Rotational-translational state-to-state collisional rate constants of N₂ at low temperature (3 < T < 16 K)

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We report an experimental determination of the state-to-state rate constants of N₂ in the vibrational ground state as a function of temperature, in the range 3 < T < 16 K. These rate constants were obtained by inversion of the master equation in a procedure not resorting to any particular fitting law. The coefficients of the master equation were obtained experimentally on the basis of Raman spectroscopic data from supersonic expansions of N₂.

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I. INTRODUCTION

State-to-state rate constants are the fundamental physical quantities governing the rotational-translational energy transfer induced in a gas by molecular collisions. Their experimental determination has largely been restricted to collisional pairs formed by a small molecule and a noble gas atom. However, the information gained has been sufficient to test different fitting laws [1], the accuracy of scattering calculations, and a number of potential-energy surfaces, leading to a good understanding of the collisional theory [2]. So far, the most straightforward experimental method to determine the rate constants in collisions between homonuclear diatomic species is based on populating selected rotational levels by stimulated Raman pumping. But it provides information only about rotational states within a ($v=1$) vibrational state, and is difficult to apply below room temperature. Rates for ortho-N₂:N₂ collisions in the ($v=1$) state have been obtained in this way [3]. N₂ ground-state ($v=0$) rate constants derived from different fitting laws have only been tested indirectly by means of other experimental methods, such as line broadening coefficients [4,5], or global relaxation time measurements [6].

In this paper we present a method capable of providing the relevant rate constants in the vibrational ground state as a function of temperature. It is not restricted to any particular fitting law, and is specially well suited for collisions between identical diatomic species at low temperatures. Its foundation is the evolution of the population kinetics along steady supersonic expansions of the probed gas, as measured by very high sensitivity Raman spectroscopy [7] with high spatial resolution ($\approx 10 \mu\text{m}$) and accuracy ($\approx 1 \mu\text{m}$) [8,9]. As an application we report the main transfer rates of N₂ in the thermal range 3 < T < 16 K.

Steady supersonic expansions are easily produced in the laboratory by expanding the sample gas through a small circular nozzle (diameter < 1 mm) into a chamber maintained at low pressure (< 1 mbar). In such expansions the remarkable properties of the expanding gas in the first section downstream from the nozzle (zone of silence) are (1) supersonic flow velocity (v), (2) fast decrease of number density (n) asymptotically tending to $n \propto z^{-2}$ for z the distance from the nozzle, and (3) sharp cooling, down to a few kelvin, with

progressive breakdown of thermal equilibrium ($T_t \neq T_r$) between translational (T_t) and rotational (T_r) temperature. This breakdown is due to the finite collisional cross sections and to the collisional deficit associated with the increasing rarefaction of the expanding gas. It plays a central role in the present method, and will be described here quantitatively in terms of a nonequilibrium parameter X defined below.

The present method relies exclusively on the experimental data derived from the rotational and vibrational intensities of linear Raman spectra recorded at consecutive points along the axis of a steady supersonic expansion of a molecular gas. Each of these points represents, by virtue of the distance (z) from the beginning of the expansion, a gas volume at different time (t), number density, and rotational, as well as translational temperatures. Since position z and time t are related in the jet by the flow velocity, an experimentally accessible quantity, the ensemble of spectra recorded at the different points of the expansion contains the information about the kinetics of the rotational energy transfer and, consequently, about the rate constants as has been recognized long ago [10,11]. How to generate and how to extract this information is the subject of the present paper. The particular case of N₂ in the low-temperature range (3 < T < 16 K), convenient from the experimental point of view, is used as illustration.

II. THEORY

The theoretical basis of the method is the master equation [12]

$$\dot{P}_i = n \sum_{j\ell m} [-P_i P_j k_{ij \rightarrow \ell m} + P_\ell P_m k_{\ell m \rightarrow ij}], \quad (1)$$

expressed in terms of the present experimental data, and of quantities derived from them; $n(t)$ is the instantaneous number density of molecules in the gas volume with translational temperature $T_t(t)$; indices i, j, ℓ, m span here the domain of the rotational quantum number J of N₂. Equation (1) describes the time derivative $\dot{P}_i = dP_i/dt$ of the normalized population P_i of a rotational energy level with quantum number $J=i$ as a function of the number density, current

rotational populations P_i, P_j, P_ℓ, P_m , and the inelastic state-to-state rotational-translational rate constants $k_{ij \rightarrow \ell m}$ for the elementary collisional process

