Low-Temperature Rotational Relaxation of N_2 in Collisions with Ne

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The rotational relaxation of nitrogen molecules in collisions with neon has been studied in supersonic expansions. N_2 rotational temperatures have been determined from resonance-enhanced-multiphoton-ionization (REMPI) spectra performed in a series of supersonic molecular beams of N_2 diluted in Ne. Terminal flow velocities and translational temperatures for the two expansion partners have been obtained from mass-selected time-of-flight measurements. From the measured data, the approximate isentropic behavior of the expansion could be verified and the thermal cross section for N_2/Ne rotational relaxation at very low temperatures could be derived. The cross section increases from a value of $\approx$35 Å^2 at 5 K, goes through a maximum of about 55 Å^2 between 10 and 20 K, and then decreases smoothly to $\approx$25 Å^2 for $T = 60$ K. The relaxation cross section for N_2/Ne collisions is larger than that for N_2/N_2 collisions below roughly 20 K and smaller above this temperature.

1. Introduction

Experimental studies of rotational energy transfer between nitrogen molecules and noble-gas atoms have been performed since the 60s.[1] An extensive investigation of the rotational relaxation of N_2 by He, Ne, Ar, and Xe, reported by Kistemaker and de Vries,[2] found the trend Ne > Ar > Xe > He for the relaxing efficiency of the different colliding partners. A comparison with previous studies (see the works cited in ref 3) showed that the relaxation rates of N_2 in collisions with Ne and Ar were somewhat larger than in self collisions, whereas on the other hand, He/N_2 collisions were less efficient for relaxation than N_2/N_2 collisions. Good agreement was obtained between the experimental data and the results of a trajectory calculation performed by the same authors[2] on a simple Morse type potential. A rationalization of the results based on a simple model relating the different masses and the moment of inertia of the molecule led to the conclusion that the relative relaxing propensity of the various noble gases was rather determined by the relation between the masses of the colliding partners than by the possible differences in the anisotropies of the intermolecular potentials. The bulk phase experiments just commented on were based on acoustic techniques and restricted to a temperature close to 300 K.

The lower temperature region was later explored in free jet experiments performed by various groups.[4−8] In all these experiments, the electron impact fluorescence (EIF) technique was used for the determination of the rotational temperatures. Even though this method has been extensively used for the measurement of rotational temperatures in supersonic jets and molecular beams of nitrogen, it turns out that the derivation of rotational state distributions is complicated and often controversial. Therefore, a comparison of the EIF data with other complementary techniques is highly desirable.[9−12] Various optical spectroscopic methods have also been used for the measurement of rotational populations in jets and beams of N_2 (see refs 9, 12, and 13 and references therein). Among these methods, the technique of resonance-enhanced multiphoton ionization (REMPI) has proven very useful[12,14−16] due to the existence of suitable schemes for the excitation and ionization of this molecule. The combination of high resolution and very high sensitivity inherent to the REMPI method makes possible the detection of individual rotational levels for very low nitrogen densities. The technique was first applied by Mazely and Smith[14] to the investigation of free jets of pure N_2 and was extended later by Smith and co-workers to the study of relaxation in binary mixtures of various small molecules and atoms.[17−19]

Most of the free jet measurements about the relaxation of N_2 in collisions with rare-gas atoms have centered on the N_2/Ar and N_2/He pairs,[4−8] but hardly any rotational temperatures are available for the N_2/Ne system,[5] and no relaxation cross sections were derived from these data.

From a theoretical point of view, a variety of cross sections relevant for a wide range of transport, relaxation, and scattering processes governed by Ne/N_2 collisions have been calculated with different theoretical methods[2,20−23] for some of the various versions of the N_2/Ne interaction potential,[2,20,24−27] but no theoretical calculations of the thermal rotational relaxation cross section have been reported for the N_2/Ne collision system at temperatures below 77 K. However, the lower temperature region is certainly of great interest. In a recent work by our group,[12] the rotational relaxation in supersonic expansions of pure molecular nitrogen was investigated in the approximately 5−80 K temperature interval and significant discrepancies were found with previous EIF data[7] for temperatures below 30 K. Whereas the EIF data led to very high relaxation cross sections (several hundred Å^2 for T < 20 K) monotonically increasing with decreasing T, our REMPI experiments indicated the

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existence of a maximum at 20−30 K with cross-section values in the 50−60 Å^2 range. The decrease in the cross section for very low translational temperatures was attributed to the reaching of the adiabatic regime for rotational energy transfer.

In the present work, we have carried out an investigation of the rotational relaxation of N_2 in collisions with Ne over a similar temperature range (≈5−60 K), which includes also the transition to the adiabatic regime for rotational energy transfer. The experimental procedure used is analogous to that of our previous work on pure nitrogen[12] and is based on a combined measurement of translational and rotational temperatures at the end of a series of supersonic expansions of mixtures of N_2 diluted in Ne. Although the REMPI experimental technique used for the measurement of rotational temperatures provides the rotational populations of the N_2 molecules, we have not attempted to extract information about the relaxation of individual levels from the data, but have rather concentrated on the determination of the average rotational relaxation cross section as a function of temperature, and on the verification of the near isentropic behavior of the translational energy in our free jets, which underlies the current model used for the derivation of the rotational relaxation cross section.

