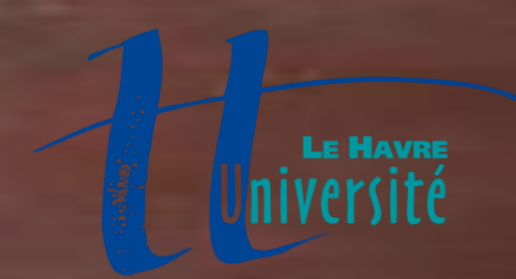


# (De-)excitation rate coefficients for collisions of O<sub>2</sub> with H<sub>2</sub>



Yulia Kalugina<sup>1,2</sup>, François Lique<sup>1</sup>

<sup>1</sup>LOMC – UMR 6294, CNRS-Université du Havre, 25 rue Philippe Lebon, BP 540, 76058 Le Havre, France

<sup>2</sup>Department of Optics and Spectroscopy, Tomsk State University, 36 Lenin Avenue, Tomsk 634050, Russia

## INTRODUCTION

Oxygen molecule - central molecule in the physical chemistry of many media. It is an important constituent of the earth atmosphere and interstellar gas. O<sub>2</sub> participated in many key reactions in ISM.

Because of the huge barrier height for branching chain oxidation of H<sub>2</sub> with O<sub>2</sub>, at low temperature (T < 1000 K), O<sub>2</sub>-H<sub>2</sub> collisions lead only to ro-vibrational energy transfer. This process is of key importance in astrophysical media since collisions compete with radiative processes in altering populations in molecular ro-vibrational levels.

Correct estimation of O<sub>2</sub> abundances in ISM from spectral data requires accurate collisional rate coefficients with the most abundant species such as H, He and H<sub>2</sub>. Determination of these rate coefficients will be an essential support in resolution of so-called "interstellar O<sub>2</sub> problem": recent measurements from the ODIN [1] satellite suggest that the abundance of O<sub>2</sub> in the cores of interstellar clouds is significantly lower than predicted by latest astrochemical models [2].

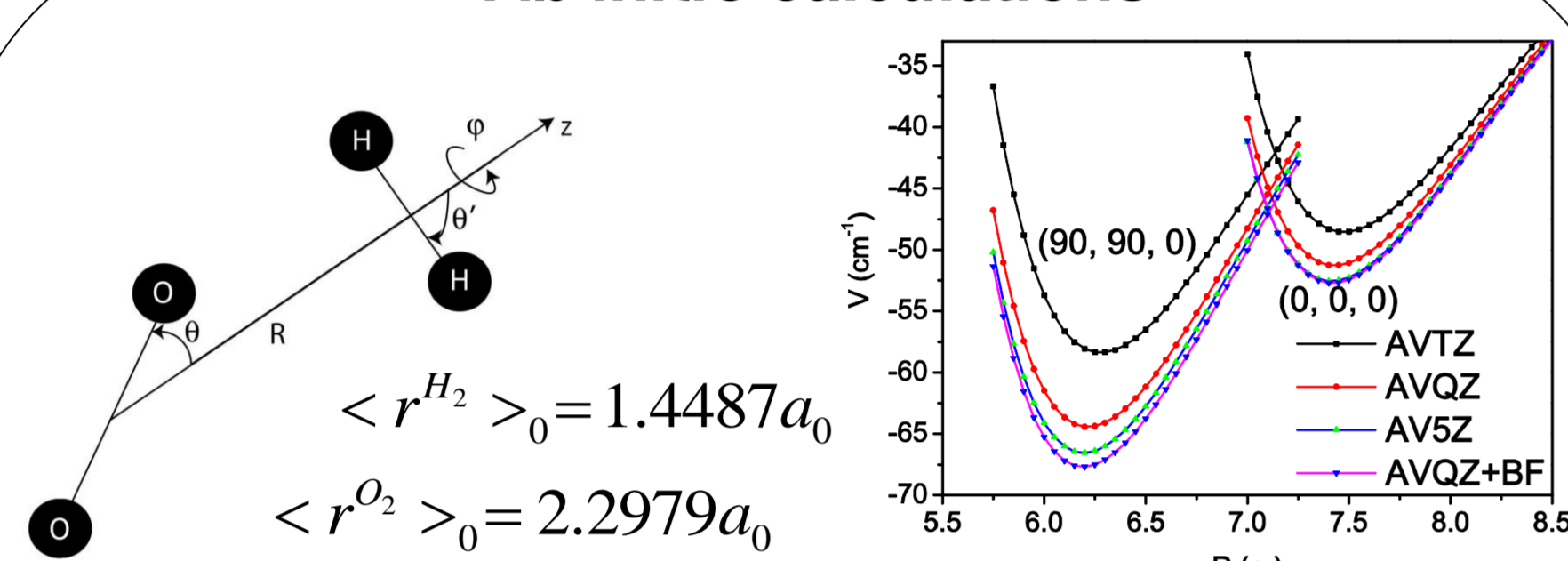
The new O<sub>2</sub>-H<sub>2</sub> rate coefficients will also be an essential support to the analysis of the recent O<sub>2</sub> observations obtained by the Herschel satellite [3, 4].

