

Low temperature rotational relaxation of N₂ in collisions with He

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Abstract

The rotational relaxation of N₂ in collisions with He has been investigated in free jets with a combination of resonance-enhanced-multiphoton ionization spectroscopy and time-of-flight techniques. From the measured data, a global cross section for rotational relaxation has been derived. The cross section grows from a value of $\approx 8 \text{ \AA}^2$ at 100 K to $\approx 18 \text{ \AA}^2$ at 5–15 K. For the weakest supersonic expansions investigated, a breakdown of the translational equilibrium between He and N₂ has been observed, that could be well accounted for by an isentropic jet model and classical collision cross sections.

1. Introduction

In their pioneering study on the rotational relaxation in nitrogen-rare gas mixtures, Kistemaker and de Vries [1] showed that, at room temperature, the relaxation of the N₂ rotation was less efficient in collisions with He than with the rest of the rare gases. Using a very simple model with a dumbbell intermolecular potential, they rationalised this result in terms of the large mass mismatch between the atom and the molecule.

Good quality potential energy surfaces (PESs) for the N₂-He system were obtained in the 1980s both from models and from empirical fits [2-5]. These PESs have very similar isotropic components but some of them differ appreciably in their anisotropies. Classical and quantum-mechanical (QM) dynamical calculations of varying accuracy, performed on these surfaces [6-12] were used for the derivation of transport and relaxation cross sections and for the simulation of crossed beam data. These works could not single out a "best" potential, but suggested that the anisotropy of the HFD1 PES of Fuchs *et al.* [2] was excessive, leading to too large rotational relaxation cross sections, σ_r , within the range of temperatures investigated, $T > 70$ K. The potential surface has been further refined in the nineties [13,14], but as far as we know, no rotational relaxation calculations have been reported on these new PESs.

Belikov *et al.* [15,16], extended the theoretical and experimental studies of N₂ rotational relaxation down to ≈ 10 K. The rotational temperatures, T_r , measured along their free jets of N₂/He mixtures, using the electron induced fluorescence (EIF) technique, could be reproduced with rotational relaxation cross sections ranging from $\sigma_r \approx 5-6.5 \text{ \AA}^2$ at 300 K to $\sigma_r \approx 12-20 \text{ \AA}^2$ at 10 K. In particular, these T_r were found to be compatible with the results of their infinite order sudden (IOS) calculations [16] on the M3SV PES [4]. The EIF technique is specially suited for the measurement of T_r of N₂ in

free jets, but the interpretation of the data is not straightforward and has lead sometimes to ambiguous or controversial results [17-19]. Complementary measurements from other spectroscopic techniques [20-25] are thus desirable.

In the present letter, we apply a combination of resonance-enhanced-multiphoton ionisation (REMPI) and time-of-flight (TOF) methods, already used in previous works [19,26,27], in order to investigate the translational and rotational cooling in free jets of N₂ diluted in He. From these data we have derived global σ_r in the ≈ 5 -100 K temperature range. The results are discussed and compared to former studies.

2. Experimental Section

The experimental arrangement used for the present measurements has been described elsewhere [19,22] and only the relevant details are given here. Free jets of N₂ diluted in He (with a 0.11 mole fraction in N₂) were generated by expanding the gas mixture from pulsed and continuous sources at room temperature. For the pulsed expansions a solenoid-driven valve (General Valve) was used with an effective diameter, $d_{eff}=0.4$ mm ($\pm 10\%$), a pulse frequency of 10 Hz and a pulse width of 0.5-1 ms. 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 thick stainless steel foil. The relevant $p_0 d_{eff}$ parameters ranged between 0.5 and 100 mbar·cm. The background pressure in the 50 l expansion chamber was kept always in the 10^{-4} - 10^{-5} mbar interval by a 2000 l s⁻¹ oil diffusion pump. Molecular beams were extracted by collimating the central part of the free jets with a skimmer at ≈ 3 -5 cm downstream from the nozzle. The beams travelled along an arrangement of interconnected vacuum chambers towards the analysers. 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 N₂ and