2. Experimental Section

The experimental arrangement used for the present measurements is described elsewhere,[12,13,28] and only the relevant details are given here. Free jets of N_2 diluted in Ne (with a 0.1 mol fraction of N_2) were generated by expanding the gases from either a pulsed or a continuous source at room temperature. For the pulsed expansions, a commercial solenoid-driven valve was used with a pulse frequency of ≈10 Hz and a pulse length of 0.5−1 ms. The gas pulses had a flat region (plateau) in the center with an effective opening diameter[13] $d_{\mathrm{eff}} = 0.4$ mm (±10%). The source of the continuous jets was a circular pinhole with a diameter of 0.195 mm (±5%) perforated in a 0.1 mm stainless steel foil. In all the experiments, the jet sources were kept at room temperature ($T_0 = 293$ K). The source pressures, p_0, were varied between ≈15 and 2500 mbar, and the relevant p_0d_{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 s^{-1} oil diffusion pump. The highest gas load to the expansion chamber was caused by the continuous nozzle, but this gas source was used only for weak expansions ($p_0d_{\mathrm{eff}} < 8$ mbar cm), where the quality of the pulses from the solenoid valve deteriorated. The background pressure of the expansion chamber was always in the 10^{-4}−10^{-5} mbar interval. Supersonic molecular beams were extracted by collimating the central part of the free jets with a skimmer placed at about 3−5 cm distance from the nozzle. These beams traveled along an arrangement of interconnected vacuum chambers toward the analyzers. Beyond the skimmer, the pressure was always lower than 5×10^{-6} mbar, and in the detection chambers, turbomolecular pumps kept the pressure in the 10^{-7} mbar range. Time-of-flight (TOF) distributions of the molecular pulses generated by the narrow (1 mm width) slits of a mechanical chopper placed in the chamber behind the skimmer were measured for the nitrogen molecules and for the Ne atoms by means of a quadrupole mass spectrometer (QMS). To synchronize the pulses of the low-frequency solenoid-driven valve with the chopper, the reference signal of the chopper (with a frequency of ≈400 Hz) was sent to a frequency divider (f/32) and then to the valve through a delay generator; the time delay was selected in such a way that the center of the pulse of molecules passed through the chopper position in coincidence with the next chopping window. This central part (plateau) of the pulse corresponds to a quasisteady flow characterized by the effective opening diameter (see ref 13 for more details). The output of the QMS was sent to a digital scope where the data could be adequately processed and stored. Extensive averaging of the TOF spectra (up to 64 000 averages) was needed for the weakest (continuous) expansions.

Terminal flow velocities, $u_{\parallel,\infty}$, and translational temperatures, $T_{\parallel,\infty}$, were determined for N_2 and Ne from the deconvolution of the TOF spectra with a Maxwellian velocity distribution along the axial ("parallel") streamline of the jet, superimposed to the flow velocity, $u_{\parallel}$. The flight path between chopper and detector was 48 cm, and the geometric gate function of this chopper was 24−29 μs (depending on the skimmer used). For a given p_0d_{eff} value, no significant variations were observed in the flow velocities or translational temperatures when changing the source, the skimmer, or the nozzle−skimmer distance.

The terminal rotational temperatures of the nitrogen molecules were obtained from REMPI spectra performed on the molecular beams.[12] A (2 + 2) REMPI scheme based on the two-photon resonant excitation of N_2 to the (1,0) vibrational band of the a $^1\Pi_g \leftarrow X\ ^1\Sigma_g^+$ transition was used. The required 283−285 nm tunable laser radiation was generated in 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} (fwhm), 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 N_2^+ ions formed were detected by means of a time-of-flight mass spectrometer of the Wiley−McLaren type provided with a dual microchannel plate. The procedure for the evaluation of rotational distributions from the N_2 REMPI spectra is described in detail in ref 12. In short, the rotational line REMPI intensities are corrected with the appropriate two-photon line strengths and are then least-squares fitted to a Boltzmann distribution. No significant deviations from Boltzmann distributions were observed, and, in particular, the same rotational temperature, $T_{r,\infty}$, fitted correctly the population of the ortho and para N_2 species.

3. Results and Discussion

Figure 1 shows three REMPI spectra of molecular nitrogen together with their best-fit simulations. These spectra correspond to three different expansions representative of the range of temperature values studied. As expected, a noticeable attenuation of the REMPI lines associated to the high rotational states of N_2 and, hence, an enhancement of the rotational cooling ultimately attained in the expansion are observed with growing p_0d_{eff}. The good agreement between the measured spectra and those simulated assuming a Boltzmann distribution for the rotational levels of N_2 in the molecular beams can be appreciated in this figure. This agreement warrants use of a rotational temperature as a measure of the rotational energy content under the present experimental conditions. Possible small deviations of some of the rotational levels from the assumed Boltzmann distribution do not invalidate the global good accordance and have not been addressed in this work.

