Inelastic Collisions of N₂, H₂, and H₂+He Mixtures in Supersonic Jets by Raman Spectroscopy

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Abstract. We present a detailed study of inelastic collisions at low temperature in several supersonic jets of N₂, H₂, and H₂+He mixtures using different nozzles and stagnation conditions. Absolute number density and rotational population data of unprecedented accuracy are measured along the jet axis by Raman spectroscopy with high spatial resolution ($< 5 \mu\text{m}$) and high-sensitivity (< 1 photon/sec). The experimental data are interpreted by means of a master equation describing the time evolution of the rotational populations in terms of the state-to-state rate coefficients derived from high-level quantum calculations. This combination of experimental and calculated data leads to a detailed understanding of the underlying physics, consistent with the assumed isentropic behaviour. The breakdown of rotational-translational thermal equilibrium, and its space-time evolution along the jet axis are accounted for by the microscopic (state-to-state rate coefficients) and macroscopic (flow velocity, number density, temperatures) physical quantities. A highly consistent picture, free from any additional parameters, bridges this way the microscopic and macroscopic approaches to fluid dynamics along the jet axis.

Keywords: Inelastic molecular collisions, supersonic jets, Raman spectroscopy, close-coupling calculations, state-to-state rate coefficients

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INTRODUCTION

Energy transfer by inelastic nonreactive collisions is responsible for many phenomena in gases, both in thermodynamic equilibrium and nonequilibrium conditions: transport properties, broadening of spectral lines, rotational and vibrational relaxation, shock waves, among others. In practice, they are of interest in aeronautics, atmospheric physics and astrophysics, as well as in molecular quantum mechanics.

At the microscopic scale, binary inelastic collisions between molecules are governed by the state-to-state cross sections (σ), and their corresponding rate coefficients (k). Much theoretical and experimental work has been done in the last decades toward obtaining accurate state-to-state cross sections and rate coefficients. Nonetheless, the problem remains elusive. This is due, in part, to the limitations of available intermolecular potential energy surfaces (PES), and, in part, to the lack of experimental methods for probing state-to-state collisional processes, i. e., not averaged *bulk* quantities. State-to-state σ 's and k 's derived from quantum calculations are very sensitive to the employed intermolecular PES. High quality PESs are very expensive (if affordable at all) to compute, even for small molecules. Therefore, accurate experimental state-to-state data are mandatory to assess or to scale the calculated k 's.

Reduced (one-body) rate coefficients have been obtained at room temperature and above for N₂ [1] from self-broadening of spectral lines measured by high-resolution spectroscopy, and rotational population distributions in free jets, measured by different laser spectroscopic techniques, have also been used [2, 3, 4]; however, in all those works some kind of empirical scaling law was imposed to relate the different k 's. So far, the most straightforward experimental method to determine rate coefficients in collisions between homonuclear diatomics is based on populating selected rotational levels by stimulated Raman pumping [5]. However, it only provides information about rotational states in an excited ($v = 1$) vibrational state, and is difficult to apply below room temperature.

In the last years, we have developed in our laboratory [6, 7, 8, 9, 10, 11] an original methodology to study rotationally inelastic molecular collisions in the vibrational ground state at very low temperature (≤ 50 K). The procedure is based on tracking the time evolution of the rotational population along supersonic gas jets by Raman spectroscopy. The method is specially suited for small molecules, including homonuclear diatomics. So far, it has been applied to N₂, H₂ (*ortho*, *o*H₂, and *para*, *p*H₂, nuclear spin species), and collisions with He.

METHODOLOGY

The equation of matter conservation in the axial region of a steady supersonic jet of a pure molecular gas, like the experimental data of the present work, adopts the form of a master equation

$$\frac{dP_i}{dt} = n \sum_{j\ell m} (-P_i P_j k_{ij \rightarrow \ell m} + P_\ell P_m k_{\ell m \rightarrow ij}), \quad (1)$$

and describes the time evolution of the population P_i (i. e., the population rate) of an internal state i as a consequence of inelastic collisions in a molecular gas at instantaneous number density n . In Eq. (1) the k 's, which depend on the translational (kinetic) temperature T_K , are the so called state-to-state collisional rate coefficients, accounting for the rate of the elementary two-body collision process

in a thermal bath at temperature T_K , where $A(i)$ and $B(j)$ are two (equal or different) molecules with internal states i and j before the collision. Constraining ourselves to linear molecules like H_2 or N_2 at temperatures below 300 K, the internal states are the rotational states, and i, j, ℓ, m may be identified with the rotational quantum number J . If the collision partner B in Eq. (2) is an atom, like He, it does not have internal states (just kinetic energy) in the energy range investigated here, and the two-index rate coefficients will be denoted $h_{i \rightarrow \ell}$.