The goal of this work is to obtain state-to-state rate coefficients between the first 7 rotational levels ( $j_1, j_2 \leq 13$ ) and the first 27 fine levels ( $N, N' \leq 17$ ) of O<sub>2</sub>(X<sup>3</sup>Σ<sup>-</sup>) for temperatures ranging from 5 to 100 K for collisions with H<sub>2</sub>.

For this purpose we have decided to determine a new 4D *ab initio* PES using the "coupled clusters" approach for the ground electronic state of the O<sub>2</sub>-H<sub>2</sub> system.

## METHODS

### Ab initio calculations



The potential was expanded in spherical functions:

$$V(R, \theta, \phi) = \sum_{l_1, l_2, l} v_{l_1, l_2, l}(R) A_{l_1, l_2, l}(\theta, \phi)$$

$$A_{l_1, l_2, l}(\theta, \phi) = \sqrt{\frac{2l_1 + 1}{4\pi}} \{ (l_1 l_2 0 | l_1 l_2 l) P_{l_1 0}(\theta) P_{l_2 0}(\phi) + 2 \sum_m (-1)^m (l_1 m l_2 - m | l_1 l_2 l) P_{l_1 m}(\theta) P_{l_2 m}(\phi) \cos(m\phi) \}$$

Here  $l, l'$  are associated with the rotational motion of O<sub>2</sub> and H<sub>2</sub>. The homonuclear symmetry of O<sub>2</sub> and H<sub>2</sub> forces the indexes  $l_1$  (0-12) and  $l_2$  (0-8) to be even.

$$v_{l_1, l_2, l}(R) = \begin{cases} a_1(l_1, l_2, l) e^{a_2(l_1, l_2, l)R}, & \text{for } R \leq R_1 \\ \sum_{n=2}^{12} b_n(l_1, l_2, l) / R^n, & \text{for } R_1 < R \leq R_2 \\ \sum_{n=6}^7 c_n(l_1, l_2, l) / R^n, & \text{for } R > R_2 \end{cases}$$

where the linking points were chosen to be  $R_1 = 4.0 a_0$  and  $R_2 = 10.0 a_0$ .

### Pure rotational (de-)excitation

We consider collisions of O<sub>2</sub> with para- and ortho-H<sub>2</sub>:  
 $O_2(j_1) + p\text{-}o\text{-}H_2 \rightarrow O_2(j_1') + p\text{-}o\text{-}H_2(j_2')$ ,  
 where  $j_1$  and  $j_2$  denote the rotational levels of O<sub>2</sub> and H<sub>2</sub>, respectively. The possible rotational excitation of H<sub>2</sub> ( $j_2 = 0 \rightarrow j_2 = 2$  or  $j_2 = 1 \rightarrow j_2 = 3$ ) has been taken into account in the calculations. Time-independent coupled scattering equations were solved using the MOLSCAT code [6] (close coupling). The calculations were performed using the propagator of Manolopoulos [7], the reduced mass of the system being  $\mu = 1.8964$  amu. Total energy grid for collision with para-H<sub>2</sub>: from 17.5 to 1000 cm<sup>-1</sup> for collisions with ortho-H<sub>2</sub>: from 136.0 to 1120 cm<sup>-1</sup>.