The experimental and simulated time-of-arrival distributions of N_2 and Ne for expansion conditions similar to those of Figure 1 are shown in Figure 2. The increasing translational cooling with growing p_0d_{eff} becomes evident from the narrowing of the corresponding time-of-flight distributions. For a given expansion, the TOF spectra of N_2 are noisier than those of Ne because of the relatively small amount of nitrogen in the mixtures and

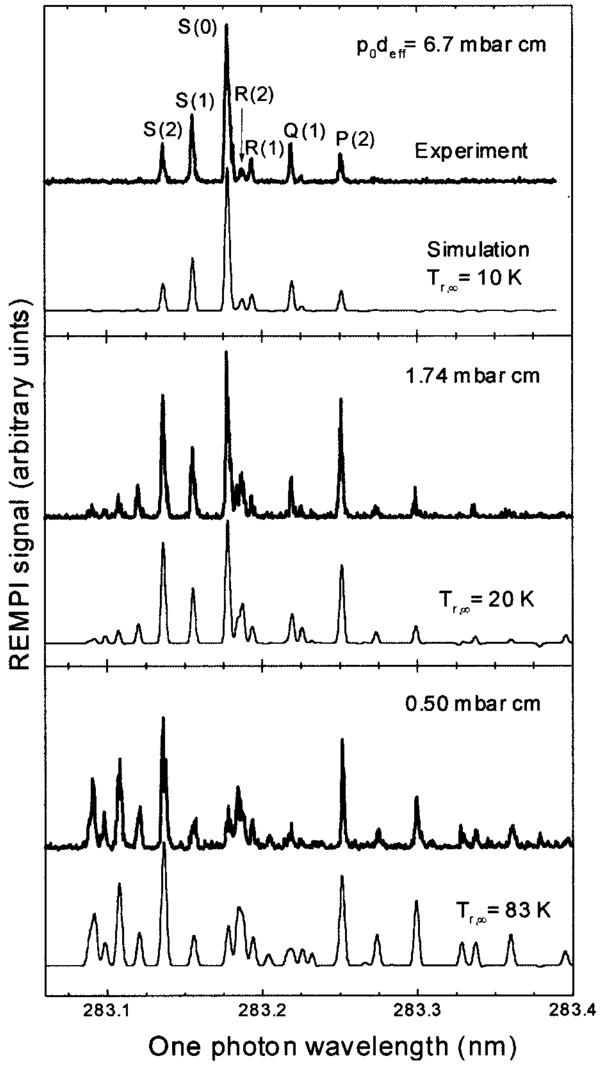

Figure 1. Molecular beam REMPI spectra of N_2 for three representative supersonic expansions of a N_2(10%)/Ne mixture. The terminal rotational temperatures determined from the simulation of the spectra are also given in each panel. The intensive cooling associated with the growing strength of the expansion, as characterized by the p_0d_{eff} parameter, is apparent in this figure.

the higher continuous background for $m/e^- = 28$. As can be seen, the functional two-parameter "drifting Maxwellian" form[12] assumed for the velocity distribution of the species in the beam reproduces the measurements satisfactorily, and no attempt has been made to improve the fits by introducing additional parameters. For the stronger expansions shown in Figure 2, the final flow velocities and translational temperatures of the two components in the expanding mixture are very similar. In the case of the weakest expansion (p_0d_{eff} = 0.5 mbar cm), the temperature obtained for N_2 is somewhat larger than that for Ne.

The whole set of experimental terminal flow velocities and translational temperatures of N_2 and Ne and the final rotational temperatures of N_2 are displayed in Figure 3 as a function of p_0d_{eff}. For the strongest expansions considered in this work, translational relaxation is very efficient and temperatures lower than 1 K are reached. For the weakest expansion, the translational temperatures are around 80−90 K. It is interesting to note that the near coincidence between the terminal flow velocities and translational temperatures of N_2 and Ne shown in the upper panels of Figure 2 extends to most of the cases studied; the terminal flow velocities of N_2 and Ne never differ by more than 5% (in fact, except for the weakest expansion studied, they never differ by more than 2%), and for p_0d_{eff} values larger than 0.5 mbar cm, the terminal translational temperatures are always quite similar, which suggests that translational equilibrium between the two mixture components is essentially maintained along the free jet. On the other hand, the terminal rotational temperatures are always higher than the corresponding translational ones, although the divergence becomes gradually smaller with increasing p_0d_{eff}. For the strongest expansions investigated (p_0d_{eff} > 30 mbar cm), the translational and rotational temperatures derived from the data are within their respective experimental errors.

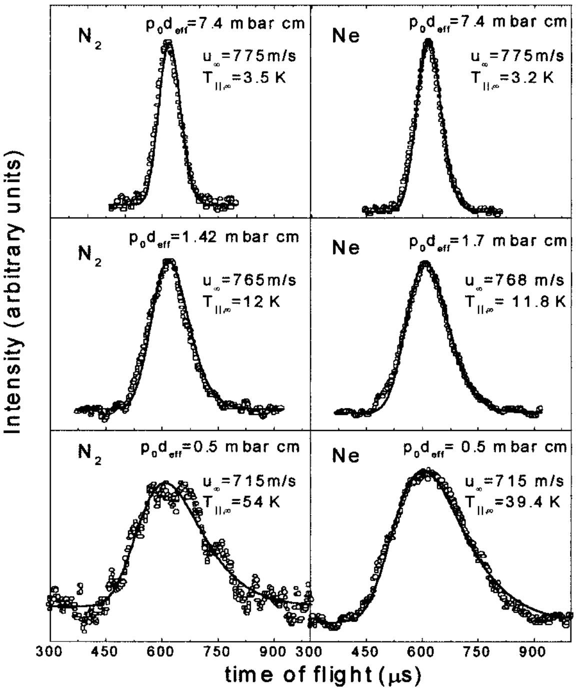

Figure 2. Molecular beam TOF spectra (symbols) of the two mixture components for expansion conditions analogous to those of Figure 1. The right panels correspond to Ne and the left ones to N_2. The terminal flow velocities and translational temperatures derived from the fit of the TOF spectra (solid lines) are also given in the figure.

