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Collisional excitation of O₂ by H₂: the validity of LTE models in interpreting O₂ observations

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ABSTRACT

Context. Oxygen molecules (O₂) are of particular interest because of their crucial role in astrochemistry. Modelling of O₂ molecular emission spectra from interstellar clouds requires the calculation of rate coefficients for excitation by collisions with the most abundant species.

Aims. Rotational excitation of O₂(X³Σ⁻) by H₂ is investigated theoretically and experimentally and we check the validity of the local thermodynamic equilibrium (LTE) approach for interpreting O₂ observations.

Methods. Using a new ab initio potential energy surface, collisional excitation of O₂ is studied using a full close-coupling approach. The theoretical calculations are validated by comparison with crossed beam scattering experiments. We also performed calculations for the excitation of O₂ from a large velocity gradient (LVG) radiative transfer code using the new rate coefficients.

Results. State-to-state rate coefficients between the 27 lowest levels of O₂ were calculated for temperatures ranging from 5 K to 150 K. The critical densities of the O₂ lines are found to be at $\geq 10^4$ cm⁻³ for temperatures higher than 50 K. This value is slightly larger than the one previously determined using previous He rate coefficients.

Conclusions. The new rate coefficients will help in interpreting O₂ emission lines observed where LTE conditions are not fully fulfilled and enable an accurate determination of the O₂ abundance in the interstellar medium.

Key words. molecular processes – molecular data – ISM: abundances – ISM: molecules

1. Introduction

Oxygen is the third most abundant element in the Universe after hydrogen and helium, which makes it very important in terms of understanding the formation and evolution of the chemistry in astronomical sources. Earlier gas-phase chemical models predicted O₂ to be a major reservoir of elemental oxygen in dense molecular clouds (Herbst & Klemperer 1973). Searches for interstellar O₂ have been one of the major goals for molecular astrophysics during the last decades. However, until recently, attempts to detect interstellar O₂ line emission with ground- and space-based observatories have failed (Combes & Wiklind 1995; Marechal et al. 1997; Pagani et al. 2003).

In 2007, Larsson et al. (2007) eventually reported the first observation of O₂ in the interstellar medium (ISM) from the satellite ODIN mission. Surprisingly, the O₂ abundance in the cores of molecular clouds was found to be ~ 1000 times lower than predicted by the astrochemical models. The low O₂ abundance has since been confirmed by other O₂ observations (Goldsmith et al. 2011; Liseau et al. 2012; Yıldız et al. 2013).

Such a low abundance for the O₂ molecule pushed physical chemists and astrochemists to review the oxygen chemistry in dense molecular clouds (Lique et al. 2009). The low abundance of O₂ in dark clouds can now be explained by gas-grain

chemical models that conclude that oxygen depletion is important (Hincelin et al. 2011).

Although low, the abundance of O₂ has still to be determined accurately. Since collisions compete with radiative processes in altering populations of molecular ro-vibrational levels, the estimation of molecular abundances in the ISM from spectral line data usually requires collisional rate coefficients with the most abundant interstellar species like He or H₂. Rate coefficients for O₂-He inelastic collisions were provided some time ago by Lique (2010). Goldsmith et al. (2011) used these rate coefficients to study the excitation of O₂ in cold molecular clouds. They concluded that O₂ abundance determination is possible assuming local thermodynamic equilibrium (LTE) (i.e. without using rate coefficients) because O₂ radiative rates are small and because the excitation of O₂ is dominated by collisions.

In the ISM, the main collisional partner is H₂ and it is well known that He and H₂ rate coefficients differ significantly, especially in the case of ortho-H₂ (Roueff & Lique 2013). It is then very important to also provide collisional data for the O₂-H₂ systems.

In this paper, we present a new study of the collisional excitation of O₂ by H₂ and we compare the theoretical results with experimental ones obtained from crossed-beam scattering experiments. Using the new data, we check the validity of the LTE approach for interpreting O₂ observations.

