

Rate Coefficients for Low-Energy Electron Dissociative Attachment to Molecular Hydrogen.

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January 24, 2003

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Abstract

Calculation of rate constants for dissociative electron attachment to molecular hydrogen is reported. The calculation is based on an improved nonlocal resonance model of Čížek, Horáček and Domcke which takes fully into account the nonlocality of the resonance dynamics and uses potentials with correct asymptotic forms. The rate constants are calculated for all quantum numbers v and J of the target molecules and for electron temperature in the range 0-30 000 K.

Keywords: dissociative attachment, hydrogen molecule, rate constant, nonlocal dynamics

1 Introduction

The system H_2^- is the most fundamental molecular anion. It is unstable, with a very short lifetime ($\tau \sim 10^{-15}$ s). The dynamics of this complex which is important in a number of collisional processes is still not well understood. As examples of the most studied processes we mention dissociative attachment (DA)



vibrational excitation (VE)



associative detachment (AD)



and, for scattering energies higher than the electron affinity of H, also collisional detachment (CD)



Understanding of these processes is important for a number of practical applications. AD and DA determine the thermal equilibrium densities of H^- ions and H_2 molecules in many astrophysical plasmas. Neutral molecules produced in AD are vibrationally excited and the emission spectra of such molecules are quite different from those of molecules excited by ultraviolet pumping or shock excitation [1]. DA of electrons to molecular hydrogen is thought to be the primary source of the H^- ions produced in hydrogen plasmas. These ions may serve for the generation of neutral particle beams, the injection of ions into controlled thermonuclear devices, or for electromagnetic propulsion of space vehicles.

In the early models of the H_2^- dynamics the interaction between the nuclei was described in the local-complex-potential approximation [2]-[4], with empirically adjustable parameters and later with *ab initio* potentials [5], [6]. The importance of nonlocal effects was pointed out in [6]. Recently, the dynamics of nonlocal models has been studied [7], [8], [9], [10], [11],[12],[13], for DA and VE in H_2 .

The present work is based on an extension of the nonlocal resonance theory to treat the DA to rotationally excited molecules. The existing nonlocal resonance model for the H_2^- dynamics [7], [9] is modified [14] to account for the long-range behaviour of the H_2^- potential-energy function. DA, VE and AD processes can thus be treated within a single model with no adjustable parameters.

We present only a brief outline of the theory here. A more detailed description of the computational procedures and results will be given elsewhere.

2 Basic theory

The calculation of the rate constants is based on the use of an improved nonlocal resonance model [14]. Let us start with a very brief description of the nonlocal resonance model (for details see [15]).

2.1 Nonlocal resonance model

The nonlocal resonance model is based on the assumption that a temporary molecular negative-ion state (resonance) is formed and that this resonance accounts for the coupling of the electronic scattering dynamics with the nuclear motion [16]. The resonance is represented by a square-integrable discrete state $|\varphi_d\rangle$ which interacts with a continuum of scattering states $|\varphi_\varepsilon\rangle$ via coupling matrix elements $V_{d\varepsilon}$. $|\varphi_d\rangle$ and $|\varphi_\varepsilon\rangle$ are assumed to be diabatic states, that is, their wave functions vary smoothly with the internuclear distance R . The second essential ingredient of the nonlocal resonance model is the explicit consideration of threshold effects which enter through the threshold expansion of the energy-dependent width function

$$\Gamma(\varepsilon) = 2\pi|V_{d\varepsilon}|^2 \quad (5)$$

and the associated level shift $\Delta(\varepsilon)$ [16].

The basic equation of the nonlocal resonance theory is the wave equation describing nuclear motion in the short-lived anion state [15]

$$[T_N + V_d(R) - E]\Psi_d(R) + \int d\varepsilon \int dR' V_{d\varepsilon}(R) G_0(R, R'; E - \varepsilon) V_{d\varepsilon}^*(R') \Psi_d(R') = -V_{d\varepsilon_i}(R) \chi_{v_i}(R) \quad (6)$$

with

$$G_0(R, R'; E) = \langle R | (E - T_N - V_0 + i\varepsilon)^{-1} | R' \rangle. \quad (7)$$

Here $V_0(R)$ and $V_d(R)$ are the potential energy functions of the target state and the discrete state, respectively. $\chi_{v_i}(R)$ is the wave function of the initial vibrational state of the target molecule, ε_i is the energy of the incoming electron, and E is the total energy of the collision complex. G_0 is the Green's function for nuclei motion in the target state, T_N being the radial nuclear kinetic energy operator.