between a N_2 molecule (active) in rotational state $J=i$, and another N_2 molecule (passive) in rotational state $J=j$, in a medium at translational temperature T_t . Recent calculations on H_2 collisions [13] show that the $k_{ij \rightarrow \ell m}$'s are quite insensitive to the rotational state of the passive molecule. This suggests the use of the reduced rates $k_{i\ell}$ as a reasonable approximation for the description of the kinetics of rotational populations along the cooling process in the supersonic expansion. Under this approximation, and taking into account that natural N_2 is a 2:1 mixture of ortho- ($J=\text{even}$) and para- ($J=\text{odd}$) noninterconverting species on the time scale of the present experiment, the master equation (1) may be reduced to the two independent master equations expressed in terms of upward collisions,

$$\begin{aligned} \dot{P}_0 &= a_{02}k_{02} + a_{04}k_{04} + \cdots + a_{0r}k_{0r} + \cdots, \\ \dot{P}_2 &= -a_{02}k_{02} + a_{24}k_{24} + \cdots + a_{2r}k_{2r} + \cdots, \\ &\vdots = \\ \dot{P}_r &= -a_{0r}k_{0r} - a_{2r}k_{2r} - \cdots + a_{r,r+2}k_{r,r+2} + \cdots. \end{aligned} \quad (3)$$

with $r=\text{even}$ for ortho- N_2 , and

$$\begin{aligned} \dot{P}_1 &= a_{13}k_{13} + a_{15}k_{15} + \cdots + a_{1s}k_{1s} + \cdots, \\ \dot{P}_3 &= -a_{13}k_{13} + a_{35}k_{35} + \cdots + a_{3s}k_{3s} + \cdots, \\ &\vdots = \\ \dot{P}_s &= -a_{1s}k_{1s} - a_{3s}k_{3s} - \cdots + a_{s,s+2}k_{s,s+2} + \cdots \end{aligned} \quad (4)$$

with $s=\text{odd}$ for para- N_2 .

The peculiar structure of the right-hand terms of Eqs. (3) and (4) reflects the properties

$$\sum_{i=\text{even}} \dot{P}_i = 0 \quad \text{and} \quad \sum_{i=\text{odd}} \dot{P}_i = 0, \quad (5)$$

which arise from the conservation of normalized populations $\sum_{i=\text{even}} P_i = 2/3$ for $o\text{-N}_2$, and $\sum_{i=\text{odd}} P_i = 1/3$ for $p\text{-N}_2$, at any point of the expansion.

Rotational populations P_i ($i \leq 6$) measured in present N_2 expansions obey, to a very good approximation, a Maxwell-Boltzmann distribution, with a well-defined rotational temperature T_r . Under this condition the coefficients $a_{i\ell}$ in Eqs. (3) and (4) can be expressed in the rigid rotor approximation as

$$a_{i\ell} = n \frac{P_i(2 - P_i - P_\ell)}{2} (-1 + e^{[\ell(\ell+1) - i(i+1)]X}), \quad (6)$$

FIG. 1. Data reduction steps and estimated uncertainties.

in terms of the nonequilibrium parameter $X = \beta B(T_t^{-1} - T_r^{-1})$, where $\beta = hc/k = 1.4388 \text{ K/cm}^{-1}$, and $B = 1.98973 \text{ cm}^{-1}$ is the rotational constant of N_2 .

Left-hand terms $\dot{P}_i$ in Eqs. (3) and (4), as well as coefficients $a_{i\ell}$, can be determined from the Raman spectra as explained below. So, obtaining the $k_{i\ell}(T_t)$'s reduces to solving numerically the system of Eqs. (3) and (4) for the dataset from point z , with translational temperature $T_t(z)$.

III. EXPERIMENT AND DATA REDUCTION

Recent progress in Raman spectroscopy of supersonic expansions [8,9] permits us to determine all the quantities needed. Following the scheme of Fig. 1, selecting a point at the position z of the expansion, in step 1 the absolute number density $n(z)$ is obtained from the integrated intensity of the Q branch of the vibrational band of N_2 at 2331 cm^{-1} ,

$$I_{2331}^{\text{vib}}(z) = K n(z), \quad (7)$$

which is proportional to the number density. The constant K is determined using static N_2 as a standard. In step 2 the populations $P_i(z)$ are determined from the intensities of the rotational lines associated with the $i \rightarrow i+2$ rotational Raman transitions, since

$$P_i(z) = G I_{i \rightarrow i+2}^{\text{rot}}(z) \frac{(2i+1)(2i+3)}{(i+1)(i+2)}, \quad (8)$$

with constant G determined from the normalization $\sum_i P_i = 1$. Rotational temperature $T_r(z)$ is determined in step 3 from populations $P_i(z)$.