The "up" and "down" rate coefficients are related by the detailed balance (microscopic reversibility principle)

$$k_{ij \rightarrow \ell m}^{\text{up}} (2i+1)(2j+1) e^{\Delta E/k_B T_K} = k_{\ell m \rightarrow ij}^{\text{down}} (2\ell+1)(2m+1) \quad (3)$$

where $\Delta E = E_\ell + E_m - E_i - E_j$ is the (positive) energy gap involved in the collision. Since "up" and "down" rate coefficients may differ at low temperature by many orders of magnitude, and the "down" rates show a far smoother thermal dependence than the "up" ones, it is convenient to rewrite the master Eq. (1) in the form

$$\frac{dP_i}{dt} = n \sum_{\tau\omega\sigma\rho} \pm a_{\tau\omega\sigma\rho} k_{\tau\omega \rightarrow \sigma\rho}^{\text{down}}, \quad (4)$$

in term of "down" rates only. The indices τ, ω, σ , and ρ run over all allowed values (considering nuclear spin statistics) of rotational quantum number J , at least one of them being equal to i . Coefficients $a_{\tau\omega\sigma\rho}$ are functions [11] of the translational temperature and rotational populations, quantities that can be determined from the experiment, as will be shown below. Each term $a_{\tau\omega\sigma\rho} k_{\tau\omega \rightarrow \sigma\rho}^{\text{down}}$ in Eq. (4) accounts in a convenient factorized form (instantaneous local properties $\times$ intermolecular properties) for the net contribution of the $\tau\omega \rightarrow \sigma\rho$ and $\sigma\rho \rightarrow \tau\omega$ time-symmetric elementary collisional processes to the population rate dP_i/dt .

The master equation can be successfully extended to gas mixtures M+O. In this case, the population rate dP_i/dt for the M species is the sum of two (or more) terms of the form of Eq. (4) [7, 11],

$$\frac{dP_i}{dt} = \chi_M(M : M) + \chi_O(M : O), \quad (5)$$

each accounting for the collisions with one of the colliding partners, weighted by their respective mole fraction χ .

The master Eqs. (4) or (5) are systems of (infinite) linear equations in the (infinite) unknown k 's; however, only a finite number of P_i 's and k 's are physically relevant at a given temperature. In favorable cases, like *para*- H_2 at low temperature [9] or H_2 :He collisions [11], it is possible to invert Eq. (4) to obtain the k 's just from the experiment. In a more general case, if some k 's are available from quantum scattering calculations or from models, the comparison between the experimental left hand side (LHS) in Eq. (4) and the combined experimental $\times$ calculated right hand side (RHS), can be used to assess the quality of the calculated rate coefficients.

EXPERIMENTAL CONDITIONS AND PROCEDURE

The experimental part of this work relies on the properties of steady supersonic gas jets and on the remarkable capability of Raman spectroscopy to measure accurately local quantities along the jet. The main properties of the

TABLE 1. Experimental conditions of supersonic gas jets employed in this work

Gas sample	Nozzle dimension	p_0 (bar)	T_0 (K)
N ₂	circular, $D = 313 \mu\text{m}$	0.2 , 0.5 , 1.0 , 2.0	297
$p\text{H}_2$	circular, $D = 50 \mu\text{m}$	1.0 to 16.0	295
$n\text{H}_2$	circular, $D = 313 \mu\text{m}$	1.28 , 2.55	295
$p\text{H}_2(25\%) + \text{He}(75\%)$	slit, $D = 130 \mu\text{m}$, $L = 3 \text{ mm}$	0.408	295
$n\text{H}_2(27\%) + \text{He}(73\%)$	slit, $D = 130 \mu\text{m}$, $L = 3 \text{ mm}$	0.400	297

