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Rate Coefficients for Dissociative Attachment and Resonant Electron-impact Dissociation Involving Vibrationally Excited O_2 Molecules

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Abstract. Rate coefficients for dissociative electron attachment and electron-impact dissociation processes, involving vibrationally excited molecular oxygen, are presented. Analytical fits of the calculated numerical data, useful in the applications, are also provided.

Keywords: Oxygen, electron-molecule collisions, rate coefficients
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INTRODUCTION

In recent work [1], referred to as I below, state-by-state cross sections for dissociative electron attachment (DEA) and electron-impact dissociation (EID) processes involving ro-vibrationally excited molecular oxygen, respectively represented by the following reactions:

$$e^- + O_2(X\,^3\Sigma_g^-; v, J) \rightarrow O_2^{-*} \rightarrow O^-(^2P) + O(^3P)\,, \tag{1}$$

$$e^- + O_2(X\,^3\Sigma_g^-; v, J) \rightarrow O_2^{-*} \rightarrow e^- + 2O(^3P)\,, \tag{2}$$

have been calculated for each oxygen vibrational level v and parameterized on the rotational quantum number J. The threshold for process (1) is 3.64 eV, corresponding to the asymptotic energy of O and O^- fragments from the level $v = 0$, whereas that for process (2) corresponds to the O_2 dissociation energy of 5.11 eV. In paper I four low-lying resonant states of O_2^- were taken into account and the *ab initio* computations of the potential energy curves and resonance widths were performed using the quantum chemistry code MOLPRO [2] and the R-Matrix method [3, 4]. The (complex) potentials were used as input data for the description of the nuclear motion which was treated within the Local-Complex-Potential model [5]. Since the present work is designed as an extension of the paper I, we refer to this paper for more details on the calculation method, results and references. The cross sections obtained, along with those for resonant vibrational-excitation, calculated in Ref. [6], represent fundamental input data for kinetic model implementation of O_2-containing plasmas in non-equilibrium conditions.

In this paper we extend the calculations of paper I to the rate coefficients for the two processes (1) and (2), by assuming a Maxwellian electron energy distribution function at a temperature T. The analytic expression for the rate coefficient $\kappa_v(T)$ is given by:

$$\kappa_v(T) = \sqrt{\frac{8}{m_e\,\pi}} \left(\frac{1}{T}\right)^{3/2} \int_{\varepsilon_{th}}^{\infty} d\varepsilon\; \varepsilon \cdot e^{-\frac{\varepsilon}{T}} \cdot \sigma_v(\varepsilon)\,, \tag{3}$$

where σ_v, ε and ε_{th} are respectively the cross section, the incident electron energy and the threshold energy of the processes (1) and (2). It is worth stressing that Eq. (3) is no longer valid in non-equilibrium condition. The rate constant κ_v can be fitted by using the following analytical expression:

$$\kappa_v(T) = \kappa_v^{max} \left(\frac{T_v^{max}}{T}\right)^{3/2} e^{-\frac{T_v^{max}}{T}}\,, \tag{4}$$

already successfully tested for electron-H_2 and -N_2 scattering [7, 8]. The formula in Eq. (4) requires only two parameters, T_v^{max} and κ_v^{max}, which are the coordinates of the maximum value of the calculated rates for each vibrational level v.

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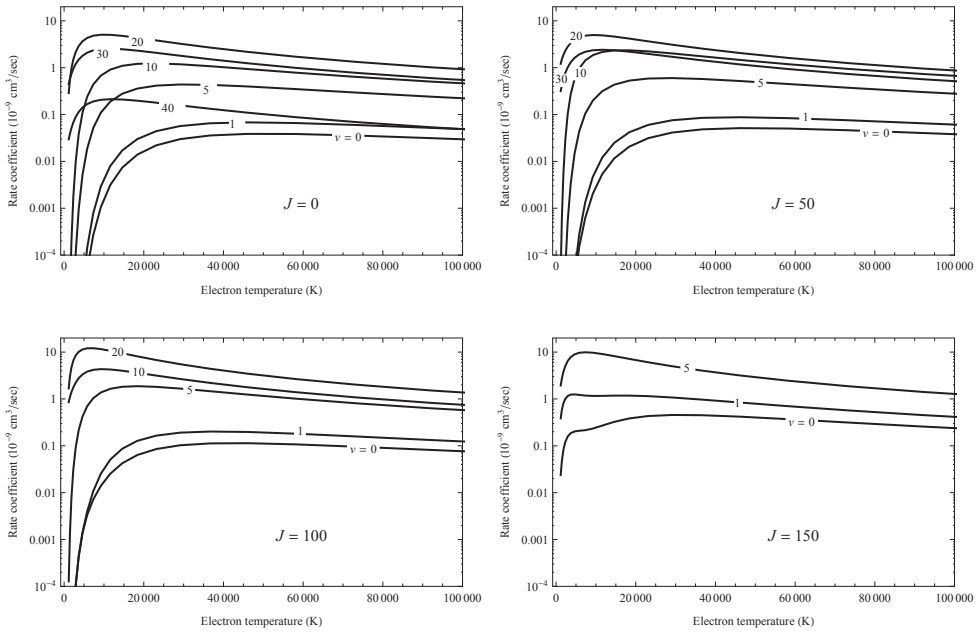

FIGURE 1. Dissociative electron attachment rate coefficients, process (1), as a function of the electron temperature, for some selected vibrational levels, indicated by v, and for some fixed values of the rotational quantum number J.