Somewhat involved is step 4, where the translational temperature T_t is estimated from the smoothed n and T_r data according to a procedure based on the conservation of momentum and total energy in the zone of silence of the super-

FIG. 2. Experimental inverse rotational and translational temperatures in supersonic expansions I and II of N_2 .

sonic expansion [14]. Inverse rotational and translational temperatures obtained here are shown in Fig. 2. In step 5 the flow velocity is determined from the conservation of total enthalpy in the zone of silence according to

$$v(z) = [R(7T_0 - 5T_t(z) - 2T_r(z))/W]^{1/2}, \quad (9)$$

for the stagnation temperature $T_0 = 295$ K, and the molar mass of N_2 $W = 0.028$ kg/mol; $R = 8.3145$ J K $^{-1}$ mol $^{-1}$ is the universal gas constant. In step 6 the time derivative of the populations are obtained from $\dot{P} = (dP_i/dz)v$, using the populations $P_i(z)$ to generate numerically the derivatives dP_i/dz . In step 7 the coefficients $a_{i\ell}(z)$ are calculated from Eq. (6) using the previously determined quantities. Finally, in step 8 the rates $k_{i\ell}$ relevant at the translational temperature $T_t(z)$ at point z are obtained numerically by solving the system of equations (3) and (4). Estimated uncertainties are given in square brackets in Fig. 1. A listing (TABLE-S.TXT) of n , T_r , and T_t is given in Ref. [15].

Some numerical aspects of the reduction of the experimental data to the determined $k_{i\ell}$'s deserve mention. In step 8 the determination of the rates $k_{i\ell}$ from Eqs. (3) and (4) is not immediate due to the peculiar structure of the system: It has an infinite number of equations, and thus it requires truncation. Furthermore, the number of unknowns is larger than the number of meaningful equations. In practice, the number of meaningful equations to be retained in Eqs. (3) and (4) depends on the experimental accuracy of $\dot{P}_i$, and on the local rotational temperature at the particular position z of the expansion. In the investigated range, $3 < T_t < 16$ K, just equations up to $\dot{P}_4$ and $\dot{P}_5$ were retained for o - N_2 and p - N_2 , respectively.

A more difficult problem is the infinite number of unknowns $k_{i\ell}$ in Eqs. (3) and (4). A common procedure for circumventing this problem is to assume a fitting law [1], relating different $k_{i\ell}$'s as functions of temperature, and a reduced number of parameters. Although there is general

FIG. 3. Experimental $k_{i\ell}$ rates of N_2 versus translational temperature T_t and average collision energy $E_{\text{coll}} = 4kT_t/\pi$.

agreement that fitting laws should include exponential functions of $\epsilon_{i\ell} = (E_\ell - E_i)/(kT_t)$, where $|E_\ell - E_i|$ is the rotational energy change in the collision, none of the models checked so far for N_2 [3–6] extends to the low temperatures investigated here. Thus, instead of using a particular fitting law, we prefer to apply the much less restrictive condition, common to all of them,

$$0 < k_{i'\ell'} < k_{i\ell} \quad \text{if} \quad (E_\ell - E_i) < (E_{\ell'} - E_{i'}), \quad (10)$$

holding separately for *ortho* and *para* subsystems, Eqs. (3) and (4), respectively. Combining the constraints (10) with the equations remaining from Eqs. (3) and (4), a mean-square solution can be obtained for the relevant $k_{i\ell}$'s at the translational temperatures of the positions z measured in the expansion.

