Inelastic Collisions of O₂ with He at low Temperatures[†]

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Abstract

Rotationally inelastic collisions of O₂ with He in the 10-34 K thermal range are investigated by means of an experimental procedure based on supersonic gas jets probed by Raman spectroscopy. The procedure employs a kinetic master equation (MEQ) that describes the time evolution of the rotational populations of O₂ along supersonic jets of O₂ and He mixtures. The MEQ is expressed in terms of experimental quantities (number density and rotational populations) measured here, and state-to-state rate coefficients for the O₂:He inelastic collisions calculated here, plus those for O₂:O₂ collisions from the literature. An agreement with the experiments is accomplished for temperatures between 10 and 34 K. Within this thermal range, the role of the fine structure due to electron spin in the collision dynamics of O₂ is discussed.

1 Introduction

Inelastic nonreactive collisions between molecules are responsible for many phenomena in gases, like the transport properties,¹ the broadening of spectral lines,² and rotational and vibrational excite-relaxation,³ among others. As such, they are of fundamental interest in molecular quantum dynamics, and of practical interest in aerospace engineering, atmospheric physics, and astrophysics.⁴

Besides being an important component of Earth's atmosphere, molecular oxygen O₂ has been detected in the interstellar medium.⁵ From the astrophysical point of view there is genuine interest on inelastic collisions of small molecules with He and H₂,⁶ the predominant collision partners in molecular clouds.⁷ Much information about such regions comes from emission lines from rotationally excited molecules. On the other hand, O₂:He collisions are also crucial to produce cold and ultracold O₂ molecules.⁸⁻¹¹ Due to this interest, various high level *ab initio* calculations of the O₂-He potential energy surface (PES) have been published.¹²⁻¹⁴

State-to-state (sts) cross sections and rate coefficients for scattering of He atoms by O₂

molecules have been calculated by Lique¹⁵ within the close coupling approach resolved in the electron spin fine-structure;¹⁶ he employed the PES by Groenenboom and Struniewicz,¹³ as obtained from high level *ab initio* calculations. Using the same PES, pressure broadening coefficients for the rotational lines of the O₂ A-band by collisions with He atoms have been calculated¹⁷ and compared with experiments. From the experimental point of view, absolute¹⁸ and differential¹⁹ cross sections (DCS) for O₂-He scattering in molecular beam experiments, for collision energies larger than 100 cm⁻¹, have been reported previously. More recently, well resolved DCS for inelastic scattering have been measured²⁰ at fixed collision energy of 660 cm⁻¹ in crossed molecular beam experiments; the relative (normalized to unity) angular dependence profiles of state-to-state DCS's were successfully compared with calculations, using the above mentioned PES. However, for practical modeling of gas regions under non thermal-equilibrium conditions, a set of absolute rate coefficients, validated by experiment, is needed.

In the last years, we have developed²¹⁻²⁹ an original methodology to study rotationally inelastic molecular collisions at low temperature, even below 50 K, in the vibrational ground state. The procedure is based on tracking the time evolution of the rotational population along supersonic gas jets by Raman spectroscopy. The method is specially well suited for small molecules, including homonuclear diatomics, and provides quantitative assessment of sts-rates calculated from first principles. So far, it has been applied to *ortho*- and *para*-H₂,^{23,24} N₂,^{21,25} and their collisions with He,^{22,26} as well as O₂:O₂²⁸ and H₂O:He²⁹ collisions. Here we report the corresponding experimental study of O₂:He collisions, complemented with close coupling scattering calculations based on the PES by Groenenboom and Struniewicz.¹³

This paper is structured as follows. The theoretical methodology is outlined in Section 2, while the experiments and the data reduction procedure are detailed in Section 3. In Section 4, the experimental results are compared with the outcome of the theoretical calculations. The paper is closed with some concluding remarks and hints for future work.

2 Methodology

The theoretical methodology employed to interpret the experimental results of this work has been described elsewhere,^{26,28} and will be only outlined here. The time evolution of the population P_i of a rotational state i of O_2 molecules, as a result of the inelastic collisions with a bath of He atoms at a translational (kinetic) temperature T_T , is given by a Master Equation (MEQ)

$$\frac{dP_i}{dt} = n \sum_{\ell \neq i} (-P_i k_{i \rightarrow \ell} + P_\ell k_{\ell \rightarrow i}), \quad (1)$$

where n is the local number density of colliders. The state-to-state rate coefficients (sts-rates in short) $k_{i \rightarrow \ell}$ in MEQ (1) account for the rate of the elementary two-body collision process

and are functions of T_T . In the absence of chemical reactions or radiative transfer, the MEQ (1) represents the conservation of matter, and is free from approximations other than neglecting three-body collisions. These conditions are satisfied in the present gas jets experiments.