H₂. Terminal flow velocities, u_∞ , and parallel translational temperatures, $T_{//,\infty}$, were derived from the time-of-arrival distributions of the molecular pulses generated by the narrow slits of a mechanical chopper placed behind the skimmer [22]. The terminal rotational temperatures, $T_{r,\infty}$, of N₂ were obtained from REMPI spectra performed on the molecular beam [19,26]. 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. The required 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 rhodamine 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 laser power of ≈ 2 mJ/pulse, which guaranteed a quadratic dependence of the signal on the pulse energy, and the formed N₂⁺ 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

The rotational temperatures of N₂, derived from the REMPI spectra, are represented in Fig. 1 (bottom). No significant deviations from Boltzmann distributions of rotational states were observed in the analysis of the spectra and the same rotational temperature fitted correctly the population the *ortho* and *para* species. The terminal flow velocities and translational temperatures of N₂ and He are also shown in Fig. 1. The rotational temperatures of nitrogen are found to be higher than the translational temperatures of both gases over the whole range of $p_0 d_{eff}$ values investigated. In addition, in the expansions with $p_0 d_{eff} < 3$ mbar·cm the terminal translational temperatures of nitrogen are larger and the final flow velocities smaller than those of

He. These differences in $T_{//,\infty}$ and in u_∞ indicate that translational equilibrium between the two mixture components is not maintained in the weakest expansions, in contrast with the behaviour observed in our former study of N₂/Ne mixtures [26].

In order to explain the observations and to obtain an estimate of the thermally averaged rotational relaxation cross section of N₂ in collisions with He, σ_{r,N_2-He} , the simple thermal conduction model used in our previous works [19,26,28] has to be suitably modified. In this case, two different local translational temperatures T_{t,N_2} and $T_{t,He}$, reflecting the breakdown of translational equilibrium between the two co-expanding gases must be considered. Given the high proportion of He (89%) in the mixture, it is assumed that the cooling of N₂ is driven by the He expansion and that the evolution of $T_{t,He}$ along the jet centreline follows a monoatomic isentrope with $\gamma = 5/3$. It is further assumed that the expansion ceases abruptly ("sudden freeze") at the point where the translational temperature of He reaches its final value, $T_{t,\infty,He}$ (Note that this assumption implies $T_{t,\infty,He} = T_{//,\infty,He}$ [19]).

With these considerations, the coupling between the relevant temperatures is given by:

$$\frac{dT_{t,N_2}}{dt} = -\frac{1}{\tau_{c,N_2-He}} \{T_{t,N_2} - T_{t,He}\} \quad (1a)$$

$$\frac{dT_{r,N_2}}{dt} = -\frac{1}{\tau_{r,N_2-N_2}} (T_{r,N_2} - T_{t,N_2}) - \frac{1}{\tau_{r,N_2-He}} (T_{r,N_2} - T_{t,He}) \quad (1b)$$

where τ_{c,N_2-He} is the characteristic collision time between N₂ and He atoms, and τ_{r,N_2-N_2} and τ_{r,N_2-He} are the rotational relaxation times for N₂ in self-collisions and in

collisions with He, respectively. The collision frequencies (τ^{-1}) corresponding to these processes can be expressed as:

$$\left(\tau_{c,N_2-He}\right)^{-1} = \left(\frac{8kT_{t,He}}{\pi}\right)^{\frac{1}{2}} n(1-\chi_{N_2})\mu_{N_2-He}^{-\frac{1}{2}}\sigma_{c,N_2-He} \quad (2a)$$

$$\left(\tau_{r,N_2-N_2}\right)^{-1} = \left(\frac{8kT_{t,N_2}}{\pi}\right)^{\frac{1}{2}} \sqrt{2}n\chi_{N_2}m_{N_2}^{-\frac{1}{2}}\sigma_{r,N_2-N_2} \quad (2b)$$

$$\left(\tau_{r,N_2-He}\right)^{-1} = \left(\frac{8kT_{t,He}}{\pi}\right)^{\frac{1}{2}} n(1-\chi_{N_2})\mu_{N_2-He}^{-\frac{1}{2}}\sigma_{r,N_2-He} \quad (2c)$$

where, k is the Boltzmann constant, n the local density, m_{N_2} the molecular mass of nitrogen, μ_{N_2-He} the reduced mass of the N_2 -He colliding pair, χ_{N_2} the mole fraction of nitrogen, σ_{c,N_2-He} the N_2 -He collision cross section and σ_{r,N_2-N_2} and σ_{r,N_2-He} the cross sections for rotational relaxation of N_2 in self collisions and in collisions with He, respectively.