The observed lack of thermal equilibrium between the terminal translation and rotation contains information about the probability of collisional relaxation of the rotational energy. To extract this information, the measured data should be reproduced with an accurate simulation of the supersonic expansions, including the exchange of energy between the various degrees of freedom of the gas and that of the hydrodynamic flow. Although in recent times significant progress is being made toward a detailed diagnostic and characterization of free jets,[29−33] a rigorous description is still beyond reach in the general case. Most studies of relaxation in supersonic expansions, carried out with axisymmetric nozzles, have centered on the axial properties of the expansion and have resorted to approximate solutions of the Boltzmann equation[34,35] or to thermal conduction models of varying complexity.[36−38] These approaches have proven in general adequate for expansions of pure gases of small molecules, and even those based on very simple models have been useful for the estimate of averaged relaxation cross sections. For expansions of binary mixtures, the situation is considerably more complex. Some attempts have been made to derive correlations for the terminal translational temperatures of the two components either from empirical data or from an extension of the Boltzmann equation formalism initially developed for free jets of monatomic gases (see refs 39 and 40 and

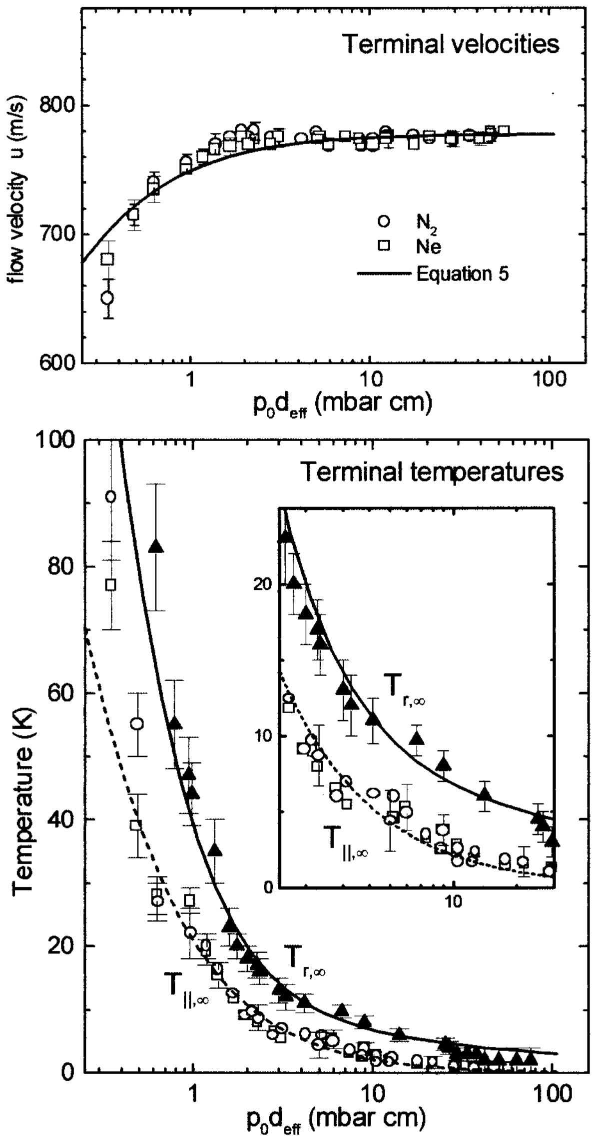

Figure 3. Terminal flow velocities and terminal temperatures derived from the REMPI and TOF measurements. The upper panel shows the terminal flow velocities of N_2 (circles) and Ne (squares) as a function of p_0d_{eff}. The solid line corresponds to the model calculation of eq 5. The lower panel and inset show the terminal translational temperatures of N_2 (circles) and Ne (squares) and terminal rotational temperatures of N_2 (triangles) as a function of p_0d_{eff}. The curves running through the measured translational and rotational temperatures correspond, respectively, to the computation of eq 6 and to the integration of eq 1 with the $\sigma_{r,N_2-Ne}(T_t)$ represented in Figure 4.

references therein). However, the correlations thus obtained are relatively complicated, and the experimental proof is scarce and mostly limited to binary mixtures of noble gases, where internal degrees of freedom do not complicate the analysis.