The rate coefficients for the “excitation” and “de-excitation” (henceforth “up” and “down” for short) collisional transfer between a given pair of levels, i and ℓ , g -fold degenerate, are related by the detailed balance

$$k_{i \rightarrow \ell}^{\text{up}} = k_{\ell \rightarrow i}^{\text{down}} \frac{g_\ell}{g_i} \cdot \exp(-\Delta E/k_B T_T) \quad (3)$$

where $\Delta E = E_\ell - E_i$ is the (positive) energy gap involved in the collision, and k_B is Boltzmann’s constant. At high enough temperatures k^{up} and k^{down} become related by the ratio of their degeneracies, but at low temperature they may differ by orders of magnitude. Since this could complicate the numerical treatment of the MEQ (1) it is convenient to rewrite it in terms of only “down” rates, which show a far smoother thermal dependence than the

“up” ones.

This MEQ formalism will be applied here to experiments on steady supersonic jets of $\text{O}_2(\alpha)+\text{He}$ mixtures, where α is the O_2 mole fraction. For a non-negligible fraction α , the population rate dP_i/dt for the O_2 molecules is the sum of two contributions {...} similar to the RHS of MEQ (1),

$$\frac{dP_i}{dt} = \alpha\{\text{O}_2 : \text{O}_2\} + (1 - \alpha)\{\text{O}_2 : \text{He}\}, \quad (4)$$

accounting for the collisions with O_2 or He colliding partners, respectively, weighted by their mole fractions.

The structure of rotational levels of the O_2 ($^3\Sigma_g^-$) molecule is more complex than that of most diatomics due to its $S = 1$ electron spin. The rotational angular momentum N couples with the electron spin S , leading to a total angular momentum $J = S + N$. As a result of such coupling, the rotational levels N are split into triads, with different $J = N, N \pm 1$, as shown, e. g., in Fig. 1 of reference 28. For $^{16}\text{O}_2$ only $N = \text{odd}$ values are allowed, due to nuclear spin statistics. Raman-active (Stokes) transitions between these fine-structure levels obey $\Delta N = +2$ and $\Delta J = 0, +1, +2$ selection rules, giving rise to six closely spaced lines. However, at the spectral resolution of the present experiments, just a triplet, split by $\pm 2 \text{ cm}^{-1}$, is observed for each $N \rightarrow N + 2$ rotational transition (see Fig. 1). On the one hand, the intensity of the side lines of the rotational triplets decreases rapidly for increasing N . On the other hand, for rotational temperatures above 10 K, the fractional populations of the $|N, J\rangle$ fine-structure levels within each N triad change by a few percent. For those reasons, the evolution of the population of the fine structure levels along the jet cannot be measured with enough accuracy in the present experiments, but only the global transfer of population between N triads. Thus, in the present work it is assumed that the O_2 molecule behaves effectively like a closed shell diatomic, with a rotational constant $B=1.43767 \text{ cm}^{-1}$ and rotational energy levels $E(N) = B N(N + 1)$. Hence, the fine structure due to electron spin will be largely ignored. This approximation is checked and theoretically justified in Section 4 below.

The theoretical sts-rates for the $\text{O}_2\text{:He}$ collisions, unresolved in the fine structure, have been calculated here by solving an atom-linear rotor scattering problem with the MOLSCAT code.³⁰ This approach has been tested by carrying out a proper comparison with averages of the rates reported by Lique¹⁵ resolved in the fine structure, as discussed in Section 4 below. We have employed the PES of Groenenboom and Struniewicz¹³ in order to be consistent with the calculations by Lique.¹⁵ The close-coupled equations were solved with the hybrid log-derivative/Airy propagator³¹ including a total of eleven rotational states in the wave function expansion (from $N=1$ to $N=21$). Integral cross sections $\sigma_{N \rightarrow N'}$ were obtained for a dense and extended grid of collision energies (468 non-uniformly distributed points, from the opening of the $N = 3$ channel at 17.28 cm^{-1} up to 660 cm^{-1}), and rate coefficients $k_{N \rightarrow N'}(T_T)$ were obtained from the standard Boltzmann-weighted integration. The corresponding sts-rates for the $\text{O}_2\text{:O}_2$ collisions were calculated in our previous work²⁸ using the ab initio PES by Bartolomei et al.³² Note that these $\text{O}_2\text{:O}_2$ rates also lack resolution in the fine structure of the O_2 molecules.