The terminal velocity and temperature of He in a supersonic expansion of a N_2 /He mixture with a small proportion of N_2 can be expressed [29] as:

$$u_{\infty,He} \approx S_{\infty,He} \left(\frac{2kT_0}{m_{eff}}\right)^{\frac{1}{2}} \left[1 - \frac{\gamma-1}{\gamma} S_{\infty,He}^2\right]^{-\frac{1}{2}} \quad (3)$$

$$T_{//,\infty,He} \approx T_0 \left[1 + \frac{\gamma-1}{\gamma} S_{\infty,He}^2\right]^{-1} \quad (4)$$

where $m_{eff} = \chi_{N_2} \cdot m_{N_2} + \chi_{He} \cdot m_{He}$ in eq. (3) is the average mass of the binary mixture

and $S_{\infty,He} = u_{\infty,He} / \left(2kT_{\infty,He} / m_{He}\right)^{\frac{1}{2}}$ is the terminal speed ratio of He. Within the model

of Beijerinck and Verster [30] (which is a “sudden freeze” model for the isentropic expansion of pure gases) the terminal speed ratio is given by:

$$S_{\infty,He} = A [Kn_0^{-1}]^B \quad (5)$$

where Kn_0 is the source Knudsen number and A and B are γ dependent constants, which take the values $A=0.527$ and $B=0.545$ for monoatomic gases ($\gamma=5/3$) [29,30] and we have assumed these values without optimization. The inverse of the Knudsen number can be written [29] as $Kn_0^{-1} = \sqrt{2}n_0 d_{eff} (53 C_{6,He}/kT_0)^{\frac{1}{3}}$, where n_0 and T_0 are the source number density and temperature and where the collision cross section, $\sigma_{c,He-He} = (53 C_{6,He}/kT_0)^{\frac{1}{3}}$ has been expressed in terms of the attractive term, $C_{6,He}$, of the interatomic potential [29,30]. Taking $C_{6,He}/k=0.154 \times 10^{-43}$ K cm⁶ for the He-He interaction [29] and substituting (5) in equations (3) and (4), the $u_{\infty,He}$ and $T_{//,\infty,He}$ can be calculated as a function of the source parameters. The results of these calculations are shown in Fig. 1 with dashed curves. The fairly good agreement found between the model predictions and the measurements for $u_{\infty,He}$ and $T_{//,\infty,He}$ over the whole range of source pressures investigated is gratifying given the lack of fit parameters in eqs.(3)-(5). Such good agreement suggests strongly that He expands indeed in an essentially isentropic way with $\gamma \approx 5/3$. The use of an average effective $\gamma_{eff} = 1.62$, in order to take into account the mole fraction of N₂ in the mixture [26], leads essentially to the same results.

For the derivation of σ_{r,N_2-He} , equation system (1) was integrated numerically for each $p_0 d_{eff}$ value along the jet axis until $T_{t,He}$ reaches $T_{//,\infty,He}$. At this point, the

calculated rotational temperature was compared to the measured $T_{r,\infty}$ and σ_{r,N_2-He} was varied until a good fit to the experimental data was obtained. The results of this fit are also shown in Fig. 1 (bottom), and the corresponding N₂-Ne rotational relaxation cross section is displayed in Fig. 2. In order to integrate equation system (1), it is necessary to introduce the values of the cross sections appearing in equations (2a) and (2b). In equation (2a), we have used $\sigma_{c,N_2-He} = \left(53 C_{6,N_2-He} / kT_0\right)^{\frac{1}{3}}$ [29,30] with $(C_{6,N_2-He}/k) = 1.27 \times 10^{-43} \text{ K cm}^6$ taken from the BTT PES [5] (the rest of the potentials available have similar values). In equation (2b), we have employed σ_{r,N_2-N_2} from our previous work [19]. The integration of equation system (1) provides also $T_{//,\infty}$ for N₂ as a function of $p_0 d_{eff}$, which are represented in the lower panel of Fig. 1 too. Note that these $T_{//,\infty,N_2}$ values have not been fitted to the points, but are directly obtained from the classical σ_{c,N_2-He} expression [29,30] using C_6 values from the literature. The good agreement between the calculated curve and the measured data lends support to the picture underlying the present model by which not only the rotation, but also the translational motion of N₂, coupled to the He cold bath through σ_{c,N_2-He} , cannot follow the rapid cooling of the rare gas when the collision frequency becomes too low.