In the present work, we will extend the simple "sudden-freeze" thermal conduction model applied in our previous works[12,28] to the present diluted binary mixtures to estimate the averaged rotational relaxation cross section of nitrogen in collisions with Ne as a function of (translational) temperature, $\sigma_{r,N_2-Ne}(T_t)$, from the observed differences between $T_{r,\infty}$ and $T_{t,\infty}$. The model allows for 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. In addition, continuous (isotropic) flow is assumed until the end of the expansion, which implies equilibrium among the translational components along and perpendicular to the beam axis (i.e., $T_{\|,\infty} = T_{t,\infty}$). For the conditions of the present work with the jet source kept at room temperature, the vibrational mode of N_2 can be obviated.[12] In the course of the expansion, the rotational temperature is assumed to be coupled to the "translational thermal bath" provided by the jet through the well-known linear equation

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

where τ_r is the rotational relaxation time. The inverse of the rotational relaxation time gives the global collision frequency for rotational relaxation which includes both N_2/N_2 and N_2/Ne collisions:

$$(\tau_r)^{-1} = (\tau_{r,N_2-N_2})^{-1} + (\tau_{r,N_2-Ne})^{-1} \qquad (2)$$

Equation 2 can be expressed as

$$(\tau_r)^{-1} = \left(\frac{8kT_t}{\pi}\right)^{1/2} n\{\sqrt{2}\chi_{N_2}{m_{N_2}}^{-1/2}\sigma_{r,N_2-N_2}(T_t) + (1-\chi_{N_2}){\mu_{N_2-Ne}}^{-1/2}\sigma_{r,N_2-Ne}(T_t)\} \qquad (3)$$

where k is the Boltzmann constant, n is the local density, m_{N_2} is the molecular mass of nitrogen, μ_{N_2-Ne} is the reduced mass of the N_2/Ne colliding pair, χ_{N_2} is the mole fraction of nitrogen, and $\sigma_{r,N_2-N_2}(T_t)$ and $\sigma_{r,N_2-Ne}(T_t)$ are the cross sections for rotational relaxation of nitrogen in self collisions and in collisions with Ne, respectively.

For the derivation of $\sigma_{r,N_2-Ne}(T_t)$, eq 1 must be integrated numerically for each p_0d_{eff} value along the jet axis; this requires a knowledge of T_t, n, and $\sigma_{r,N_2-N_2}(T_t)$. In general, when dealing with free jets of pure gases, T_t and n are computed from current isentropic relations.[40] The hypothesis of isentropic behavior can be extended to binary mixtures, but, in this case, additional assumptions are needed and it is worth addressing the jet translational properties in some more detail.

Given the similarity of the final flow velocities and translational temperatures commented on above, it is reasonable, in principle, to describe the expansions of the N_2/Ne mixture studied with a single effective adiabatic coefficient, γ_{eff}, and a single effective molecular mass, m_{eff}. The value $m_{eff} = 20.98$ is readily obtained from the average

$$m_{eff} = \sum_i \chi_i m_i$$

where χ_i and m_i are the mole fraction and molecular mass of species i (i = Ne or N_2), respectively. The adequate value for γ_{eff} has been calculated by weighting the constant-pressure heat capacities of N_2 and Ne with their respective mole fractions in the form suggested by Miller:[40]

$$C_{eff} = R\frac{\gamma_{eff}}{\gamma_{eff} - 1} = \sum_i \chi_i C_i = R\sum_i \chi_i \frac{\gamma_i}{\gamma_i - 1} \qquad (4)$$

where R is the gas constant. The mole average specific heat of the expanding gas is finally given by $c_{eff} = C_{eff}/m_{eff}$. Equation 4 yields the value $\gamma_{eff} = 1.625$, which indicates that the evolution of T_t during the expansion will be thus much closer to the monatomic gas limit ($\gamma = {}^5/_3 = 1.67$) than to the "frozen-vibration" diatomic gas limit ($\gamma = {}^7/_5 = 1.4$).

The assumption of an approximate isentropic behavior corresponding to γ_{eff} can be assessed by considering the measured values of the terminal flow velocities and translational temperatures. At a given point of the jet, the degree of translational relaxation, i.e., the effective conversion of the random translational energy of the atoms and molecules into directed kinetic energy of the flow in the course of the continuous supersonic expansion, is often expressed in terms of the local speed ratio, which is defined as the quotient $S = u/(2kT_t/m)^{1/2}$, where u is the local flow velocity. The ultimate degree of translational relaxation attained in a supersonic expansion is thus given by the terminal speed ratio, S_∞. If we assume that the end of the expansion is essentially determined by the ceasing of the predominant Ne−Ne collisions, the terminal flow velocity and translational temperature for the expansions of our N_2/Ne mixture can be expressed approximately as functions of $S_{\infty,\mathrm{Ne}}$.

$$u_\infty \approx S_{\infty,\mathrm{Ne}}\left(\frac{2kT_0}{m_{\mathrm{eff}}}\right)^{1/2}\left[1 + \frac{\gamma_{\mathrm{eff}} - 1}{\gamma_{\mathrm{eff}}}S_{\infty,\mathrm{Ne}}{}^2\right]^{-1/2} \tag{5}$$

$$T_\infty \approx T_0\left[1 + \frac{\gamma_{\mathrm{eff}} - 1}{\gamma_{\mathrm{eff}}}S_{\infty,\mathrm{Ne}}{}^2\right]^{-1} \tag{6}$$