2. Methodology of calculations

2.1. Potential energy surface (PES)

The PES used in this work was described in detail in Kalugina et al. (2012, hereafter Paper I). The PES was calculated in the supermolecular approach with a partially spin-restricted coupled cluster with single, double, and perturbative triple excitations [RCCSD(T)] (Knowles et al. 1993, 2000). The collision partners were considered to be rigid [$r_{\text{O-O}} = 2.297$ bohr and $r_{\text{H-H}} = 1.449$ bohr]. The four atoms were described by augmented correlation-consistent quadruple zeta (aug-cc-pVQZ) basis set of Dunning (1989) augmented with bond functions. Details of computations, analytical representation, and plots of the PES are given in Paper I. For the scattering calculations, we used the original PES of Paper I and not the scaled one of Chefdeville et al. (2013).

2.2. Scattering calculations

As noticed in Paper I and confirmed by the experiments of Chefdeville et al. (2013), the rotation of H₂ has almost no influence on the magnitude of O₂–H₂ integral cross sections (ICS). Thus, we performed calculations only for the $j = 0$ level of H₂ (i.e. the PES was averaged over both orientation θ' and dihedral ϕ angles describing the H₂ geometry) and considered that our results are valid for both para- and ortho-H₂. Collisions with H₂($j = 0$) are equivalent to collisions with a structureless atom. Then, the scattering problem is equivalent to atom-diatom inelastic collisions.

In the O₂(³Σ⁻) electronic ground state, the rotational levels are split by spin-rotation coupling. In the intermediate coupling scheme, the rotational wave function of O₂ can be written for $j \geq 1$ as (Lique et al. 2005)

$$\begin{aligned} |F_1 jm\rangle &= \cos\alpha|N = j - 1, S jm\rangle + \sin\alpha|N = j + 1, S jm\rangle \\ |F_2 jm\rangle &= |N = j, S jm\rangle \\ |F_3 jm\rangle &= -\sin\alpha|N = j - 1, S jm\rangle + \cos\alpha|N = j + 1, S jm\rangle, \end{aligned} \quad (1)$$

where $|N, S jm\rangle$ denotes pure Hund's case (b) basis functions and the mixing angle α is obtained by diagonalisation of the molecular Hamiltonian. In this relation corresponding to Hund's case (b), the total molecular angular momentum j is defined by:

$$j = N + S, \quad (2)$$

where N and S are the nuclear rotational and the electronic spin angular momenta. The rotational energy levels of the O₂ molecule were computed with the use of the experimental spectroscopic constants of Endo & Mizushima (1982).

All calculations were carried out with the exact energy levels including the fine structure interaction. However, in the present paper, we will use the usual astrophysical level labelling N_j where $N = j - 1$, $N = j$, and $N = j + 1$ correspond to the F_1 , F_2 , and F_3 levels as defined in Eq. (1). The quantal coupled equations were solved in the intermediate coupling scheme using the MOLSCAT code (Hutson & Green 1994) modified to take into account the fine structure of the energy levels. We used a fine collisional energy grid for the calculations so that the resonances (shape and Feshbach) that appear in the ICS at low and intermediate energies were well represented.

By averaging over a Maxwellian distribution of collision velocities, we can use the calculated ICS to obtain thermal rate coefficients for (de-)excitation transitions between O₂ levels

$$k_{\alpha \rightarrow \beta}(T) = \left(\frac{8}{\pi \mu k_B^3 T^3} \right)^{\frac{1}{2}} \int_0^{\infty} \sigma_{\alpha \rightarrow \beta} E_k e^{-\frac{E_k}{k_B T}} dE_k, \quad (3)$$

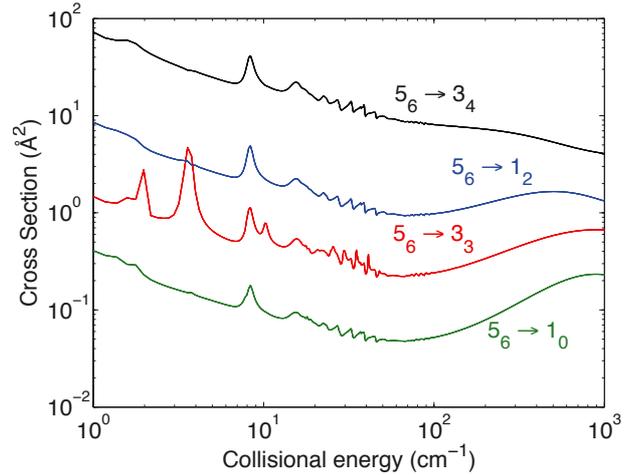


Fig. 1. Collisional excitation ICS of O₂ by H₂ out of the $N_j = 5_6$ state.

where $\sigma_{\alpha \rightarrow \beta}$ is the cross section from initial level α (i.e. N_j) to final level β (i.e. N'_j), μ is the reduced mass of the system and k_B is the Boltzmann constant.