Rate constants $k_{i\ell}$ only depend on the kinetic energy of the collision, given in the average by the translational temperature, and are invariant with respect to the number density and the rotational temperature. In order to check for this invariance, an important test of present method, the $k_{i\ell}$'s were derived independently from two different expansions of N_2 , henceforth referred to as I and II, with associated number densities differing by a factor of 2, and rotational temperatures differing by up to 22% at identical translational temperature. Expansions I and II were generated through an axisymmetric nozzle of diameter $D = 313$ μm at stagnation temperature $T_0 = 295$ K and stagnation pressures $P_0^I = 1$ bar, and $P_0^{II} = 2$ bars, respectively. For the present purpose only the zone of silence of the expansion matters. In order to ensure the quality of the experimental data, the Raman spectra were recorded at discrete points of the expansions in the following ranges: $10D < z^I < 44D$ for expansion I, and $10D < z^{II} < 70D$ for expansion II. For $z < 10D$, the temperatures and densities may be perturbed by turbulences in the flow,

TABLE I. Coefficients $C_{i\ell}$ and $b_{i\ell}$ for the $k_{i\ell}$ (up) rates of N_2 between 3 and 16 K.

i	ℓ	$10^{20}C_{i\ell}$ m ³ /s	$b_{i\ell}$ dimensionless
0	2	10900 ± 850	0.886 ± 0.010
1	3	8210 ± 450	0.920 ± 0.015
2	4	8930 ± 260	0.988 ± 0.018
3	5	5600 ± 50	0.948 ± 0.016
0	4	7050 ± 750	0.865 ± 0.031
4	6	4580 ± 1200	0.971 ± 0.018
2	6	8150 ± 1800	0.964 ± 0.055

and for $z^I > 44D$, or $z^{II} > 70D$, by the shock waves associated with the expansions. In the unperturbed region translational temperatures are between 3 and 16 K.

IV. RESULTS

Due to the very low population of the rotational levels with $J > 4$ at $T_r < 16$ K, the rates k_{02} and k_{13} are determined best, while k_{24} , k_{35} , k_{04} , k_{15} , k_{26} , k_{06} , etc, have increasingly larger uncertainties. A sample of the determined rate constants is shown in Fig. 3. It must be stressed that very nearly the same values are obtained from expansions I and II, experimentally confirming the invariance of $k_{i\ell}$'s with respect to the number density and rotational temperature. In the thermal range $3 < T_r < 16$ K we found empirically that $k_{i\ell}$'s expressed as a function of the parameter $\epsilon_{i\ell}$ defined above obey, to a very good approximation, the exponential law

$$k_{i\ell} = C_{i\ell} e^{-b_{i\ell}\epsilon_{i\ell}}, \quad (11)$$

consistent with the energy-corrected sudden approximation [1]. The coefficients $C_{i\ell}$ and $b_{i\ell}$, averaged over expansions I and II, are given in Table I jointly with their estimated uncertainties.

As an additional proof of consistency of the reported method and results, the rotational population kinetics along the expansions has been recalculated from Eq. (11) and Table I. The result for expansion II is shown in Fig. 4. For expansion I the result is as good.

A comparison of present $k_{i\ell}$'s of N_2 with literature data is not too meaningful at present, since the values so far reported are for room temperature and above, either for $v = 1$ [3] or for $v = 0$ vibrational states [4,5]. Nonetheless extrapo-

FIG. 4. Population derivatives $\dot{P}_i$ recalculated with $k_{i\ell}$'s derived from Eq. (11) and Table I, compared to experiment.

lation of Eq. (11) and Table I to room temperature leads to $k_{i\ell}$'s in between those from Refs. [5] and [3].

V. CONCLUSIONS

The experimental state-to-state rate constants of N_2 are reported here as a function of temperature, between 3 and 16 K. These data provide a test not only for the $N_2:N_2$ potential-energy surface, but also for dynamical models of collisions between diatomic molecules, associated scaling laws, and advanced scattering computational codes.

Extending the method outlined here to expansions of N_2 generated under stagnation conditions $T_0 > 600$ K, and $P_0 < 0.5$ bar, may help improve the accuracy of the results in Table I, widening also the set of rates that can be determined and their thermal range, perhaps up to room temperature. Similar studies on other systems, including molecular mixtures, and mixtures with noble gases, are, in principle, possible as soon as the $k_{i\ell}$'s for the pure species become determined. However a complete evaluation of the method and its variants, for instance, for expansions with ill determined rotational temperatures, will require a considerable amount of experimental and computational work.

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the experimental data n , T_r , T_t , and v , of expansions I and II of N_2 as a function of $\tilde{z}=z/D$. This document may be retrieved via the EPAPS homepage <http://www.aip.org/pubservs/epaps.html> or from [ftp.aip.org](ftp://ftp.aip.org) in the directory /epaps/. See the EPAPS homepage for more information.