FIGURE 1. Raman spectra at $z = 300 \mu\text{m}$ on the jet axis of H₂+He mixtures through a $0.13 \times 3 \text{ mm}^2$ slit nozzle. Spectral resolution $\Delta\nu = 0.4 \text{ cm}^{-1}$; recording time 150 s; space resolution $\Delta z = 15 \mu\text{m}$.**FIGURE 2.** Rotational Raman spectra of N₂ in a jet at different distances z from nozzle ($D = 313 \mu\text{m}$). Stagnation conditions: $p_0 = 2000 \text{ mbar}$; $T_0 = 297 \text{ K}$. ZS zone of silence; NS normal shock (Mach disk); BS barrel shock.

expanding gas in the zone of silence are: i) laminar flow, with supersonic flow velocity V ; ii) marked decrease in number density n , of several orders of magnitude, iii) fast cooling, down to few degrees Kelvin, with progressive breakdown of thermal equilibrium between translational (T_K) and rotational (T_R) temperature.

Supersonic jets are produced in the laboratory by expanding a gas (pure or mixture) from a reservoir at known stagnation pressure p_0 and temperature T_0 through a nozzle into an expansion chamber, kept at low pressure ($< 1 \text{ mbar}$) by means of a high pumping speed ($> 400 \text{ litre/s}$) vacuum system (turbomolecular or Roots-blower pumps). Different nozzles and stagnation conditions have been used in this work; they are summarized in Table 1.

High-sensitivity (few photons/s) Raman spectroscopy with high spectral ($\sim 1 \text{ cm}^{-1}$) and spatial ($\sim 5 \mu\text{m}$) resolution is used as a quantitative diagnostic technique. Raman spectroscopy provides, among all spectroscopic techniques, the most direct and accurate measurements of absolute number densities and rotational populations along a gas jet [12, 13], signal being linear with density along several orders of magnitude. The experimental setup is described with more detail elsewhere [14].

Absolute number density n and rotational populations P_J are the primary experimental quantities measured at a number of points at different distances z from the nozzle along the axis of the zone of silence of the jet. Representative Raman spectra recorded along the jet axis of N₂ and of mixtures of H₂+He are shown in Figs. 1 and 2. The number

densities $n(z)$ were derived from the integrated Raman intensity I_Q of the Q branch ($\Delta J = 0$) of the vibrational fundamental band. For N_2 this is the unresolved band at 2331 cm^{-1} , while in H_2 it corresponds to the sum of the resolved rotational lines $Q(J)$ at $4161.2, 4155.3, 4143.5, 4125.9$ and 4102.6 cm^{-1} (see Fig. 1). For a very wide range of conditions $I_Q = Cn(z)$ is strictly proportional to the number density of the sample at the focal spot of the exciting laser beam. The proportionality constant C depends only on exciting wavelength and irradiance, scattering geometry, and molecular polarizability, quantities that remain constant along the experiment. Thus C is determined by recording the spectrum, under the same irradiance conditions, of a static sample of the same gas at a known pressure, measured with a MKS Baratron 690A of 0.08% nominal accuracy.

The rotational populations P_J can be derived from the Raman intensity of rotationally resolved lines. In the case of H_2 , the $Q(J)$ lines referred above were used, their intensity being $I_{Q(J)} = Cn P_J$. For N_2 the $S(J)$ Raman lines from 12 to $\sim 160 \text{ cm}^{-1}$ (see Fig. 2), associated with the $J \rightarrow J+2$ rotational transitions, were used,

$$I_{S(J)} = GP_J \frac{(J+1)(J+2)}{(2J+1)(2J+3)}. \quad (6)$$

The constant G is determined from the normalization condition $\sum_J P_J = 1$.

From the primary experimental data n and P_J , other local quantities needed in Eq. (4) like rotational temperature T_R , translational temperature T_K , and flow velocity V can be derived as follows. T_R is obtained from the populations P_J , since the vast majority of the molecules do obey a Boltzmann distribution under the present experimental conditions. T_K is determined from the statistical definition of entropy, assuming its invariance $\Delta S = 0$ along the jet axis. For H_2 the most general expression was used [9],

$$T_K(z) = T_0 \left[\left(\frac{n(z)}{n_0} \right) \prod_J \left(\frac{P_J(z)}{g_J(2J+1)} \right)^{P_J(z)} \left(\frac{g_J(2J+1)}{P_J^0} \right)^{P_J^0} \right]^{2/3}, \quad (7)$$

where no rotational distribution is imposed; assuming a classical rotational partition function, like for N_2 , it turns