3 Experimental and Data Reduction

Three jets of $\text{O}_2(\alpha)\text{+He}$ mixtures with different α have been investigated in this work. Their experimental conditions are summarized in Table 1. Stagnation pressure p_0 was measured with a piezoresistive gauge of 4 mbar accuracy, and stagnation temperature T_0 with a calibrated RhFe resistor. The gas mixtures were prepared in continuous flow by means of two mass-flow controllers, and were expanded into a vacuum chamber through a circular airbrush nozzle of diameter $D = 0.358 \text{ mm}$. The chamber was evacuated by a (nitrogen-purged) 2000 liter/s turbomolecular pump, backed by a $400 \text{ m}^3/\text{hour}$ roots blower and a $65 \text{ m}^3/\text{hour}$ rotary pump, both lubricated with a special oil for pumping pure oxygen. Residual gas background pressure p_b was measured with a MKS Baratron 690A of 100 Torr full scale and nominal accuracy 0.08% of reading. The O_2 mole fraction α was measured by Raman spectroscopy,

Table 1: Experimental conditions of supersonic gas jets of $O_2(\alpha)+He$ mixtures studied in this work.

Jet	α	$W(\text{g/mol})$	γ	$p_0(\text{mbar})$	$T_0(\text{K})$	$n_0(10^{24} \text{ m}^{-3})$	$p_b(\text{mbar})$
A	0.02345	4.657	1.656	280.9	295.4	6.887	0.0075
B	0.1145	7.206	1.619	238.5	294.8	5.860	0.0056
C	0.4747	17.292	1.506	277.4	293.7	6.841	0.0037

as explained below for O_2 number density. The adiabatic coefficient $\gamma = C_P/C_V$ of the gas mixtures was calculated as $\gamma = (5+2\alpha)/(3+2\alpha)$, and the molar mass as $W = 32\alpha + 4(1-\alpha)$.

Under these conditions, a well defined zone of silence (ZS) was established for the three jets, surrounded by a structure of shock waves (BS, NS), as shown in Fig. 1. In the zone of silence the flow is laminar, and no significant penetration from residual background gas in the expansion chamber was observed, as checked by comparison with the isentropic model.^{33,34}

The jet axes were probed with a spatial resolution of a few microns by Raman scattering. It was excited by the sharply focused (15 μm) beam of a single-mode cw Ar^+ laser (4 W at 514.5 nm), perpendicular to the jet axis. The Raman signal was collected at 90° from both the jet axis and the laser beam, and was projected with a $\times 10$ magnification onto the entrance slit of the spectrometer. This is equipped with a 2360 groove/mm grating, and a CCD detector with 1430×400 pixels (20 μm) refrigerated by liquid nitrogen. For all the measured quantities, the space resolution of the Raman scattering experiment was high enough to avoid interferences from the regions surrounding the jet axis.

The primary experimental quantities $n(z)$, and $P_N(z)$ were measured along the jet axis at increasing distances z from the nozzle, like in our previous work on $O_2:O_2$ collisions,²⁸ and can be summarized as follows. The number densities of O_2 , $n^*(z)$, were measured from the integrated Raman intensity of the Q branch of the vibrational band of O_2 at 1555 cm^{-1} ,

$$I^Q(z) = K n^*(z), \quad (5)$$

Figure 1: Rotational Raman spectra of the $\text{O}_2(47\%) + \text{He}$ jet, showing the $N \rightarrow N+2$ triplets. ZS= zone of silence; NS=normal shock; BS=barrel shock.

Figure 2: Experimental number densities $n(z)$, and flow velocities $V(z)$, at increasing axial distance z from the nozzle, for the three O_2 +He jets studied in this work. Continuous lines are best fits to analytical functions. Dashed vertical lines bound the $34 \text{ K} \geq T_T \geq 10 \text{ K}$ thermal ranges.

which is, to a very good approximation, proportional to the number density of O_2 molecules at the focal spot of the exciting laser beam for a wide range of conditions. The constant K was determined by comparison with a static sample of pure O_2 at a known pressure as a reference. The total O_2 +He number densities were then calculated as $n(z) = n^*(z)/\alpha$. The raw experimental $n(z)$ values measured in this work are plotted in Fig. 2 for the three jets. A statistical uncertainty (2σ) of $\pm 5\%$ was estimated from the residuals of the fits to model functions (see below).