This grid allow to obtain rate coefficients after averaging over collisional energy up to 100 K.

Integration range was set from  $4.0 a_0$  to  $50 a_0$ .

O<sub>2</sub> rotational basis was extended to  $j_1 = 17$  to ensure convergence of rotational levels of with  $j_1 \leq 13$ . The maximum value of the total angular momentum  $J$  was set to be large enough that the inelastic cross-sections were converged to 0.005 Å<sup>2</sup>.

From the rotationally inelastic cross sections  $\sigma_{j_1 j_2 \rightarrow j_1' j_2'}(E_c)$ , one can obtain the corresponding thermal rate coefficients at temperature  $T$  by an average over the collision energy [8]:

$$k_{j_1 j_2 \rightarrow j_1' j_2'} = \left( \frac{8}{\pi \mu k_B^3 T^3} \right)^{1/2} \int_0^\infty \sigma_{j_1 j_2 \rightarrow j_1' j_2'}(E_c) \times E_c e^{-E_c/k_B T} dE_c$$

### Fine structure (de-)excitation

Quantum close coupling calculations were performed for the fine-structure resolved inelastic cross sections and rate coefficients of O<sub>2</sub> in collision with para-H<sub>2</sub>( $j=0$ ) using MOLSCAT code modified by Lique [9].

Total molecular angular momentum  $j$  is defined by (Hund's case (b)):  
 $j = N + S$   
 $N$  and  $S$  are nuclear rotational and electronic spin angular momenta.

In intermediate coupling scheme rotational wave function for  $j \geq 1$  is [10]:

$$|F_1 j m\rangle = \cos \alpha |N = j - 1, S j m\rangle + \sin \alpha |N = j + 1, S j m\rangle$$

$$|F_2 j m\rangle = |N = j, S j m\rangle$$

$$|F_3 j m\rangle = -\sin \alpha |N = j - 1, S j m\rangle + \cos \alpha |N = j + 1, S j m\rangle$$

where  $|N, S j m\rangle$  denotes pure Hund's case (b) basis functions and mixing angle  $\alpha$  is obtained by diagonalization of molecular Hamiltonian.

The fine structure levels of oxygen are defined by  $N, F_i$

Calculations were carried out for the first 27 fine levels of O<sub>2</sub> for total energies up to 1500 cm<sup>-1</sup>.

Inelastic cross sections from  $F_i, j$  to  $F_i', j'$  are obtained at each kinetic energy  $E_k = E - E_{F_i', j'}$  [11]:

$$\sigma_{F_i, j \rightarrow F_i', j'}(E_k) = \frac{\pi}{(2j+1)k_{F_i, j}^2} \sum (2J+1) |T^J(F_i j l; F_i' j' l')|^2$$

By overaging over Maxwellian distribution of collision velocities, we obtain thermal rate coefficients for transitions between fine-structure level of O<sub>2</sub>:

$$k_{F_i, j \rightarrow F_i', j'}(T) = \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \left( \frac{1}{k_B T} \right)^2 \int_0^\infty E_k \sigma_{F_i, j \rightarrow F_i', j'}(E_k) e^{-E_k/k_B T} dE_k$$