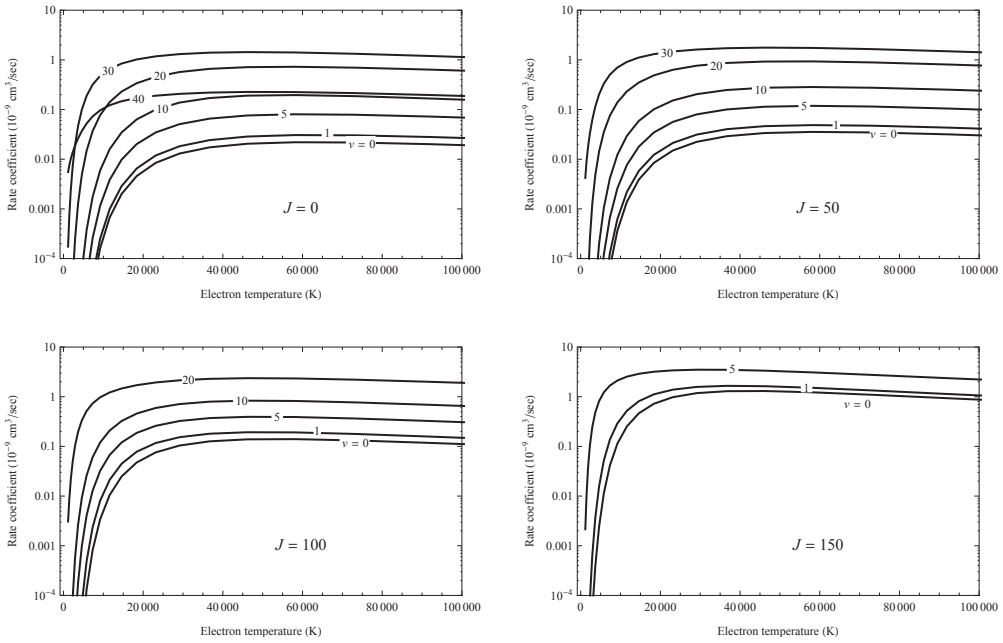

FIGURE 2. As Fig. 1 but for electron-impact dissociation, process (2).

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RESULTS

Figures 1 and 2 summarize the results for the rate coefficients for the processes of DEA and EID, respectively. In particular, in Fig. 1 shows the DEA rate coefficients as a function of the electron temperature for some values of the vibrational quantum number, v, and for a fixed rotational level J as indicated in the figures. In the left-upper panel the $J = 0$ rates show an increasing trend with vibrational excitation up to $v = 20$, then for $v \geq 30$ the trend is inverted. This reflects the behavior of the corresponding cross sections observed in I. The other panels show the rates coefficients for $J = 50, 100$ and 150. The number of the vibrational levels, with eigenenergy below the DEA threshold, reduces as J increases. Figure 2 shows the rate coefficients for process (2) for selected values of v and fixed rotational levels as in Fig. 1. Again the rates for $J = 0$ present an inverted trend for large v, while a regular behavior is observed in the other panels ($J > 0$).

Figure 3 shows finally the rate fits obtained by Eq. (4), for some v and for DEA processes. The fits are provided for $J = 0$ only. T he values of κ^v_{Max} and T^v_{Max}, required in Eq. (4), are given in Tables 1. The quality of the fits is quite good for $v \leq 10$, while some discrepancy is observed at high temperature for $v = 20$. All the calculated rate coefficients for DEA and EID processes, along with the corresponding cross sections [1, 6], are freely available in the Phys4Entry database [9].

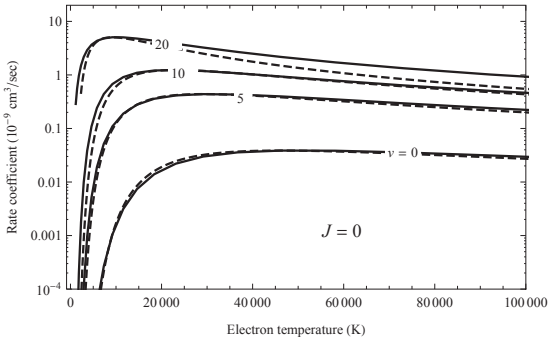

FIGURE 3. Calculated (full lines) and fitted (dashed lines) rate coefficients for dissociative electron attachment process as a function of the electron temperature and for some selected v values and $J = 0$.

TABLE 1. $\kappa^v_{Max}(10^{-9}cm^3/s)$ and T^v_{Max} (eV) fitting parameters for DEA rate coefficients.

v	T^v_{Max}	κ^v_{Max}	v	T^v_{Max}	κ^v_{Max}
0	5.9700	9.43(-02)	21	1.1900	1.14(+01)
1	5.9700	1.66(-01)	22	1.1900	1.16(+01)
2	5.9700	2.86(-01)	23	1.5000	1.05(+01)
3	4.7400	4.55(-01)	24	1.5000	9.58
4	4.7400	7.13(-01)	25	1.5000	9.56
5	3.7700	1.07	26	1.5000	8.37
6	3.7700	1.49	27	1.5000	8.43
7	2.9900	1.90	28	1.5000	7.35
8	2.9900	2.20	29	1.5000	7.08
9	2.9900	2.50	30	1.5000	6.21
10	2.9900	3.01	31	1.5000	5.85
11	2.3800	3.92	32	1.5000	5.73
12	2.3800	5.25	33	1.5000	4.76
13	1.8900	7.06	34	1.5000	3.58
14	1.8900	9.19	35	1.5000	3.51
15	1.5000	1.08(+01)	36	1.5000	2.92
16	1.5000	1.10(+01)	37	1.5000	2.01
17	1.5000	1.12(+01)	38	1.5000	1.35
18	1.5000	1.27(+01)	39	1.5000	6.19(-01)
19	1.1900	1.35(+01)	40	1.5000	5.19(-01)
20	1.1900	1.23(+01)	41	1.5000	3.38(-01)

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