ for the M3SV. Our experimental cross section ($\sigma_r^{N_2-He} \approx 15 \text{ \AA}^2$) is consistent with the σ_r from the two later potentials, but is smaller than the σ_r corresponding to the HFD1 one, thus corroborating the results of Belikov and Sharafutdinov.

4. Summary and Conclusions

Molecular relaxation in supersonic free jets of pure N₂ and of N₂ diluted in He and Ne has been investigated at low temperatures using a combination of REMPI and TOF techniques. The strong translational cooling observed and the different evolution of the terminal translational temperatures between pure N₂ and N₂-rare gas mixtures can be approximately accounted for by assuming isentropic behaviour and a sudden freezing of the flow properties. The populations of N₂ rotational states found at the end of the expansions correspond to Boltzmann distributions describable by a $T_{r,\infty}$, which is

always larger than the corresponding $T_{t,\infty}$. The cross-sections for rotational relaxation in the low T (<60-80 K) range are larger than those at $T = 300$ K but maintain the qualitative trend observed at room temperature, namely $\sigma_r^{N_2-N_2} \approx \sigma_r^{N_2-Ne} > \sigma_r^{N_2-He}$.

Very simple considerations can be of help for the rationalization of these results. The increase in σ_r with decreasing T_t is a general behaviour in gas phase rotational relaxation, related to the fact that the collision time gets closer to the rotational period of the molecule, facilitating energy transfer until the adiabatic limit is reached [2]. When comparing the different collision pairs, two factors should be taken into account: the anisotropy of the potential and the mismatch between the masses of the colliding partners. The larger the anisotropy and the more similar the masses, the higher the probability for rotation-translation transfer [13]. In the present case the large difference between the masses of He and N_2 prevails. The picture presented here is obviously too simple and invites improvement. Further experimental work and refinements of the model are underway in our group.

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Figure Captions

Figure 1 Experimental REMPI spectra of nitrogen in molecular beams extracted from $p_{0\text{eff}} \approx 0.9$ mbar cm expansions (solid lines) together with their theoretical simulations (dashed lines). Upper panel: expansion of pure nitrogen; middle panel expansion of a 10% mixture of N_2 in He; lower panel expansion of a 10% mixture of N_2 in Ne.

Figure 2 Evolution of the terminal rotational and translational temperatures in free jets of pure nitrogen (upper panel) and of its binary mixtures with He (middle panel) and with Ne (lower panel). The solid triangles represent the N_2 terminal rotational temperatures; the open circles, the terminal N_2 translational temperatures and the solid squares, the terminal translational temperatures of the corresponding noble gas.

Figure 3 Comparison of the evolution of the terminal rotational (upper panel) and translational (lower panel) temperatures of free jets of pure nitrogen (solid line) and of its 10 % mixtures with He (dashed line) and Ne (dotted line). The lines displayed correspond to the experimental fits shown in Fig. 2. Note the differences between the “nearly” monoatomic mixtures and the diatomic expansions of pure N_2 .

Fig 1

Fig. 2

Fig. 3