## RESULTS

### POTENTIAL ENERGY SURFACE

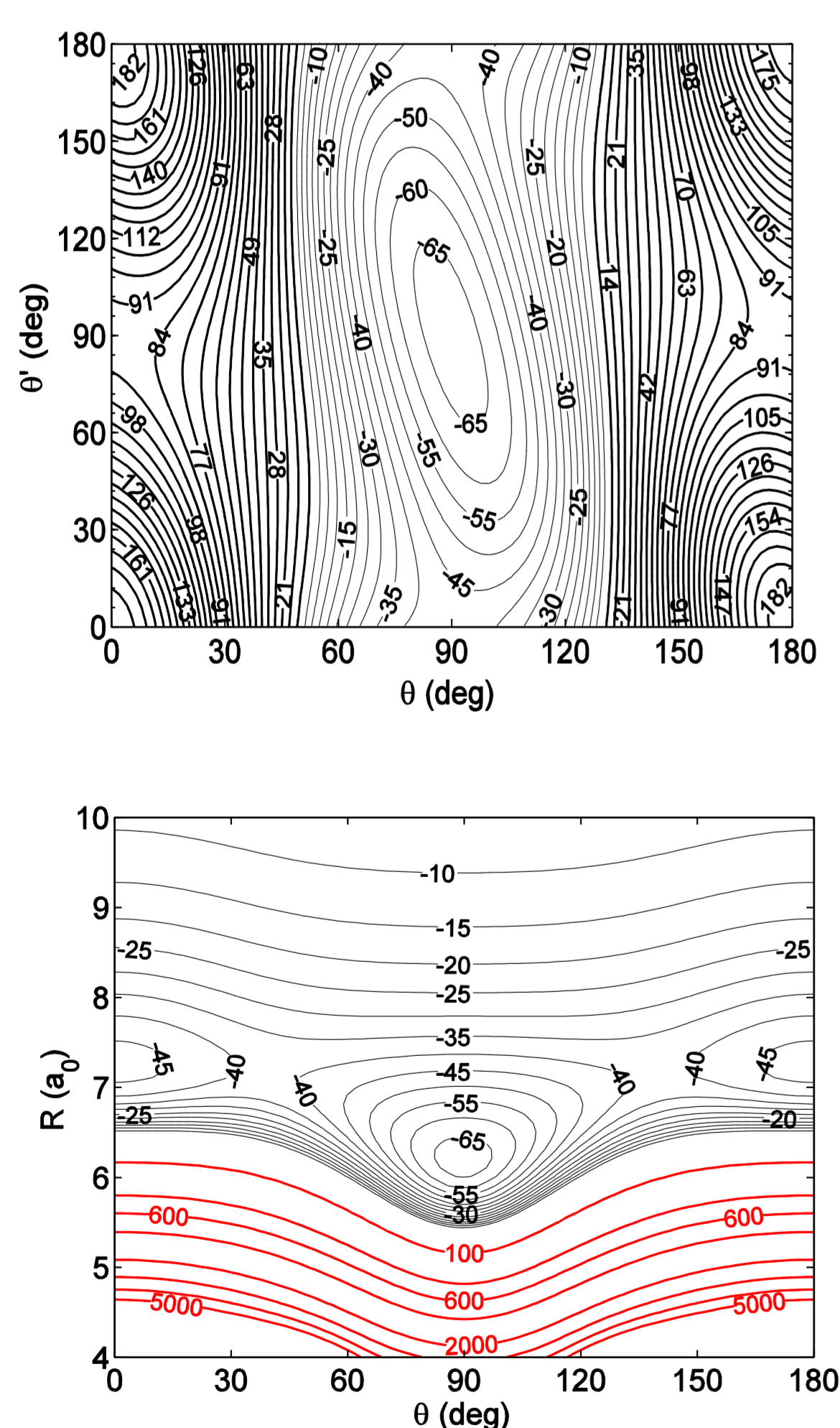


Fig. 1 Contour plots of the O<sub>2</sub>-H<sub>2</sub> PES for fixed equilibrium parameters.

The global minimum of the PES occurs for  $R = 6.19 a_0$ ,  $\theta = 90^\circ$  and  $\phi = 0^\circ$  and is of 67.69 cm<sup>-1</sup>. A saddle point ( $\Delta E = -49.80$  cm<sup>-1</sup>) between two equivalent minima ( $\theta = 90^\circ, \theta' = 90^\circ$  and  $\theta = 90^\circ, \theta' = -90^\circ$ ) corresponds to the T-shaped geometry with  $\theta = 90^\circ, \theta' = 0^\circ$  and  $R = 6.54 a_0$ .