Fig. 2, compares the present results for σ_{r,N_2-He} , with the cross sections for rotational relaxation of N₂ in self-collisions and in collisions with Ne obtained in our previous works [19,26]. With decreasing temperature, σ_{r,N_2-He} shows initially a monotonic growth, then it levels off and hints even at a very smooth maximum in the $T \approx 5\text{-}15 \text{ K}$ range. This change of behaviour is probably associated with the reaching of the adiabatic regime of inefficient rotational-translational transfer [19]. Over the whole

temperature range investigated, σ_{r,N_2-He} is much smaller than σ_{r,N_2-N_2} and σ_{r,N_2-Ne} , maintaining the trend observed previously at room temperature [1].

The theoretical cross sections available for $T < 300$ K, are compared to the present data in Fig. 3. At room temperature, all the calculations lead to σ_{r,N_2-He} within the $\approx 3-7$ \AA^2 interval, in agreement with the sound absorption experiment of Holmes *et al.* [31]. In the 100-77 K interval, which corresponds to the upper temperature sensitivity limit of our experiment, most theoretical σ_{r,N_2-He} are within the experimental uncertainty. The only exception corresponds to the IOS calculations [16] on the M3SV PES [4], which go down to 10 K and yield always too low cross sections as compared with the present measurements. Classical trajectory (CT) calculations [9] performed on this same PES do not extend below 77 K, but it is interesting to observe that between 200 and 77 K these CT σ_{r,N_2-He} are higher than the IOS ones and closer to the present experimental data.

Belikov *et al.* [15,16] performed EIF measurements along the centreline of free jets of N_2/He mixtures. Using a power law of the type $\sigma_r = AT^{-B}$, these authors fitted the results of various theoretical approaches [7,9,16] and extrapolated to the low temperature range. The $\sigma_r(T)$ thus obtained were then used to simulate the measured T_r as a function of the distance to the nozzle exit. This extrapolation to very low temperatures is, in principle, not warranted and although it can be used to derive a plausible range of σ_{r,N_2-He} values for comparison with the measurements, it should not be taken as a rigorous check of a given potential. The measurements were best reproduced with relaxation cross sections extrapolated from the results on the BTT PES and the M3SV PES (ranging from 6 \AA^2 at 100 K to $\approx 16-20$ \AA^2 at 10 K) and were even compatible with the IOS results (5 \AA^2 at 100 K to ≈ 13 \AA^2 at 10 K). The extrapolation of

the classical trajectory results on the BTT and M3SV PESs lies always within our experimental uncertainty and indicates thus the approximate agreement between the EIF measurements [15,16] and the present results. The values extrapolated from the calculations on the HFD1 potential (10 \AA^2 at 100K to 30 \AA^2 at 10 K) were too high for the simulation of the EIF experiments [15,16] and are also higher than those derived from our measurements over most of the temperature range. Results from other experimental techniques have not yet been published, but a recent experiment using Raman spectroscopy in free jets and sensitive to the 2-20 K temperature range, yields values of σ_{r,N_2-He} which are lower by 30 % than the present ones and lie within the mutual experimental uncertainty [25].