The rotational populations $P_N(z)$ were determined from the summed Raman intensities $I(z)$ over the triplets associated with the $N \rightarrow N + 2$ rotational transitions,^{35,36} which can be reduced to

$$P_N(z) = G I(z)_{N \rightarrow N+2} \frac{(2N+1)(2N+3)}{(N+1)(N+2)}, \quad (6)$$

for an ensemble of randomly oriented O_2 molecules. The constant G is determined from the normalization condition $\sum_N P_N = 1$. Representative rotational Raman spectra recorded along the jet axis of one of the expansions are shown in Fig. 1. Previous experiments on diluted jets of O_2 in He have reported partial rotational alignment of the O_2 molecules.^{37,38}

Figure 3: Experimental (symbols) and fitted (lines) populations P_N of the $N = 1$ to 9 rotational levels of O_2 for the $O_2(2.4\%)+He$ jet. Continuous lines are the calculated Boltzmann populations at the fitted T_R (see text). Dashed vertical lines bound the $34\text{ K} \geq T_T \geq 10\text{ K}$ thermal range.

However, its effect on the relative intensities of the $N \rightarrow N + 2$ Raman lines will be hardly detectable as long as the alignment of the O_2 molecules would be similar in all the observed rotational levels, as expected in the present experiments. The raw populations in the jet A are shown in Fig. 3 (symbols).

The measured rotational populations summed over the fine structure, $P_N = \sum_J P_{NJ}$, obey, to a good approximation, a Boltzmann distribution for a diatomic rigid rotor. Only minor deviations from that distribution were observed for the highest levels, which are scarcely populated. Thus, the vast majority of the molecules can be represented by a (rigid rotor) rotational temperature T_R . The raw experimental $T_R(z)$'s are plotted in Fig. 4 (red symbols)

Figure 4: Experimental rotational, $T_R(z)$ (in red), and translational, $T_T(z)$ (in blue), temperatures for the three O_2+He mixture jets studied in this work. The data at lower z are scaled by $\times 0.2$. Continuous lines are best fits to analytical functions. Dashed vertical lines bound the $34\text{ K} \geq T_T \geq 10\text{ K}$ thermal ranges.

for the three mixtures measured in this work. Statistical uncertainties (2σ) of $\pm 1.7\text{ K}$ for the jet A, and $\pm 1\text{ K}$ for the jets B and C, were estimated from the residuals of the fits to model functions (see below).

Following the empirical finding of our previous work on pure O_2 jets,²⁸ the translational temperatures have been first determined from the local number densities $n(z)$ by means of the isentropic condition ($\Delta S = 0$) along the jet for an ideal gas

$$T_T(z) = T_0 [n(z)/n_0]^{\gamma-1}, \quad (7)$$

where n_0 is the stagnation number density. These T_T temperatures were then checked against a more rigorous approach: for a real gas mixture of monatomic plus diatomic molecules, the $\Delta S = 0$ condition leads to an isentropic (*i*) translational temperature³⁹

$$T_T^{(i)}(z) = T_0 \left(\frac{n(z)}{n_0} \right)^{2/3} \left(\frac{T_0}{T_R(z)} \right)^{2\alpha/3}, \quad (8)$$

but any $\Delta S \neq 0$ raises it to

$$T_T^{(*)}(z) = T_T^{(i)}(z) \exp(2\Delta S/3R), \quad (9)$$

where $R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant. For an inviscid-adiabatic (i. e., no dissipation) gas flow, the entropy due to $T_R \neq T_T$ non-equilibrium is given by⁴⁰

$$\Delta S(z) = \alpha R \int_0^z \left(\frac{1}{T_R} - \frac{1}{T_T} \right) \left(\frac{dT_R}{dz} \right) dz. \quad (10)$$

The $T_T^{(*)}(z)$'s of Eq. (9), calculated numerically from the local quantities of the present jets, turned out to be very close to the T_T 's from Eq. (7), their difference being less than 0.25 K for the oxygen-rich jet C, and much smaller for the more diluted A and B jets. The raw experimental $T_T(z)$ are plotted with blue symbols in Fig. 4 where the $T_T < T_R$ breakdown of local thermal equilibrium can be clearly noticed. From the rated uncertainty of $n(z)$ and $T_R(z)$, the $T_T(z)$'s are estimated to be accurate (2σ) to ± 1 K for the three jets.