### SCATTERING CALCULATIONS

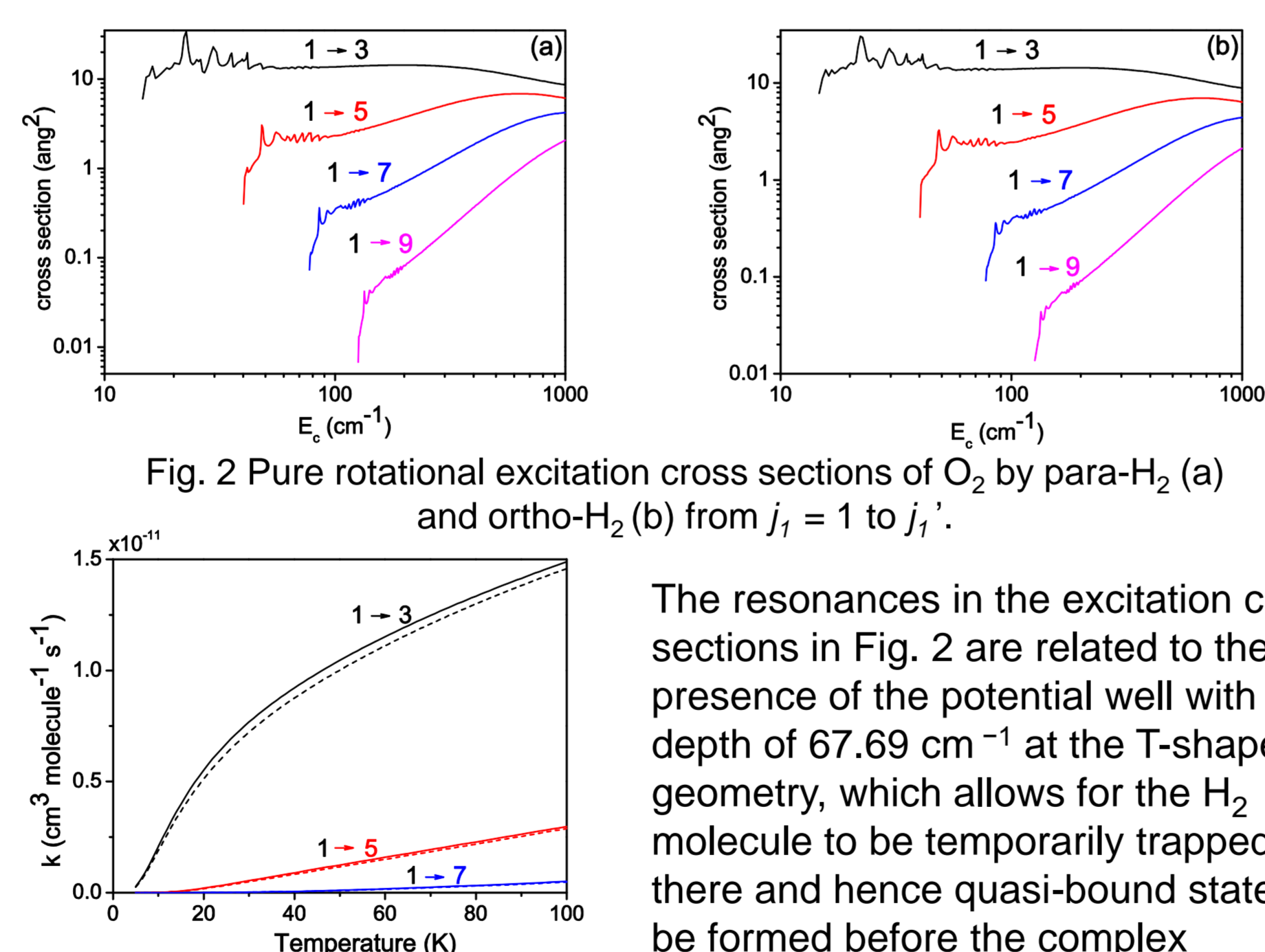


Fig. 2 Pure rotational excitation cross sections of O<sub>2</sub> by para-H<sub>2</sub> (a) and ortho-H<sub>2</sub> (b) from  $j_1 = 1$  to  $j_1'$ .

Fig. 3 Temperature dependence of pure rotational excitation rate coefficients of O<sub>2</sub> by H<sub>2</sub> from  $j_1 = 1$  to  $j_1'$ . Dash lines – para-H<sub>2</sub>; solid lines – ortho-H<sub>2</sub>.