S_∞ depends on the total number of binary collisions taking place in the expansion, as well as on the relevant collision cross sections. This twofold dependence can be expressed in terms of the Knudsen number at the source exit, Kn_0. Using a "sudden-freeze" model for isentropic expansions of pure gases, Beijerinck and Verster[36] have derived a simple expression for the terminal speed ratio:

$$S_\infty = A[Kn_0{}^{-1}]^B \tag{7}$$

where A is a γ-dependent constant[40] ranging from 0.527 for $\gamma = {}^5/_3$ to 0.783 for $\gamma = {}^7/_5$ and $B = 3(\gamma - 1)(\gamma + 2)$. The main dependence of the terminal speed ratio on the source Knudsen number is contained in the B exponent, which takes the value 0.545 for $\gamma = {}^5/_3$ and 0.353 for $\gamma = {}^7/_5$. Correlations similar to that of eq 7, based on simple models or on empirical data, have been derived by other authors both for atoms[34,41,42] and for small molecules.[12,43] These works lead also to a B exponent close to 0.5 for atoms and to 0.3 for small molecules.

The above considerations suggest that the terminal speed ratio of Ne appearing in eqs 5 and 6 may be estimated by applying eq 7 to the experimental conditions of the present work:

$$S_{\infty,\mathrm{Ne}} \approx A(\gamma_{\mathrm{eff}})[Kn_{0,\mathrm{Ne}}{}^{-1}]^{B(\gamma_{\mathrm{eff}})} \tag{8}$$

where $Kn_{0,\mathrm{Ne}} = \lambda_{0,\mathrm{Ne}}/d_{\mathrm{eff}}$ is the quotient between the source mean free path for Ne and the effective nozzle diameter. The inverse of this number can thus be expressed as

$$Kn_{0,\mathrm{Ne}}{}^{-1} = n_0 d_{\mathrm{eff}} m_{\mathrm{Ne}}{}^{1/2}\{\sqrt{2}\chi_{\mathrm{Ne}} m_{\mathrm{Ne}}{}^{-1/2}\sigma_{\mathrm{c,Ne-Ne}}(T_0) + (1 - \chi_{\mathrm{Ne}})\mu_{\mathrm{Ne-N_2}}{}^{-1/2}\sigma_{\mathrm{c,Ne-N_2}}(T_0)\} \tag{9}$$

where n_0 is the source molecular density, $\mu_{\mathrm{N_2-Ne}}$ is the reduced mass of the Ne/N_2 pair, and $\sigma_{\mathrm{c,Ne-Ne}}(T_0)$ and $\sigma_{\mathrm{c,N_2-Ne}}(T_0)$ are the source temperature cross sections for Ne atom collisions and for collisions between Ne atoms and N_2 molecules, respectively. For the calculation of the collision cross sections, we have used the expression[36,40] $\sigma_c(T_0) = (53C_6/(kT_0))^{1/3}$, where C_6 corresponds to the isotropic long-range interaction coefficients of the potential. For the present analysis, the following literature values were taken:[26,40] $(C_{6,\mathrm{Ne-Ne}}/k) = 0.76 \times 10^{-43}$ K cm^6 and $(C_{6,\mathrm{Ne-N_2}}/k) = 4.54 \times 10^{-43}$ K cm^6, which correspond to room-temperature collision cross sections of 24 and 43.5 Å^2, respectively.

The terminal velocities and temperatures calculated using eqs 5 and 6 with the $S_{\infty,\mathrm{Ne}}$ values obtained from eq 8 with $A = 0.57$ and $B = 0.51$ are represented in Figure 3. Except for the lowest $p_0 d_{\mathrm{eff}}$ values, the calculated curves give a good account of the experimental observations. For $p_0 d_{\mathrm{eff}}$ between 1 and 3, the observed terminal velocities are larger by 2−3% than those from the model, and only for $p_0 d_{\mathrm{eff}}$ values lower than 0.4−0.5 mbar cm, that is, for the two weakest expansions covered in the experiments, do the calculated curves deviate significantly from the measured values of temperature and velocity. It is also in this region where smaller velocities and higher temperatures are recorded for N_2 than for Ne, which suggests that the simple picture of a gas mixture characterized by a single γ_{eff} can be dubious for these low Knudsen number expansions. It is worth noting that the good global agreement observed between the calculations and the measurements requires A and B parameters close to the model values for $\gamma = {}^5/_3$ and in contrast with those obtained for expansions of pure nitrogen in previous works.[12,43] In fact, the assumption that the translational energy characteristics of the diluted free jets under study are entirely driven by Ne is also a fairly good approximation. Neglecting N_2/Ne collisions altogether in the model, i.e., dropping the corresponding term in eq 9 and using $\gamma = {}^5/_3$ instead of γ_{eff}, leads to terminal translational temperatures and flow velocities similar within 5−10% to those given by the curves of Figure 3.