4. Conclusions

Translational and rotational cooling taking place in supersonic expansions of N_2 diluted in He has been investigated by means of REMPI and TOF techniques. In all the cases studied the final rotational temperatures of nitrogen were found to be higher than the translational temperatures of both mixture components. In the weakest expansions, the terminal translational temperatures of N_2 were also higher than those of He. By application of a thermal conduction model to describe the energy-momentum exchange in the gas expansion, σ_{r,N_2-He} were derived in the ≈ 5 -100 K temperature interval. The cross section grows with decreasing temperature from $\approx 8 \text{ \AA}^2$ at 100 K to $\approx 18 \text{ \AA}^2$ at 5-15 K. The same model could reproduce well the translational disequilibrium between N_2 and He by assuming a classical collision cross section (with a $T^{-\frac{1}{3}}$ dependence) and using literature values for the attractive term of the N_2 -He interaction. The σ_{r,N_2-He} values are in rough agreement with other inferred from previous EIF measurements, and

also with the prediction of calculations on the state-of-the-art potential energy surfaces. However, the present σ_{r,N_2-He} are significantly higher than those from the only theoretical calculation (performed within the IOS approximation on the M3SV PES) available over the temperature range relevant for this experiment.

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Figure Legends

Figure 1. Terminal flow velocities (top) and temperatures (bottom). Symbols: experimental data. Long-dash lines: model calculations for $u_{\infty, He}$ and $T_{//, \infty, He}$ using equations (3) and (4). Solid and short-dash lines: result of the integration of equation system (1) for T_{t, N_2} and T_{r, N_2} with the rotational relaxation cross section σ_{r, N_2-He} of Fig. 2 and the classical collision cross section $\sigma_{c, N_2-He} = \left(53 C_{6, N_2-He} / kT_0\right)^{1/3}$, with C_{6, N_2-He} from [5].

Figure 2. Comparison of σ_{r, N_2-He} (present work) with σ_{r, N_2-N_2} [19] and σ_{r, N_2-Ne} [25].

Figure 3. Comparison of σ_{r, N_2-He} with the results of theoretical calculations on three different potential energy surfaces for the N_2He system. CC: close coupling calculation; CT: classical trajectories; IOS: infinite order sudden approximation.