In order to ensure convergence of the inelastic ICS, it was necessary to include in the calculations several energetically inaccessible (closed) levels. At the largest energies considered in this work, the O₂ rotational basis was extended to $N = 29$ to ensure convergence of the rotational ICS of O₂.

3. Results

3.1. Cross sections

We have obtained the (de-)excitation ICS between the first 27 fine structure levels of O₂ by H₂. Figure 1 presents the typical kinetic energy variation of the ICS for de-excitation transitions from the $N_j = 5_6$ level of O₂. As expected, the de-excitation ICS decrease with increasing energy. Noticeable resonances appear at low collisional energies. This is related to the presence of an attractive potential well, which allows for O₂–H₂ bound and quasi-bound states to be formed before the complex dissociates (Smith et al. 1979; Christoffel & Bowman 1983).

The quality of the theoretical results strongly depends on the accuracy of the PES employed for the quantum scattering calculations, especially at very low energy and for low O₂ quantum numbers where the ICS can be significantly dominated by resonances. The energy position, width and magnitude of the resonances are so dependent on the calculated potential well that their experimental observation offers a stringent test for the theory. We already obtained a strong positive sign in previous combined theoretical and experimental work on the ICS of the $1_0 \rightarrow 1_1$ transition with complete resolution of the partial-wave resonances (Chefdeville et al. 2013). In this work, we extend the study to the $1_2 \rightarrow 3_2$ transition.

Using the same apparatus as the one described in Chefdeville et al. (2013), we measured the ICS corresponding to the $1_2 \rightarrow 3_2$ transitions by probing the collision induced population in the 3_2 level as a function of the collision energy using the $2+1(^3\Sigma_1^-, v = 2 \leftarrow ^3\Sigma_0^-, v = 0) Q_{23}(2)$ resonance-enhanced multiphoton ionisation transition at 88.874 cm^{-1} (Yokelson et al. 1992). The experiments were performed with normal-H₂; they can nevertheless be directly compared with the theoretical results since the O₂–H₂ ICS have been proven not to depend on the