The second term on the left hand side of Eq.(6) plays the role of a complex, energy-dependent and nonlocal effective potential for the radial nuclear motion. It accounts for the decay of the electronic resonance state through the coupling with the electronic scattering continuum.

The cross section for dissociative attachment of an electron of energy ε_i to a molecule in the vibrational state $|\chi_v\rangle$ is given by [15]

$$\sigma_{DA}(E) = \frac{4\pi^3}{k_i^2} |\langle \Psi_d | V_{d\varepsilon_i} | \chi_v \rangle|^2, \quad (8)$$

where Ψ_d is now the solution of Eq.(2) in which the right hand side is set to zero.

In practice, the nuclear wave function $\Psi_d(R)$ is represented by a partial wave expansion with respect to rotational angular momentum and the Lippmann-Schwinger equation corresponding to the wave Eq.(6) is solved for the individual partial wave components. For this purpose, the very efficient Schwinger-Lanczos continued-fraction method [17] is

employed. The efficiency of this method allows the cross sections to be calculated on a very fine mesh of collision energies.

The nonlocal resonance model is characterized by the three functions $V_0(R)$, $V_d(R)$ and $V_{d\epsilon}(R)$. The target potential - energy function $V_0(R)$ can directly be obtained by ab initio calculations or by fitting spectroscopic data. The functions $V_d(R)$ and $V_{d\epsilon}(R)$ representing the H_2^- resonance (at short internuclear distance) and the H_2^- bound state (at intermediate and large internuclear distances) have been obtained [14] by a joint fitting of the ab initio $^2\Sigma$ eigenphase sum and accurate ab initio calculations of the H_2^- potential energy function at intermediate internuclear distance. All parameters of the model are thus determined by ab initio calculations.

2.2 Rate constants

Generally, the rate constant for the reaction in gas is defined as

$$k = \int_0^{\infty} v f(v) \sigma(v) dv \quad (9)$$

where $f(v)$ is a normalized distribution of the relative velocities v and $\sigma(v)$ is the cross section of the reaction. Here the Maxwellian distribution is assumed for electrons

$$f(v) = 4\pi v^2 \left(\frac{\mu}{2\pi kT} \right)^{3/2} e^{-\frac{\mu v^2}{2kT}} \quad (10)$$

where μ is the reduced mass of the particles.

3 Dissociative attachment

3.1 Dissociative attachment cross sections.

The main emphasis of this work is on the calculation of rate constants for DA process. It is however instructive to discuss briefly the underlying cross sections. In Figure 1, the calculated DA cross sections are plotted assuming nonrotating molecular target for some values of the vibrational quantum number v . A typical feature of DA process in molecular hydrogen is the rapid increase of the cross sections with increasing vibrational energy of the target. This feature is clearly demonstrated in Figure 1. The peak cross section increases at increasing vibrational excitation v up to $v=8$. This feature is used for example as a diagnostic tool in [18].

In Figure 2 the DA cross sections are plotted for rotationally excited target molecules, $J=10$. As observed the rotational excitation also makes the DA process more efficient. At this rotational state the highest DA cross section is obtained at a lower vibrational excitation state, $v=7$. This trend continues and at $J=15$, the highest DA cross section is obtained at $v=5$, see Figure 3.

In Figure 4 the DA cross sections are shown for vibrationally excited target, $v=1$, and a set of rotational quantum numbers J . At high J the DA cross section attains huge values.

3.2 Calculated rate constants

The calculated rate constants are plotted in Figure 5 as a function of the electron temperature T for hydrogen molecules in their ground vibrational state, $v=0$, and $J=0, 1, \dots, 30$.

The calculated rate constants are in Tables 1-51. The data tables in electric files are available at URL=<http://dpc.nifs.ac.jp/DB/DA/>.

4 Conclusions

Rate constants for the process of dissociative attachment are calculated at a range of electron temperatures $T=0-30\,000$ K for hydrogen molecules by the means of an improved nonlocal resonance model for all rotational and vibrational states (v, J) of the hydrogen molecules.