The radial coefficients contributing mainly to cross sections with  $j_2 \rightarrow j_2'$  transitions are those with  $l_2$  in the  $|j_2 - j_2'| < l_2 < |j_2 + j_2'|$  range. Hence, for collisions with para-H<sub>2</sub>( $j_2 = 0$ ), only the  $l_2 = 0$  terms contribute whereas for collisions with ortho-H<sub>2</sub>( $j_2 = 1$ ), the  $l_2 = 0, 2$  terms contribute. This means (and we checked it by inspecting the radial coefficients) that the radial expansion terms with  $l_2 = 2$  are significantly lower the one with  $l_2 = 0$ . The weak anisotropy of the PES compared to  $\theta'$  and  $\phi$  angles probably explain this behavior.

Table. Rotational cross sections calculated using averaged 2D potential and 4D potential.

Ec, cm-1	transition	4D H2(j=0,2)	4D H2(j=0)	2D H2(j=0)
20	1-3	10.7812	10.6437	10.6348
100	1-3	13.6759	13.6077	13.6072
	1-5	2.2991	2.6531	2.2662
	1-7	0.3135	0.3053	0.3052
300	1-3	13.8794	13.8877	13.8853
	1-5	5.0436	4.9932	4.9940
	1-7	1.208	1.1700	1.1698

As we consider collisions with only para-H<sub>2</sub>( $j_2 = 0$ ) at low temperatures, we can restrict ourselves to  $j_2 = 0$ .

4D PES → 2D PES

The 2D potential was expanded as follows:  $V_{av}(R, \theta) = \sum_l V_l(R) P_l(\cos \theta)$

where  $V_{av}(R, \theta)$  is obtained by an average of  $V(R, \theta, \phi)$  over the angular motion of the H<sub>2</sub> molecule.

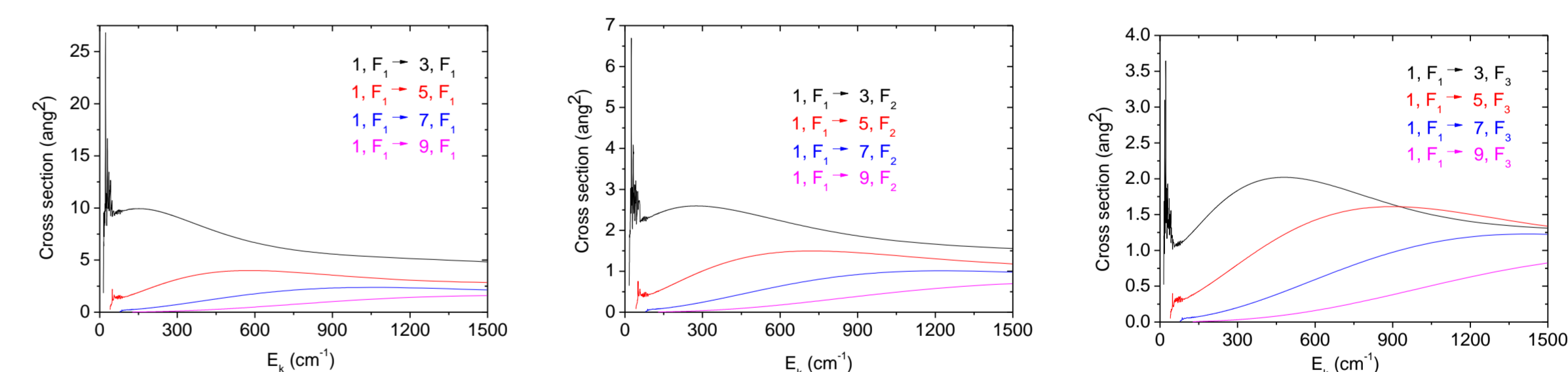


Fig. 4 Collisional de-excitation fine-structure resolved cross sections of O<sub>2</sub> by H<sub>2</sub> from  $N, F=1, F_i$ .