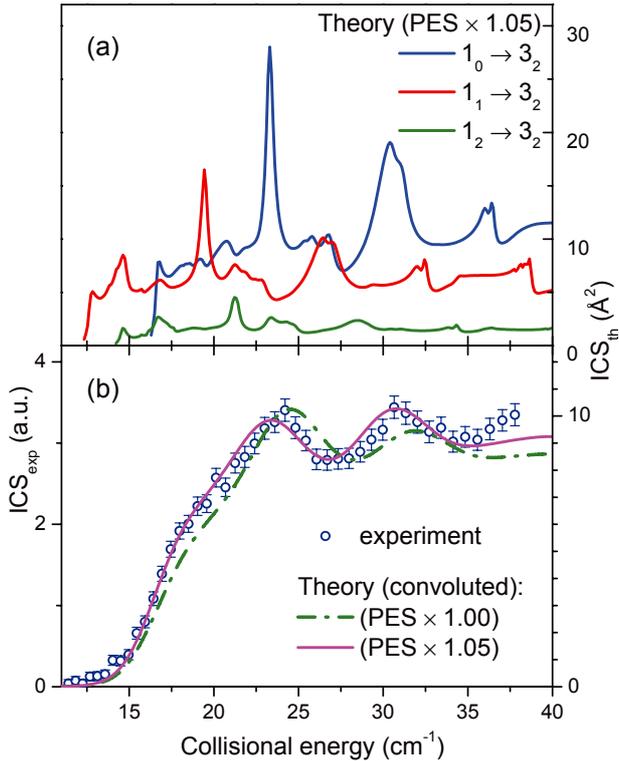


Fig. 2. Collisional energy dependence of the integral cross sections for O₂ excitation $N_j = 1_0 \rightarrow N_{j'} = 3_2$. **a)** Theoretical ICS calculated with modified PES; **b)** theoretical ICS convoluted with the experimental collision energy spread calculated with the original PES (dashed line) and the modified PES (solid line); experimental data (open circles), obtained when crossing a beam of normal-H₂ from a first pulsed nozzle at ≈ 45 K propagating at velocity $v_1 = 951$ ms⁻¹ with a beam of 0.5% O₂ in Ne from a second pulsed nozzle at 300 K propagating at $v_2 = 803$ ms⁻¹; crossing angle χ was varied from 22.5° to 45°, resulting in a collision energy $E_k = \frac{1}{2}\mu(v_1^2 + v_2^2 - 2v_1v_2\cos\chi)$ where μ stands for the reduced mass of the collision partners.

rotational levels of H₂. The initial residual population in 3₂ level was offset by shot-to-shot background subtraction when triggering the probe laser and the O₂ beam at 10 Hz with the H₂ beam at 5 Hz. The ICS were recovered from the measured intensities using the procedure described in the Supplementary Materials of Chefdeville et al. (2013).

The ICS obtained for O₂–H₂ collisions are displayed in Fig. 2. The theoretical results obtained with a slightly modified PES (the original PES scaled by a factor of 1.05; see Chefdeville et al. 2013) for the three possible transitions from the $N = 1$ state ($1_{j=0-2} \rightarrow 3_2$) are given in the upper panel (Fig. 2a). The experimental data obtained between $E_k = 11.4$ cm⁻¹ and 37.8 cm⁻¹ are displayed in the lower panel (Fig. 2b) along with the theoretical ICS convoluted with the experimental collision energy spread to allow for comparison with the experimental values. Excitation of any $1_{j=0-2}$ state can contribute to the signal. However, the observed signal is probably due mainly to the 1₀ state for the following reasons: (i) the rotational temperature within the molecular beam for CO (Chefdeville et al. 2012) and O₂ (Chefdeville et al. 2013) beams was proven to be below 1 K; a similar behaviour is then expected for the O₂ source in the present work, resulting in relative populations ($P(0) \approx 0.8$, $P(2) \approx 0.2$ and $P(1) \leq 0.01$); (ii) the calculated cross section for excitation of the $N_j = 1_1$ state ($\Delta j = \Delta N - 1$) is only slightly less intense than for the $N_j = 1_0$ state ($\Delta j = \Delta N$); a significant population

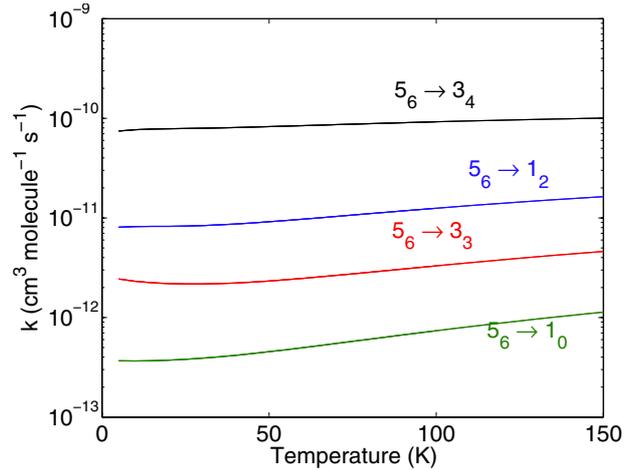


Fig. 3. O₂–H₂ rate coefficients out of the $N_j = 5_6$ state.

of the $N_j = 1_1$ level would result in a significant signal below the 1₀ → 3₂ threshold at 16.3 cm⁻¹, which is not observed; and (iii) the calculated cross section for excitation from the 1₂ level is much weaker ($\Delta j = \Delta N - 2$); a 20% population results in a small contribution. The theoretical data displayed in Fig. 2b are the sum of the contributions of excitation from the 1₀, 1₂, and 1₁ states, weighted to their relative populations at 1 K, and convoluted to experimental energy resolution.