The results commented on in the previous paragraphs support the hypothesis of nearly isentropic translational behavior corresponding to a single γ_{eff}. Consequently, eq 1 has been integrated numerically in a way analogous to that described in our previous works.[12,28] Isentropic relations, with $\gamma_{\mathrm{eff}} = 1.625$ and the corresponding Mach number values $M(\gamma_{\mathrm{eff}})$ interpolated between those tabulated in reference,[40] are used for the derivation of u, n, and T_t along the jet axis, as a function of the distance to the nozzle exit. The integration is pursued until the translational temperature reaches the experimental value for $T_{t,\infty} = T_{||,\infty}$. At this point, the calculated set of rotational temperatures as a function of $p_0 d_{\mathrm{eff}}$ is compared to the measured $T_{r,\infty}$, and $\sigma_{\mathrm{r,N_2-Ne}}(T_t)$ is varied until a good fit to the experimental data is obtained. The results of this fit to the experimental $T_{r,\infty}$ values are shown in the lower panel of Figure 3, whereas the corresponding best-fit of N_2/Ne rotational relaxation cross section, $\sigma_{\mathrm{r,N_2-Ne}}(T_t)$, is displayed in Figure 4. The $\sigma_{\mathrm{r,N_2-N_2}}(T_t)$ appearing in eq 3 has been taken from our previous work[12] on pure N_2 and is also shown in Figure 4 for comparison.

As can be seen in Figure 4, the N_2/Ne relaxation cross section determined in the present work grows initially with decreasing T_t until it reaches a maximum of ≈55 Å^2 for $T_t = 10-20$ K; below this temperature, the cross section decreases slightly to a value of about 35 Å^2 at 5 K. This decrease in the cross section observed at the lowest temperatures is most probably associated with the beginning of the adiabatic regime for the transfer of energy between rotation and translation (see discussion in ref 12). For T_t values below ≈20 K, the rotational relaxation of N_2 is more efficient in collisions with Ne than in self collisions, and the opposite is true for $T_t > 20$ K; however, the error bars of the two cross sections are large and the comparison should be taken with care. The experimental data are not sensitive to temperatures characteristic of the beginning of the expansions (100−300 K), where a relatively high number of collisions guarantees an equilibrium between translation and rotation for a wide range of values of the rotational relaxation cross section. In fact, the sensitivity of the experiment to the actual value of

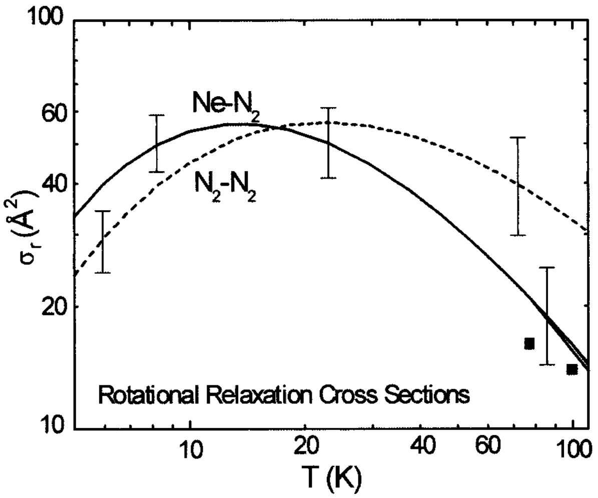

Figure 4. Rotational relaxation cross sections as a function of temperature: (solid line) cross section for the rotational relaxation of N_2 in collisions with Ne, $\sigma_{\mathrm{r,N_2-Ne}}(T_\mathrm{t})$, derived from the measurement of the present work (see Figure 3), as indicated in the text; (dashed line) rotational relaxation cross section for N_2/N_2 collisions from ref 12; (squares) rotational relaxation cross section for N_2/Ne collisions from the classical trajectory calculations of Wong et al.[21]

$\sigma_{\mathrm{r,N_2-Ne}}(T_\mathrm{t})$ decreases rapidly with growing temperature for T_t values higher than $\approx$60 K.

Few studies of the rotational relaxation in N_2/Ne mixtures have been reported thus far. Kistemaker and de Vries investigated the rotational relaxation of N_2−rare gas mixtures at 308 K with acoustic methods;[2] from the relaxation times determined by these authors, a Ne/N_2 cross section of about 10−16 Å^2 can be inferred. Unfortunately, our present experiment is insensitive to this high temperature. These measurements suggested that the relaxation of nitrogen in collisions with Ne was somewhat more efficient than in self collisions[3] and, in fact, the $\sigma_{\mathrm{r,N_2-N_2}}(T_\mathrm{t} \approx 300\ \mathrm{K})$ values obtained by various groups with different techniques lie between 8 and 12 Å^2 (see the references cited in ref 28). Over the low-temperature range investigated in the present work, this apparent trend is not maintained, as commented on in the previous paragraph. Faubel and Weiner[5] used the EIF technique for the determination of N_2 rotational temperatures in supersonic expansions of mixtures of neon and nitrogen. These authors, however, did not provide σ_r values, and in addition, their measurements were performed with different N_2 mole fractions, which renders difficult a comparison with our data. Over the whole p_0d_eff interval (11−84 mbar cm) investigated by Faubel and Weiner, the terminal translational temperatures of the two mixture components (with N_2 mole fractions ranging from 0.18 to 0.28) were very similar, which suggests that also for these conditions the two mixture components maintain translational equilibrium throughout the expansion and the corresponding free jets can be characterized by a single γ_eff. For N_2 mole fractions around 0.20, the terminal translational temperatures were found to decrease from $T_{\|,\infty} =$ 6−7 K at $p_0d_\mathrm{eff} = 11$ mbar cm to $T_{\|,\infty} = 2-3$ K at $p_0d_\mathrm{eff} = 29$ mbar cm. These values are somewhat higher than those of the present work, which is consistent with the higher proportion of nitrogen (lower γ_eff) in the mixtures used. Furthermore, the rotational temperatures of these experiments were estimated to lie in all cases below 10−11 K, but the uncertainty associated with the data reduction scheme chosen for the EIF data precludes any conclusion on the likelihood of rotational relaxation. Faubel and Weiner stress the possibility of aggregation processes in their supersonic expansions, some of which could raise the jet temperature and perturb the interpretation of the data; in fact, they observe a small amount of N_2 dimers for N_2/Ne expansions with p_0d_eff values larger than 27 mbar cm. No dimers were found in our experiments, which extend to higher p_0d values, because we worked with much larger nozzle diameters (0.2−0.4 mm as compared with 0.02−0.05 mm) and the probability of dimerization depends on the frequency of ternary collisions and scales approximately as $p_0^2d_\mathrm{eff}$.