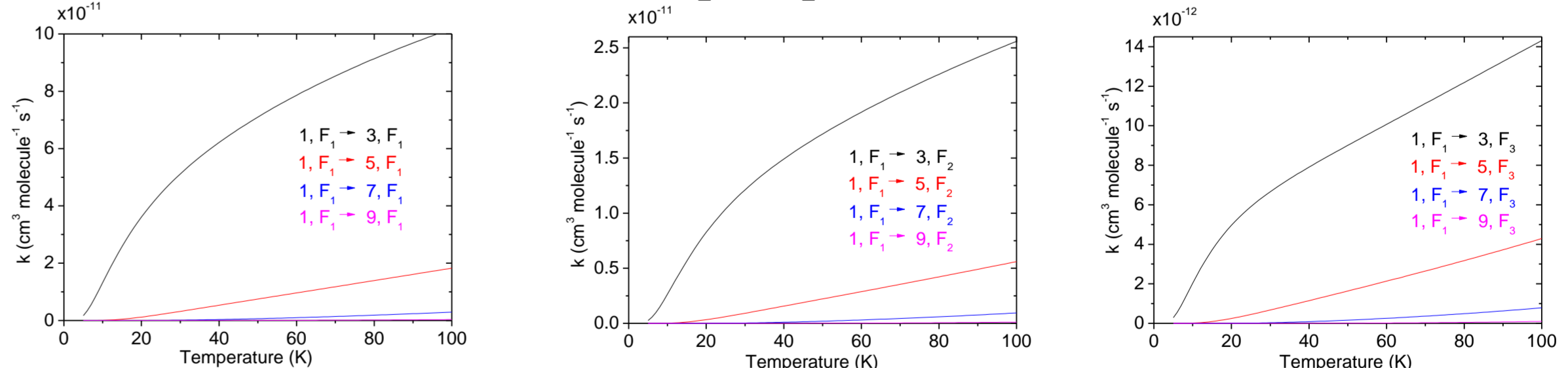


Fig. 5 Collisional de-excitation fine-structure resolved rate coefficients of O<sub>2</sub> by H<sub>2</sub> from  $N, F=1, F_i$ .

• The cross sections decrease with increasing  $\Delta N$

• A strong propensity rule exists for F-conserving transitions [ $\Delta F = \Delta N$  for pure Hund's case (b)]

• Rate coefficients display the same propensity rules as cross sections

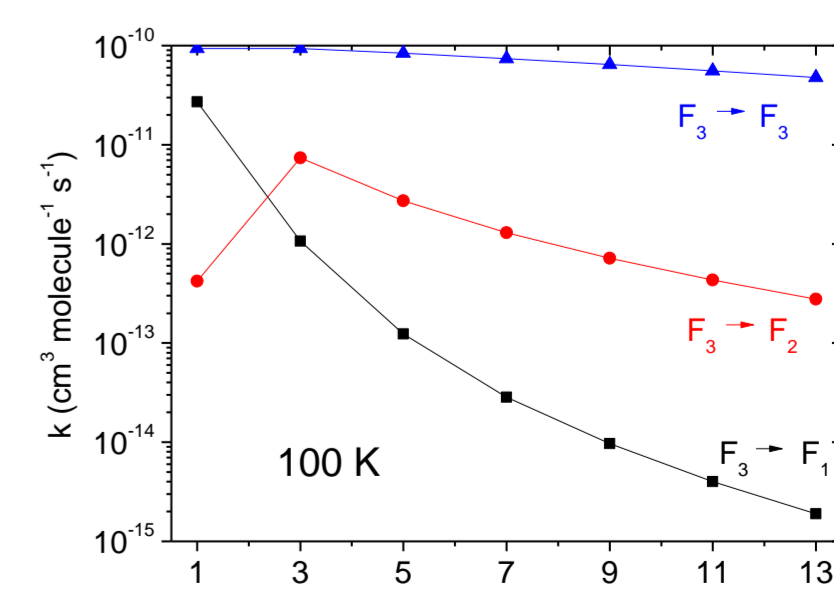


Fig. 6 Collisional excitation rate coefficients of O<sub>2</sub> by H<sub>2</sub> at 100 K for  $\Delta N = N' - N = 2$

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