The agreement between experimental values and present theory is good. The agreement becomes almost perfect as for the 1₀ → 1₁ transition when using the slightly modified PES. However, this modified PES, tailored for very low collisional energies, can hardly be used for the determination of rate coefficients for temperatures above 30–50 K. This PES accurately describes the bound state energies but the scaling factor of 1.05 leads to an overestimation of the interaction energies in the repulsive wall. For the original PES, the overall good agreement again confirms the accuracy of the calculated PES and of the theoretical approach. We found that rate coefficients obtained from both the original and the modified PES differ by less than 10% at 10 K. It suggests that the rate coefficients obtained here are accurate enough to allow improved astrophysical modelling.

3.2. Rate coefficients

By performing a thermal average of the collision energy dependent ICS, we have obtained rate coefficients between the first 27 fine structure O₂ levels for temperatures up to 150 K. This complete set of (de-)excitation rate coefficients is available on-line from the LAMDA (Schöier et al. 2005) and BASECOL (Dubernet et al. 2013) websites. The thermal dependence of the state-to-state O₂–H₂ rate coefficients is illustrated in Fig. 3 for transitions out of the $N_j = 5_6$ level.

A strong propensity rule exists for $\Delta j = \Delta N$ transitions. A propensity rule of this kind was predicted theoretically (Alexander & Dagdigan 1983) and is general for molecules in the ³Σ⁻ electronic state. It was also observed previously for the O₂(X³Σ⁻)–He (Lique 2010), SO(X³Σ⁻)–H₂ (Lique et al. 2007) or NH(X³Σ⁻)–He (Toboła et al. 2011) collisions.

Collisions with He are often used to model collisions with H₂. It is generally assumed that rate coefficients with H₂ should be larger than He rate coefficients; a scaling factor of 1.4 being often used (Schöier et al. 2005). In Table 1, we show,

Table 1. Comparison between O₂–He and present O₂–H₂ rate coefficients.

$N_j \rightarrow N'_j$	10 K		50 K		150 K	
	He	H ₂	He	H ₂	He	H ₂
$1_1 \rightarrow 1_0$	0.14	0.76	0.04	0.17	0.01	0.04
$3_3 \rightarrow 1_1$	1.75	3.76	2.35	3.99	3.06	5.29
$3_3 \rightarrow 1_2$	1.08	1.95	1.38	1.96	1.90	2.65
$3_4 \rightarrow 1_0$	0.18	0.28	0.21	0.27	0.37	0.51
$3_4 \rightarrow 1_2$	2.56	5.76	3.37	5.95	4.28	7.72
$5_4 \rightarrow 1_0$	0.21	0.28	0.27	0.31	0.44	0.53
$5_4 \rightarrow 1_2$	0.19	0.24	0.28	0.28	0.61	0.60
$5_4 \rightarrow 3_2$	3.27	6.39	3.89	6.84	4.64	8.14
$9_{10} \rightarrow 5_6$	0.87	1.58	1.29	1.81	2.21	2.84
$9_{10} \rightarrow 7_7$	0.06	0.09	0.10	0.10	0.22	0.19

Notes. The rate coefficients are in units of $10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

on a small sample, a comparison of our rotational O₂–H₂ rate coefficients versus the O₂–He ones of Lique (2010).

As one can see, differences exist between the two sets of data. Globally, the H₂ results are larger by a factor of ≈ 2 than the He ones at low temperature and for transitions between the first rotational states. The ratio can even be larger (see e.g. the $1_1 \rightarrow 1_0$ transition). However, for transitions between higher energy levels and for temperature above 50 K, He rate coefficients can be equal to or larger than the H₂ rate coefficients. Therefore, using He rate coefficients scaled by a factor of 1.4 results in an overestimation of the collisional process in modelling of O₂ emission.

4. Discussion and astrophysical applications

We have presented quantum mechanical calculations of rate coefficients for the collisional excitation of O₂ by H₂ molecules. The accuracy of the theoretical calculations has been checked by comparing theoretical and experimental ICS. The rotationally inelastic energy transfer in O₂ is more efficient with H₂ molecules than with He atoms at low temperature, but is similar at high temperatures and for high rotational states.

As a first application and in order to test the impact of the new rate coefficients, we have performed radiative transfer calculations for typical physical conditions from where O₂ emission is detected. Non-local thermodynamic equilibrium (non-LTE) calculations were performed with the RADEX code (van der Tak et al. 2007) using the large velocity gradient (LVG) approximation for an expanding sphere. Both collisional and radiative processes are taken into account.