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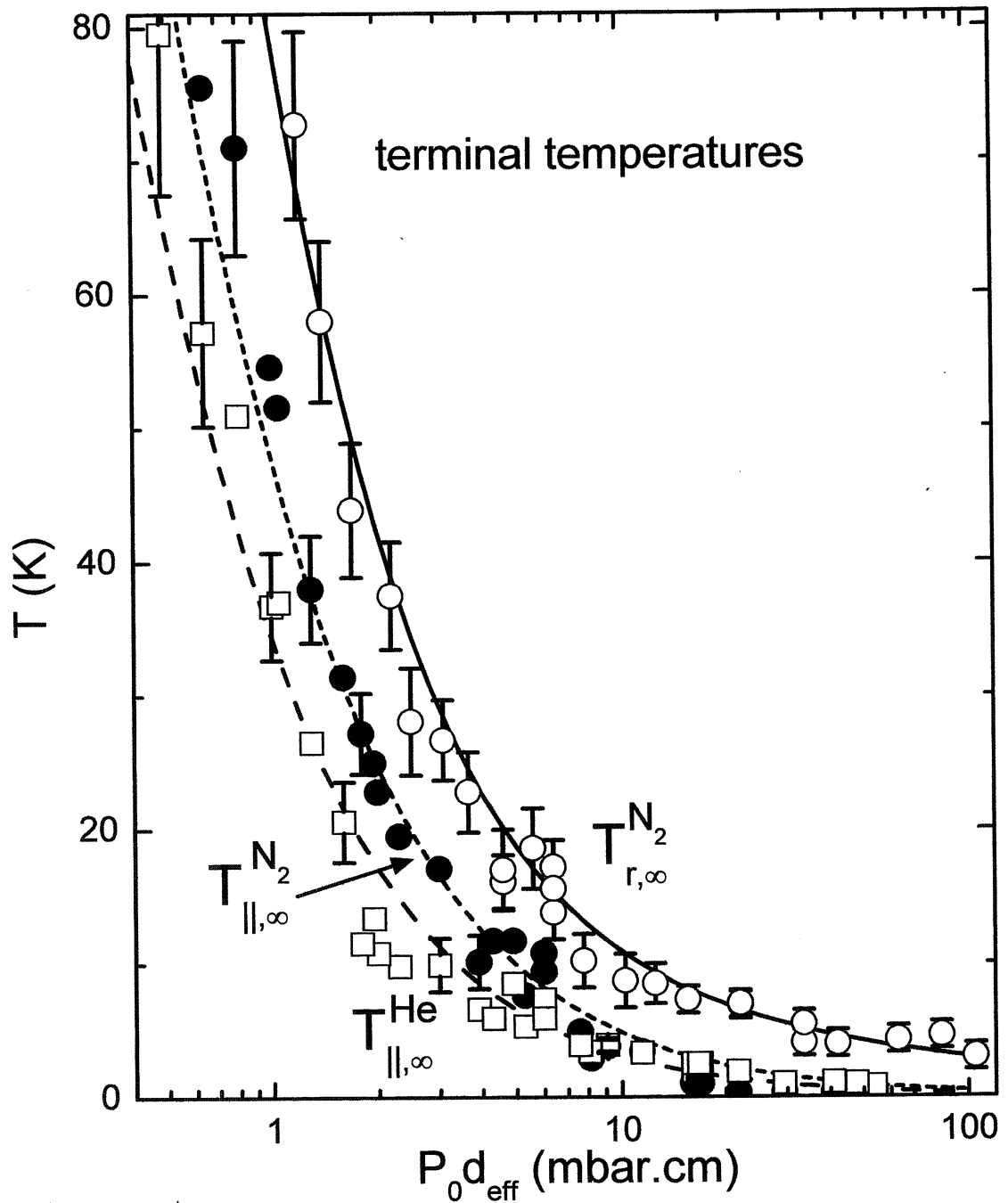
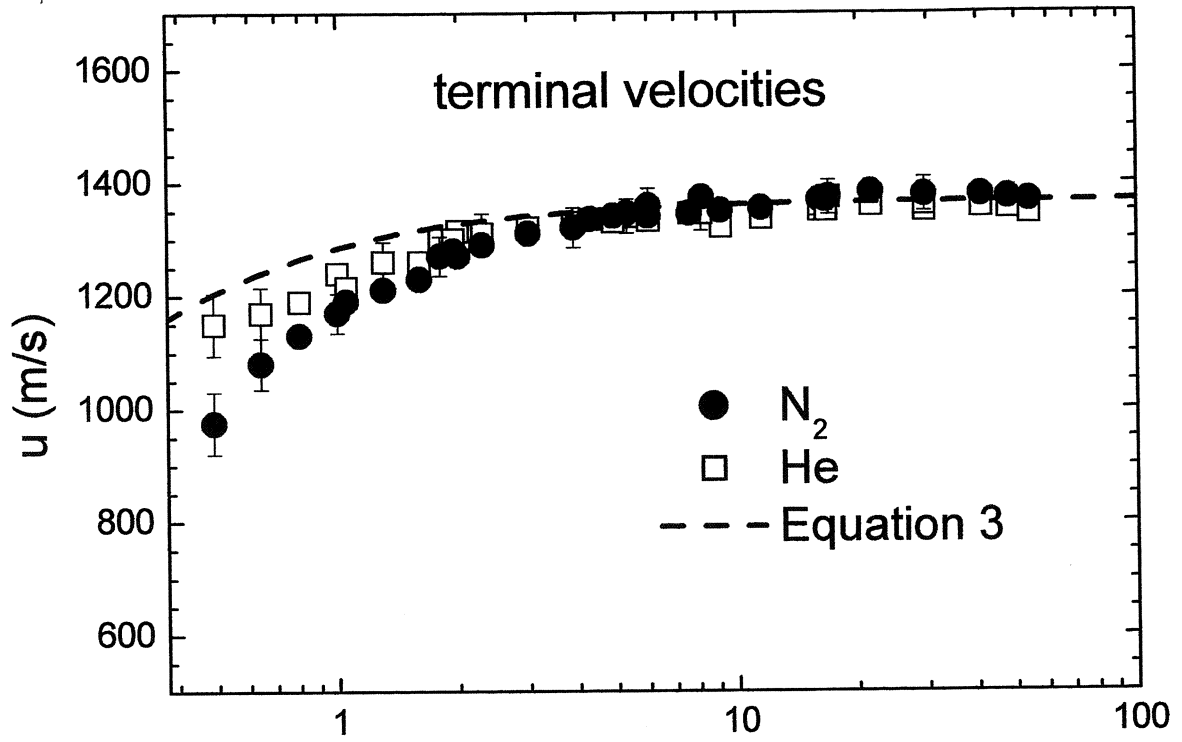


Fig. 1 Aoi et al.