Analytical functions have been fitted to the raw experimental data $n(z)$ and $T_R(z)$ of Figs. 2 and 4, where they are plotted as continuous lines. The rotational populations $P_N(z)$ for $N = 1$ to 9 have been re-calculated from the fitted $T_R(z)$. For the jet A they are shown in Fig. 3 (continuous lines). From these functions, the gradients dP_N/dz can be obtained numerically at any z point. The flow velocities $V(z)$ are needed to transform them into time derivatives $dP_N/dt = V dP_N/dz$. They have been calculated from the conservation of enthalpy along the flow streamlines as

$$V^2(z) = \frac{R}{W} [5(T_0 - T_T(z)) + 2\alpha(T_0 - T_R(z))], \quad (11)$$

and they are plotted in Fig. 2.

The time derivatives $dP_N(z)/dt$ of the jet A obtained that way are shown in Fig. 5 along the full z -range. For the three jets, the $dP_N(z)/dt$ at selected z points corresponding to

Figure 5: Time derivatives dP_N/dt of the populations of the $N = 1$ to 9 rotational levels of O_2 , as retrieved from the experimental P_N of the $O_2(2.4\%)+He$ jet. Dashed vertical lines bound the $34\text{ K} \geq T_T \geq 10\text{ K}$ thermal range.

translational temperatures $T_T = 10, 14, 18, 22, 28$, and 34 K , will be compared next with the outcome of the theoretical calculations. Their uncertainties (2σ) have been estimated from those of the slopes of straight lines fitted locally (± 5 points) to the experimental $P_N(z)$, being on average 24000 s^{-1} , 8200 s^{-1} , and 5200 s^{-1} for the jets A, B, and C, respectively.

The probed thermal range is not limited, in principle, by our experimental set-up or methodology. However, in practical terms, the cold limit is determined by the sensitivity of the experiments, because the lowest temperatures are reached far away from the nozzle, where the severe density drop impedes to measure the decreasing population gradients with the required accuracy (see Figs. 2–4). Conversely, the warm limit is not much conditioned by the experiment (closer to the nozzle, the density is high and the population gradients are

large) but by the increasing number of involved rates, which can render unmanageable the analysis of the MEQ. In the present case, the 10-34 K thermal range was also determined by the availability of the O₂:O₂ collision data.

4 Discussion

The time derivatives dP_N/dt obtained through the data reduction procedure described above constitute the left-hand side (LHS) of the MEQ (1), and proceed solely from the present experimental data. The corresponding RHS can be calculated from the experimental n 's and P_N 's, along with a set of theoretical sts-rates $k_{N \rightarrow N'}$. In the case of the present mixtures, there are two contributions, one from the O₂:He hetero-collisions, and another one from the O₂:O₂ homo-collisions, weighted by their corresponding mole fractions, as shown in Eq. (4). The later contribution has been calculated here from a set of sts-rates validated in our previous experimental study on O₂:O₂ collisions.²⁸

For the O₂:He collisions, a set of theoretical down sts-rates in the 5-35 K thermal range is displayed in Fig. 6; the complete set employed in the present work is listed in Table 2. In order to assess the validity of omitting the fine structure in the collision dynamics of O₂ we have proceeded as follows. The rates calculated here can be compared with those resolved in the electron spin fine structure, $k_{NJ \rightarrow N'J'}$, calculated by Lique¹⁵ using the same PES, by summing these rates over the final triad levels (J'), and averaging over the initial ones (J),

$$k_{N \rightarrow N'}(T_T, T_R) = \sum_J \xi_{NJ}(T_R) \sum_{J'} k_{NJ \rightarrow N'J'}(T_T), \quad (12)$$

where

$$\xi_{NJ}(T_R) = \frac{(2J+1) \exp(-E_{NJ}/k_B T_R)}{\sum_{J'} (2J'+1) \exp(-E_{NJ'}/k_B T_R)} \quad (13)$$

is the fractional population of the $|N, J\rangle$ fine-structure state within the N triad at a rotational temperature T_R .

Figure 6: State-to-state rate coefficients for various $N \rightarrow N'$ processes computed here by neglecting the O_2 fine structure in the close-coupling calculations (solid lines), and compared with the fine-structure rates $k_{NJ \rightarrow N'J'}$ reported by Lique¹⁵ averaged according to Eq. (12) for the $O_2(2.4\%)+He$ jet (symbols).