Theoretical calculations of rotational energy transfer for the Ne/N_2 system have been performed by several groups using different versions of the intermolecular potential. These calculations range from quantum mechanical approximations of varying accuracy[20,21,23] to the application of scaling laws and simple models.[2,23] The comparison of some of these results as well as other calculations of macroscopic transport properties with experimental measurements has been the usual way to assess the quality of the various potential energy surfaces (PES) proposed for this system (see refs 20 and 24−26 and the references therein). The most thorough multiproperty check of an intermolecular potential energy surface for the N_2/Ne interaction was performed by Wong et al.[21] on the HFD3 PES.[25] These authors performed classical trajectory (CT) and infinite order sudden (IOS) calculations of an extensive set of effective cross sections governing a wide variety of transport and relaxation phenomena for Ne/N_2 mixtures. As far as we know, the only theoretical $\sigma_{\mathrm{r,N_2-Ne}}(T_\mathrm{t})$ data available are the CT values reported in this work, corresponding to the 77−673 K temperature interval; over this range, the CT cross sections grow also with decreasing T_t. The two lowest points of this calculation, corresponding to $T_\mathrm{t} = 100$ K and $T_\mathrm{t} = 77$ K, are shown in Figure 4. The calculated cross sections are somewhat lower than those of the present experimental determination, which suggests that the anisotropy of the HFD3 potential is nearly correct or slightly weak, although this indication should be taken with care, given the low sensitivity of our experiment for temperatures $T_\mathrm{t} > 60$ K (see error bars in Figure 4). At this point, it is interesting to observe that the conclusion of the global comparison of transport and relaxation properties carried out by Wong et al.[21] was exactly the opposite, namely, that the anisotropy of the HFD3 surface was too high, a conclusion that was also corroborated by the more sensitive experimental differential cross sections measured in the crossed beam experiments of Beneventi et al.[20] However, Wong et al.[21] also noted disagreement in the comparison of their CT $\sigma_{\mathrm{r,N_2-Ne}}(T_\mathrm{t})$ with experiment (which at the time was limited to the sound absorption experiment of Kistemaker and de Vries[2] at 308 K), and the present results seem to extend those discrepancies in the rotational relaxation cross section toward lower temperatures. Further experiments with improved resolution at higher temperatures as well as dynamical calculations of the cross sections over the 5−60 K temperature range on the various intermolecular potentials available would certainly help to clarify this point.

4. Summary and Conclusions

Thermally averaged rotational relaxation cross sections of N_2 in collisions with Ne have been obtained at very low temperatures from time-of-flight and resonance-enhanced-multiphoton-ionization measurements performed in molecular beams of N_2/Ne mixtures. Diluted mixtures (10% N_2 in Ne) were chosen to optimize the proportion of nitrogen−neon collisions.

The experimental results show that translational equilibrium between the two mixture components is maintained over most of the range studied. Hints of separation appear just for the lowest Knudsen number expansions, but a more thorough investigation would be needed in order to draw conclusions.

The rotational relaxation cross section derived from our measurements grows with decreasing temperature from roughly 25 Å^2 at 60 K up to a value of approximately 55 Å^2 at 10−20 K. For lower temperatures, the cross section decreases slightly, probably because of the onset of the adiabatic regime for energy transfer between translation and rotation. A comparison with our previous work[12] indicates that rotational relaxation in N_2/Ne collisions is more efficient than in self collisions at very low temperature (T_t < 20 K), but less efficient for higher temperature.

No theoretical rotational relaxation cross sections have been reported in the 5−60 K temperature range, where the sensitivity of the present experiment is highest, but an approximate comparison can be made with the classical trajectory results from Wong et al.[21] on the HFD3 potential surface,[25] which go down to 77 K. The higher values of the experimental cross section suggest a correct or slightly insufficient anisotropy of the potential, which is however in contradiction with the conclusion drawn from an extensive comparison of experimental and theoretical observables calculated using this potential. This interesting discrepancy is worth investigating in deeper detail.

An extension of the measurements toward higher temperatures would be very interesting in order to bridge the gap between the present data and the results of other calculations and measurements. Further work in this direction as well as investigations on the rotational relaxation in other binary gas mixtures are currently in progress in our laboratory.

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