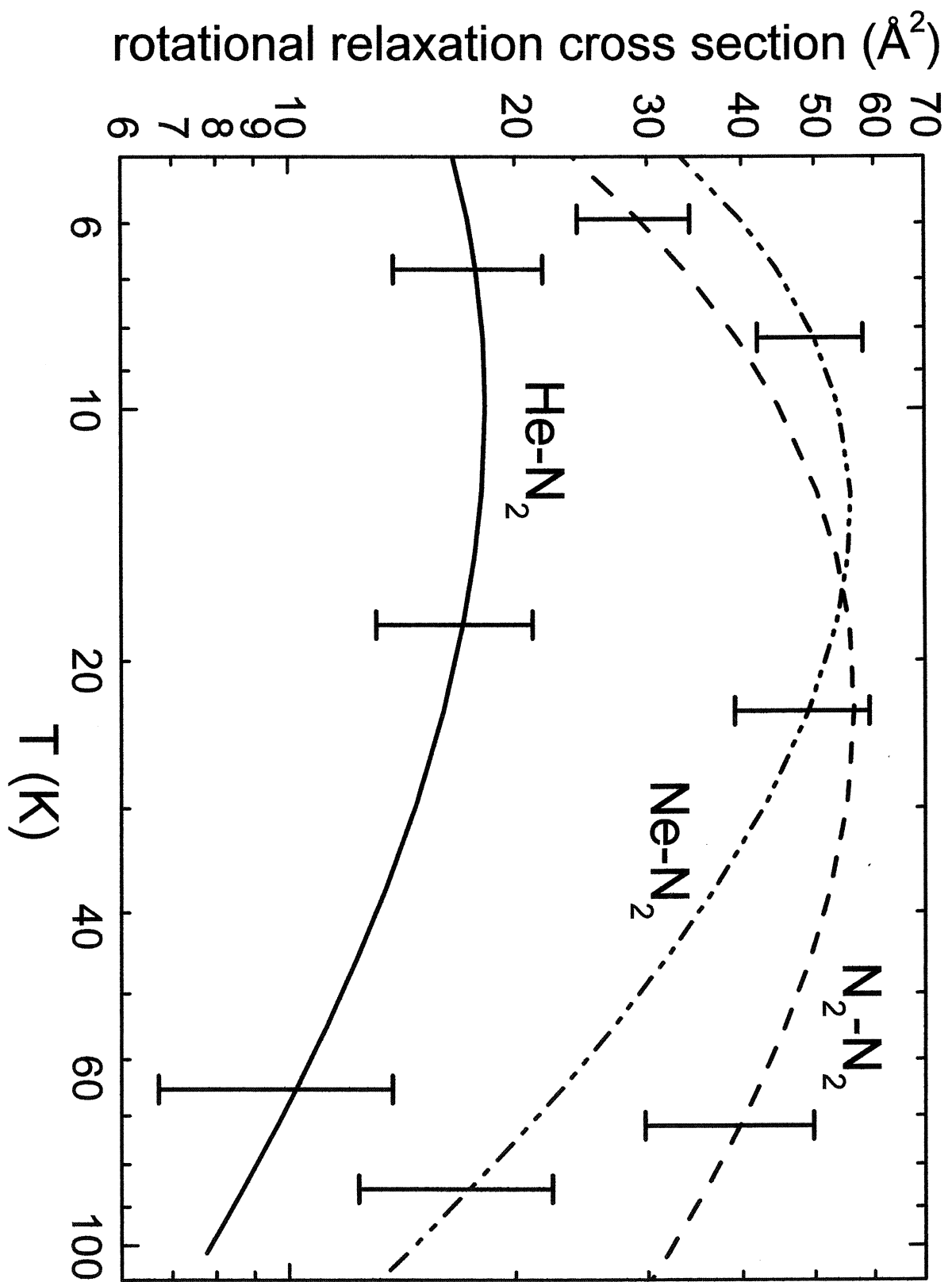


Fig. 2 Aoi et al.