As shown in Fig. 6, the present calculated rates (solid lines) are in very good agreement with the averaged rates (symbols) given by Eq. (12) for T_T and T_R of the $O_2(2.4\%)+He$ jet; similar plots are obtained for the other two jets. These results are consistent with the conclusion by Corey and McCourt⁴¹ that the collision dynamics of $^{2S+1}\Sigma$ molecules with lack of resolution in the spin multiplets is equivalent to that of spinless $^1\Sigma$ molecules, as long as the ratio between the statistically averaged energy for the N multiplet and the energy of the N level in the spinless approximation is close to one. Thus, deviations from the spinless approximation are only expected for sufficiently low collision energies or temperatures. Re-

sults of Fig. 6 indicate that, for O₂:He collisions, such deviations become noticeable around $T_T = 5$ K. Therefore, neglecting the O₂ fine structure for the collision dynamics provides here a safe approximation for translational temperatures above 10 K.

To compare the LHS with the RHS of the MEQ (1) we have proceeded as follows. As shown elsewhere,^{21,42} for the O₂:He collisions the MEQ (1) leads to the linear system

$$\begin{aligned}
 dP_1/dt &= a_{31}k_{3 \rightarrow 1} + a_{51}k_{5 \rightarrow 1} + a_{71}k_{7 \rightarrow 1} + \dots \\
 dP_3/dt &= -a_{31}k_{3 \rightarrow 1} + a_{53}k_{5 \rightarrow 3} + a_{73}k_{7 \rightarrow 3} + \dots \\
 \vdots &= \vdots \\
 dP_N/dt &= -a_{N1}k_{N \rightarrow 1} - a_{N3}k_{N \rightarrow 3} - \dots + a_{N+1,N}k_{N+1 \rightarrow N} + \dots,
 \end{aligned} \tag{14}$$

expressed in terms of only “down” rates. The system of Eq. (14) can be written in the general form

$$dP_N/dt = - \sum_{i < N} a_{Ni}k_{N \rightarrow i} + \sum_{\ell > N} a_{\ell N}k_{\ell \rightarrow N}, \tag{15}$$

with coefficients

$$a_{\ell i} = n P_\ell (1 - \exp[-\Delta E (T_T^{-1} - T_R^{-1})/k_B]), \tag{16}$$

where $\ell > i$ holds; thus $\Delta E = E_\ell - E_i$ is the *positive* energy difference of the $N = \ell$ and $N = i$ rotational levels. For atom-molecule collisions, the $a_{\ell i}$ coefficients are always positive for $T_R > T_T$, condition that holds in the zone of silence of supersonic jets. The actual computation of RHS in Eq. (14) involves differences of larger quantities, and thus the calculated dP_N/dt might be prone to significant error. To minimize them, the system of Eq. (14) can be re-arranged by linear combinations into the cumulative sums $S_N = \sum_{j=1}^N dP_j/dt$

$$\begin{aligned}
 dP_1/dt &= a_{31}k_{3 \rightarrow 1} + a_{51}k_{5 \rightarrow 1} + a_{71}k_{7 \rightarrow 1} + \dots \\
 dP_1/dt + dP_3/dt &= a_{51}k_{5 \rightarrow 1} + a_{71}k_{7 \rightarrow 1} + \dots
 \end{aligned}$$

$$\begin{aligned}
& +a_{53}k_{5\rightarrow3} + a_{73}k_{7\rightarrow3} + \dots \\
& \vdots = \vdots \\
\sum_{j=1}^N dP_j/dt &= \sum_{i=1}^N \sum_{\ell>N} a_{\ell i} k_{\ell\rightarrow i}.
\end{aligned} \tag{17}$$

As opposed to Eq. (14), the RHS in Eq. (17) are sums of positive terms only, because the negative ones in Eq. (14) cancel out. Something similar occurs in the MEQ accounting for the O₂:O₂ homo collisions, although in this case not all the negative terms cancel out.

Again, the LHS in Eq. (17) is a purely experimental quantity (sums of dP_N/dt), while the corresponding RHS is a combination of experimental quantities (n 's and P_N 's) and theoretical sts-rates. The experimental S_N (LHS in Eq. (17)) at selected z points corresponding to translational temperatures $T_T = 10, 14, 18, 22, 28$, and 34 K, for the four lowest rotational levels $N = 1, 3, 5, 7$, are plotted as cyan bars in Figs. 7 and 8, along with their estimated uncertainties (2σ) as propagated from those of the dP_N/dt . The contributions of the O₂:He collisions to the RHS of Eq. (17) at the same z points are plotted as white bars in Figs. 7 and 8, while those of the O₂:O₂ collisions are plotted as pink bars. The uncertainties of the calculated RHS were estimated through error propagation⁴³ from those of n , T_R and T_T .