We focus on the calculation of the excitation temperature determined for O₂ transitions that have been already observed. Figure 4 shows some results of our calculations for a column density of O₂ fixed at 10^{15} cm^{-2} .

At very low volume densities, the excitation temperature of four lines tends to be equal to the adopted value of the background radiation field (2.7 K). This parameter rises to higher values as collisional excitation becomes more important. At volume densities above a critical value, the excitation temperature approaches the kinetic temperature, at which point the LTE approximation may be used. At low temperatures (10 K) the critical density lies at $\approx 10^3 \text{ cm}^{-3}$, while for higher temperatures, the critical density can be up to $2\text{--}3 \times 10^4 \text{ cm}^{-3}$ for transitions between highly excited states. This conclusion is in reasonable agreement

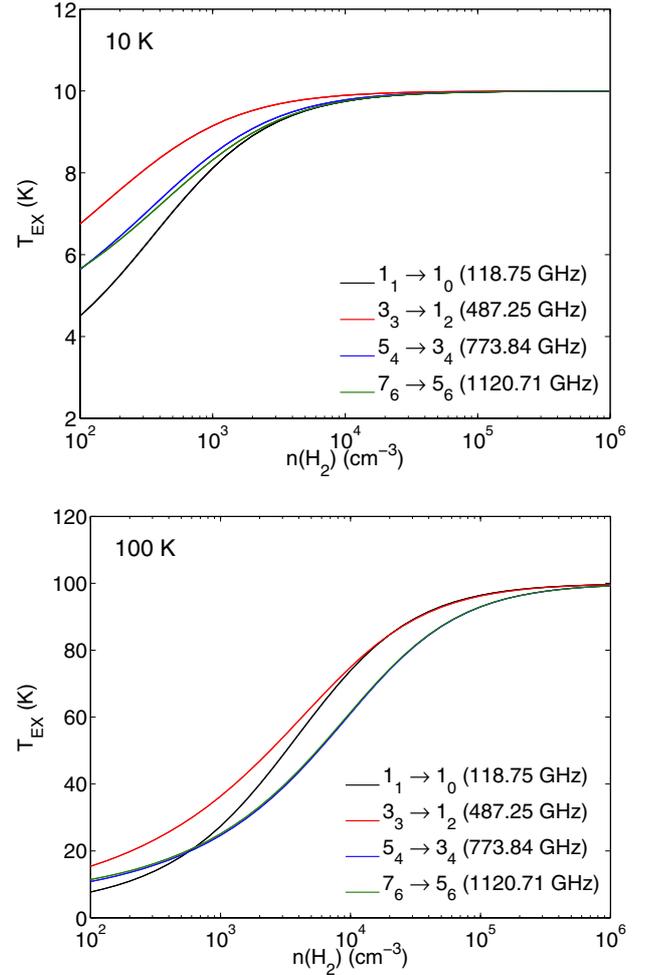


Fig. 4. Excitation temperature for the $1_1 \rightarrow 1_0$, $3_3 \rightarrow 1_2$, $5_4 \rightarrow 3_4$ and $7_6 \rightarrow 5_6$ lines of O₂, as a function of volume density for $T = 10$ and 100 K. The column density of O₂ is 10^{15} cm^{-2} .

with the one found by Goldsmith et al. (2011) although we found critical densities a bit larger than in their study. This can certainly be explained by the magnitude of H₂ rate coefficients between high energy levels of O₂ that is smaller than the corresponding He ones (scaled by a factor of 1.4) used by Goldsmith et al. (2011).

We also vary the column density of O₂ (from 10^{14} to 10^{16} cm^{-2}) and we have also found although not shown here that the column density has almost no impact on the magnitude of the excitation temperature. This can certainly be explained by the fact that the O₂ lines are optically thin.

To conclude, at typical physical conditions of molecular clouds where O₂ is observed ($n(\text{H}_2) > 3 \times 10^4 \text{ cm}^{-3}$, $T = 10\text{--}100 \text{ K}$), O₂ lines are mainly thermalised. However, if O₂ can survive in slightly lower density and/or higher temperature molecular clouds, non-LTE analysis will be required in order to enable an accurate determination of O₂ abundance.

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