$$T_K(z) = T_0 \left(\frac{n(z) T_0}{T_K(z) n_0} \right)^{2/3}. \quad (8)$$

Within the zone of silence of the jet the flow is laminar, and the distance z and the time t from the nozzle are related by means of the flow velocity $V(z) = dz/dt$. This way, the population rates can be derived from the experimental data as

$$dP_J/dt = V(z) dP_J/dz. \quad (9)$$

Flow velocity can be determined from the conservation of energy $h_0 = h + \frac{1}{2}V^2$ along the jet axis, which leads to

$$V(z) = \sqrt{R(7T_0 - 5T_K(z) - 2T_R(z))/W} \quad (10)$$

where R is the universal gas constant and W the mole mass of the gas.

CALCULATED CROSS SECTIONS AND RATE COEFFICIENTS

The two body state-to-state collisional cross sections $\sigma_{ij \rightarrow \ell m}$ have been calculated in the close-coupled (CC) approach, up to total energy $E = E_K + E_R(J)$ relevant for the experimental data, using high-level quantum scattering calculations with the MOLCOL [16] and MOLSCAT [15] codes. For N_2 the PES by Cappelletti *et al* [17] was used, up to total energy $E < 263 \text{ cm}^{-1}$ to account for the experimental k 's up to 35 K. For H_2 the PES by Diep and Johnson [18] was employed, up to total energy $E < 5000 \text{ cm}^{-1}$ relevant for $T_K < 300 \text{ K}$. In these cases, quantum interference effects were checked to be negligible for distinguishable molecules. Finally, calculations at the converged close-coupled (CCC) level were carried out for H_2 -He using two recent PESs [19, 20] up to 7000 K.

State-to-state rate coefficients were calculated from cross sections by thermal average,

$$k_{ij \rightarrow \ell m}(T_K) = \frac{\langle v \rangle}{(k_B T_K)^2} \int_{E_s}^{\infty} \frac{\sigma_{ij \rightarrow \ell m}(E)}{\exp(E/k_B T_K)} E dE, \quad (11)$$

assuming a Maxwell-Boltzmann velocity distribution, where $\langle v \rangle = (8k_B T_K / \pi \mu)^{1/2}$ is the mean relative velocity of the colliding partners of reduced mass μ , and E_s is the minimum kinetic energy for the internal states ℓ and m to become accessible.

TABLE 2. CC calculated rate coefficients $k_{ij \rightarrow \ell m}^{\text{down}}$ scaled to experiment, for $\text{N}_2:\text{N}_2$ collisions at several temperatures T_K . Units of $10^{-20} \text{ m}^3/\text{s}$.

$ij \rightarrow \ell m$	35 K	18 K	8 K	4 K
03 $\rightarrow$ 21	8971	7348	8184	10674
41 $\rightarrow$ 23	7722	5943	5778	6970
20 $\rightarrow$ 00	1084	907	1052	1436
21 $\rightarrow$ 01	3050	2390	2532	3313
22 $\rightarrow$ 02	2684	2094	2123	2679
30 $\rightarrow$ 10	1868	1533	1693	2244
31 $\rightarrow$ 11	3824	2942	2897	3645
32 $\rightarrow$ 12	4799	3648	3729	4826

TABLE 3. CC calculated rate coefficients $k_{ij \rightarrow \ell m}^{\text{down}}$ for $\text{H}_2:\text{H}_2$ collisions at several translational temperatures T_K . Units of $10^{-20} \text{ m}^3/\text{s}$.

$ij \rightarrow \ell m$	300 K	100 K	40 K	20 K	5 K
03 $\rightarrow$ 21	864	452	319	330	979
41 $\rightarrow$ 23	631	350	279	359	3601
20 $\rightarrow$ 00	167	63	40	39	63
21 $\rightarrow$ 01	283	104	65	60	83
22 $\rightarrow$ 02	281	106	68	64	94
30 $\rightarrow$ 10	135	42	27	28	89
31 $\rightarrow$ 11	164	45	26	27	83
32 $\rightarrow$ 12	164	47	29	27	95

FIGURE 3. Experimental and CCC-calculated $h_2 \rightarrow 0$ rate coefficient for *para*- H_2 :He collisions.

FIGURE 4. Experimental and CCC-calculated $h_3 \rightarrow 1$ rate coefficient for *ortho*- H_2 :He collisions.