For any of the three jets, the overall correlation coefficient between the corresponding LHS and RHS of MEQ (4) is better than 0.98 for the four lowest rotational levels in the 10-34 K thermal range. It should be stressed that such an agreement between experiment and theory is accomplished despite the large range of O₂ content (2.34% to 47.5%), densities (10 to $30 \times 10^{22} \text{ m}^{-3}$), and flow velocities (900 to 1600 m/s, see Fig. 2) of the current experiments.

At a given translational temperature T_T , the root mean squared (rms) differences (LHS-RHS), $\sqrt{\sum(\text{LHS}_N - \text{RHS}_N)^2/12}$, for the four lowest rotational levels over the three jets, range from 25000 s^{-1} at $T_T \leq 18$ K to 54000 s^{-1} at 34 K. The relatively high latter value might be due to the lack of sufficient sts-rates being considered here, since at $T_T = 34$ K the number of inelastic channels contributing to the total population rates dP_N/dt is quite large, especially for the O₂:O₂ homo collisions. On the contrary, the rms of the (LHS-RHS)

difference at lower T_T is comparable to the uncertainty of the experimental dP_N/dt for the most diluted jet A, where the $\text{O}_2\text{:He}$ collisions are dominant over the $\text{O}_2\text{:O}_2$ collisions.

At the low T_T 's probed in the current experiments, only a few $a_{\ell i} k_{\ell \rightarrow i}$ terms contribute significantly to the calculated S_N , one of them usually being dominant. Thus, S_1 depends mostly on $3 \rightarrow 1$ plus a minor contribution from $5 \rightarrow 1$; S_3 is mostly due to $5 \rightarrow 3$ plus smaller contributions from $5 \rightarrow 1$ and $7 \rightarrow 3$; and S_5 is mostly due to $7 \rightarrow 5$ plus a minor contribution from $7 \rightarrow 3$. This situation is more pronounced the lower the T_T : at $T_T = 10$ K, $3 \rightarrow 1$ amounts to 94% of dS_1/dt , plus a residual 6% due to $5 \rightarrow 1$, while at $T_T = 34$ K these contributions are 71% and 25%, respectively. By comparing the experimental (LHS) and calculated (RHS) S_N 's, one could attempt to track some correlations to individual sts-rates, like in our previous work on $\text{H}_2\text{:He}$ collisions,²⁶ or to scale all the sts-rates to minimize the LHS-RHS difference, like in our works on $\text{O}_2\text{:O}_2$ ²⁸ and $\text{H}_2\text{O:He}$ ²⁹ collisions. Unfortunately, the large uncertainty of some of the bars in Figs. 7 and 8, along with the fact that the observed (total) population rates in the mixtures include the corresponding weighted contribution from $\text{O}_2\text{:O}_2$ homo-collisions, impairs carrying out such an exercise with confidence.

Finally, it should be noticed that the previous experiments²⁰ on differential cross sections for inelastic collisions of O_2 and He were carried out at a fixed collision energy of 660 cm^{-1} , much higher than the ΔE probed in this work, and thus no direct comparison with the present results is possible.

5 Concluding remarks

A study of the $\text{O}_2\text{:He}$ inelastic collisions from 10 to 34 K is presented. For that purpose, a number of supersonic microjets of $\text{O}_2\text{:He}$ mixtures free from O_2 condensation, with O_2 fractions spanning from about 2.5% to 50%, have been quantitatively characterized in terms of variations in densities $n(z)$ and rotational populations $P_N(z)$ along the jet axis z by means of their rotational and vibrational Raman spectra. From these primary data, rotational

temperature, translational temperatures, and flow velocity were determined. All these experimental data are linked to theoretically calculated sts-rate coefficients by means of the kinetic Master Equation which accounts for the time evolution of the rotational populations. A detailed analysis of the Master Equation, which combines experimental and theoretical data, allows us to assess the accuracy of the rate coefficients: the agreement, within the experimental uncertainty, between experimental and theoretical population rates validates the employed potential energy surface¹³ to a large extent. Although our analysis was done by summing over the O₂ fine structure, our results indirectly validate as well the existing collision rates resolved in the fine structure¹⁵ employed in the radiative transfer models. The present results are meant as a guide for future experiments and astrophysical observations.