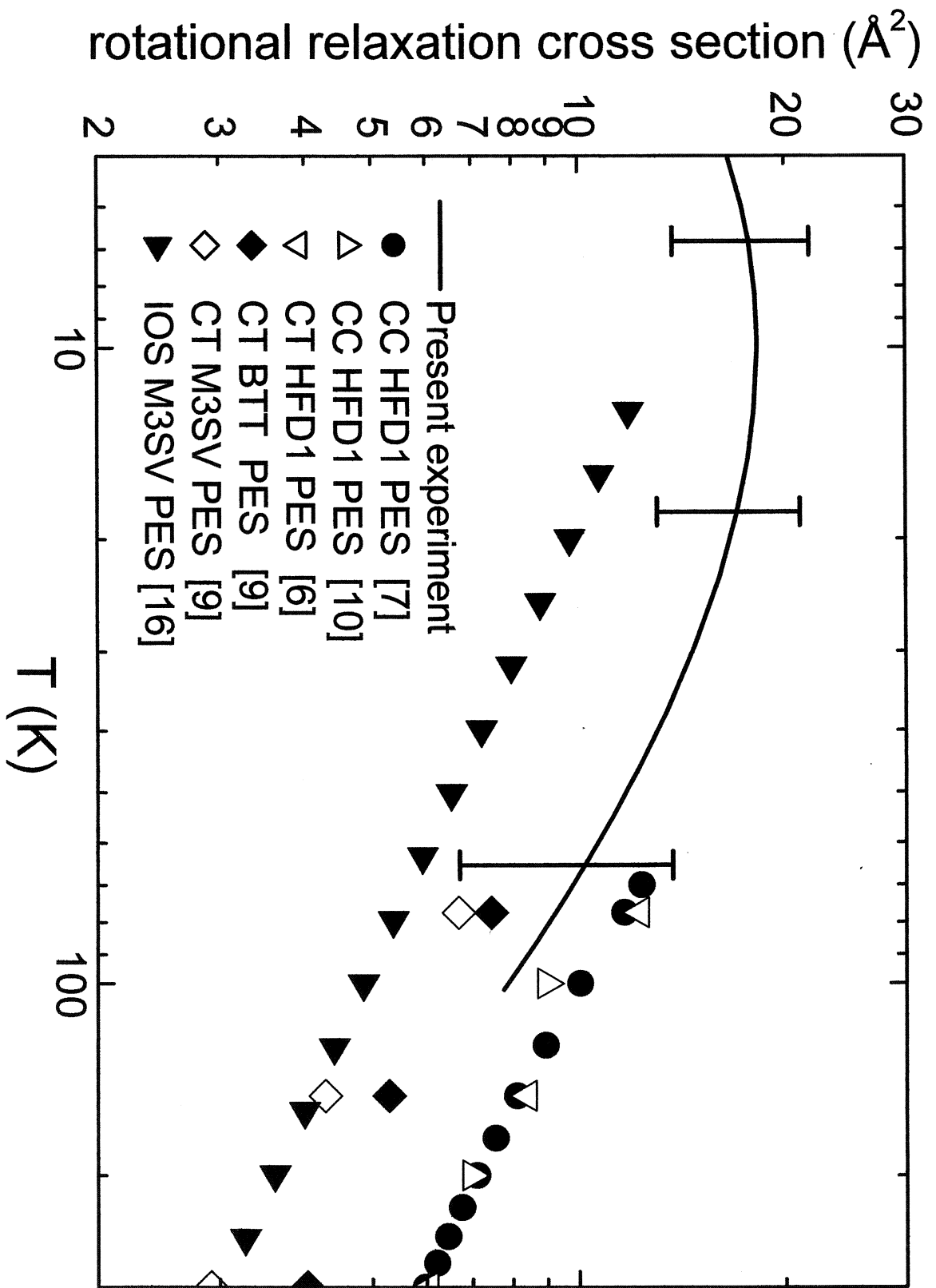


Fig 3 Aoi7 et al.