RESULTS AND CONCLUSIONS

Calculated CC rate coefficients for N_2 have been assessed by the ratio LHS/RHS of Eq. (4), using the experimental values of n , P_J , dP_J/dz , T_K , T_R and V at fixed points corresponding to translational temperatures from 35 to 4 K [10]. The ratio LHS/RHS ranged from 0.61 to 0.87 in all cases, and for a fixed T_K the ratio was almost constant for all P_J 's. This suggests that the calculated k 's are off by about the same amount, so that they can be scaled to match the experimental P_J 's to better than 10%. Some rate coefficients scaled that way are shown in Table 2.

For H_2 species only two rotational levels are involved in the temperature range investigated here: $J = 0, 2$ for $p\text{H}_2$, and $J = 1, 3$ for $o\text{H}_2$. Thus, a more detailed analysis is possible [9]. The direct approach, similar to that used for N_2 , is to assess the calculated rate coefficients by the ratio LHS/RHS of Eq. (4), which in this case ranged between 0.99 and 1.06 for the whole thermal range $10 < T_K < 140$ K. Some CC calculated rate coefficients are shown in Table 3. Because of the few k 's physically relevant in this case, the inverse approach is also possible: to invert the master Eq. (4) to determine $k_{20 \rightarrow 00}$ and $(k_{30 \rightarrow 12} + 5k_{31 \rightarrow 11})$ just from experimental data at different temperature ranges, in good agreement with the calculated values. The calculated k 's were also checked to reproduce, better than 10%, the relaxation times from independent acoustic experiments of ultrasonic absorption/dispersion between 77 and 300 K [21, 22, 23].

In the case of H_2+He mixtures, the master Eq. (5) has two terms, one for $\text{H}_2:\text{H}_2$ self collisions with four-index $k_{ij \rightarrow \ell m}$'s, and one for $\text{H}_2:\text{He}$ collisions with two-index $h_{i \rightarrow \ell}$'s [11]. Only $h_{2 \rightarrow 0}$ (for $p\text{H}_2$) and $h_{3 \rightarrow 1}$ (for $o\text{H}_2$) are physically relevant at the temperatures of the experiment, and thus can be determined from experiment, assuming

the $k_{ij \rightarrow \ell m}$'s are known from the previous work [9]. The comparison between the experimental and calculated rate coefficients $h_{i \rightarrow \ell}$ employing several PES is shown in Figs. 3 and 4 (note the different ordinate scales), along with some independent acoustic measurements [21, 22, 23]. Experimental data for $h_{2 \rightarrow 0}$ are consistent with Muchnick and Russek (MR) PES [19] but not with Boothroyd et al. (BMP) PES [20].

All the information implicit in Eq. (4) can be displayed in the so-called *collisional spectra* [9, 10]. These are graphical representations of the contribution (positive or negative) of each collision $\tau\omega \rightarrow \sigma\rho$ to a given population rate dP_j/dt versus the energy gap (positive or negative) of the collision. It is interesting to discuss the role of mixed "up-down" collisions like $30 \rightarrow 12$, in which one molecule relaxes ($3 \rightarrow 1$) and other molecule gets excited ($0 \rightarrow 2$). The total energy gap is negative, and thus the net effect of the collision is to cool the gas, but in N_2 or H_2 (with two non-interconverting nuclear spin species) it *heats* one of the spin species. Mixed "up-down" collisions of this kind play an important role at low T_K , when few collisional channels are relevant, and cannot be described by reduced (one-body) rate coefficients $k_{i \rightarrow \ell}$ assuming a "passive" role for the colliding partner B in Eq. (2). That precludes any rigorous reduction of state-to-state (four-index) rate coefficients in Eq. (1) into one-body "effective" ones.

To conclude, Raman intensity measurements in supersonic gas jets are proven suited to study the rotation-translation energy transfer by inelastic collisions in a thermal range hardly accessible to any other experimental method. The experimental data on the breakdown of rotational-translational equilibrium, and its time evolution along the jet axis, are interpreted within the gas-dynamic conservation equations of matter, energy, and entropy, in terms of microscopic (state-to-state rate coefficients) and macroscopic (flow velocity, number density, temperatures) physical quantities, leading to a detailed understanding of the underlying physics. The accuracy of calculated state-to-state rate coefficients can be experimentally assessed this way. The method here described is planned to be applied to other diatomics of atmospheric and astrophysical interest, like O_2 and CO , and to be extended to triatomics like H_2O .

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