The feasibility of the experimental set-up and methodology for studying collisions of O₂ molecules with He atoms has been demonstrated. This is based on Raman spectroscopy of supersonic gas jets combined to a kinetic Master Equation. Although there is no specific limitation in our experimental set-up or methodology, it is especially well suited for low temperatures, where just a few rate coefficients come into play in the Master Equation. Within the thermal range studied here ($T > 10$ K), the fine structure due to electron spin can be ignored for the average rotational dynamics of O₂ in collisions with He. Preliminary experiments on O₂:He jets with $T_T \leq 4$ K show that the current experimental approach can also be used to study the change in population within the rotational N -triads due to (*quasi*)elastic collisions, where the fine structure due to electron spin will be necessarily taken into account.

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Figure 7: Experimental (cyan) and calculated (white $O_2:He$ and pink $O_2:O_2$) time derivatives S_N of the populations of the rotational levels of O_2 at $T_T = 10, 14, 18$ K, for the three jets studied in this work.

Figure 8: Experimental (cyan) and calculated (white $\text{O}_2:\text{He}$ and pink $\text{O}_2:\text{O}_2$) time derivatives S_N of the populations of the rotational levels of O_2 at $T_T = 22, 28, 34\text{ K}$, for the three jets studied in this work.

Table 2: State-to-state rate coefficients, averaged over the electron spin fine structure, for “down” rotational inelastic collisions of O₂ with He, employed in the Master Equation of this work. Units: 10⁻²⁰ m³/s.

$N \rightarrow N'$	Δ/B	$T = 34$ K	28	22	18	16	14	12	10
3 $\rightarrow$ 1	10	3513.38	3375.32	3236.47	3143.89	3097.17	3049.48	2999.79	2946.37
5 $\rightarrow$ 1	28	769.08	732.55	701.33	684.24	677.00	670.67	665.26	660.61
5 $\rightarrow$ 3	18	4611.28	4473.45	4338.72	4254.01	4214.30	4176.95	4142.32	4110.11
7 $\rightarrow$ 1	54	201.64	187.08	174.18	166.72	163.41	160.44	157.83	155.62
7 $\rightarrow$ 3	44	1006.15	950.98	900.22	869.83	855.99	843.23	831.65	821.13
7 $\rightarrow$ 5	26	5257.24	5127.73	5003.40	4928.53	4895.24	4865.57	4839.74	4816.35
9 $\rightarrow$ 1	88	46.03	41.62	37.82	35.68	34.75	33.93	33.21	32.60
9 $\rightarrow$ 3	78	278.00	257.63	239.46	228.97	224.34	220.19	216.56	213.43
9 $\rightarrow$ 5	60	1146.04	1077.54	1013.49	974.88	957.33	941.21	926.60	913.27
9 $\rightarrow$ 7	34	5540.73	5396.27	5255.93	5170.51	5132.02	5096.94	5064.80	5032.76
11 $\rightarrow$ 1	130	10.35	9.19	8.22	7.69	7.46	7.26	7.09	6.95
11 $\rightarrow$ 3	120	67.09	60.70	55.21	52.15	50.84	49.68	48.70	47.89
11 $\rightarrow$ 5	102	319.04	294.37	272.40	259.82	254.32	249.45	245.25	241.70
11 $\rightarrow$ 7	76	1222.63	1145.08	1073.21	1030.70	1011.77	994.72	979.70	966.49
11 $\rightarrow$ 9	42	5546.92	5380.75	5219.90	5122.84	5079.56	5040.58	5005.65	4972.21
13 $\rightarrow$ 1	180	2.22	1.93	1.70	1.58	1.53	1.48	1.44	1.41
13 $\rightarrow$ 3	170	15.63	13.91	12.47	11.69	11.36	11.07	10.82	10.62
13 $\rightarrow$ 5	152	80.30	72.57	65.97	62.30	60.73	59.35	58.16	57.16
13 $\rightarrow$ 7	126	335.08	307.70	283.49	269.71	263.69	258.33	253.64	249.55
13 $\rightarrow$ 9	92	1240.69	1158.68	1083.61	1039.69	1020.22	1002.66	987.06	973.07
13 $\rightarrow$ 11	50	5359.28	5174.61	4997.11	4889.93	4841.64	4797.45	4756.78	4716.65

Figure 9: TOC Graphic