Acknowledgement

We acknowledge Mr. Masatoshi Kato for his help to make tables.

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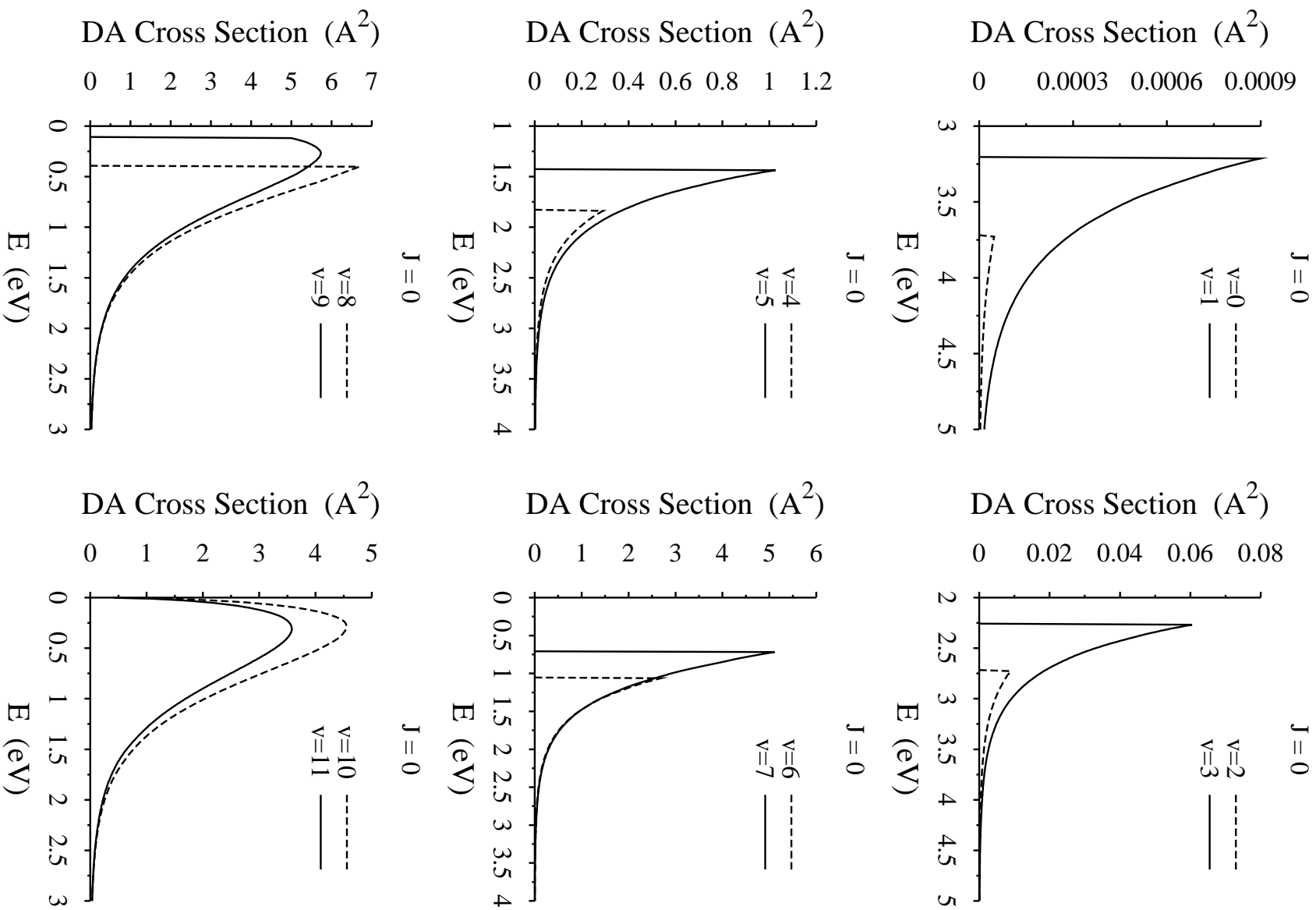


Figure 1: DA cross section for initial vibrational target states $v = 0, 1, \dots, 11$ for nonrotating hydrogen molecule.

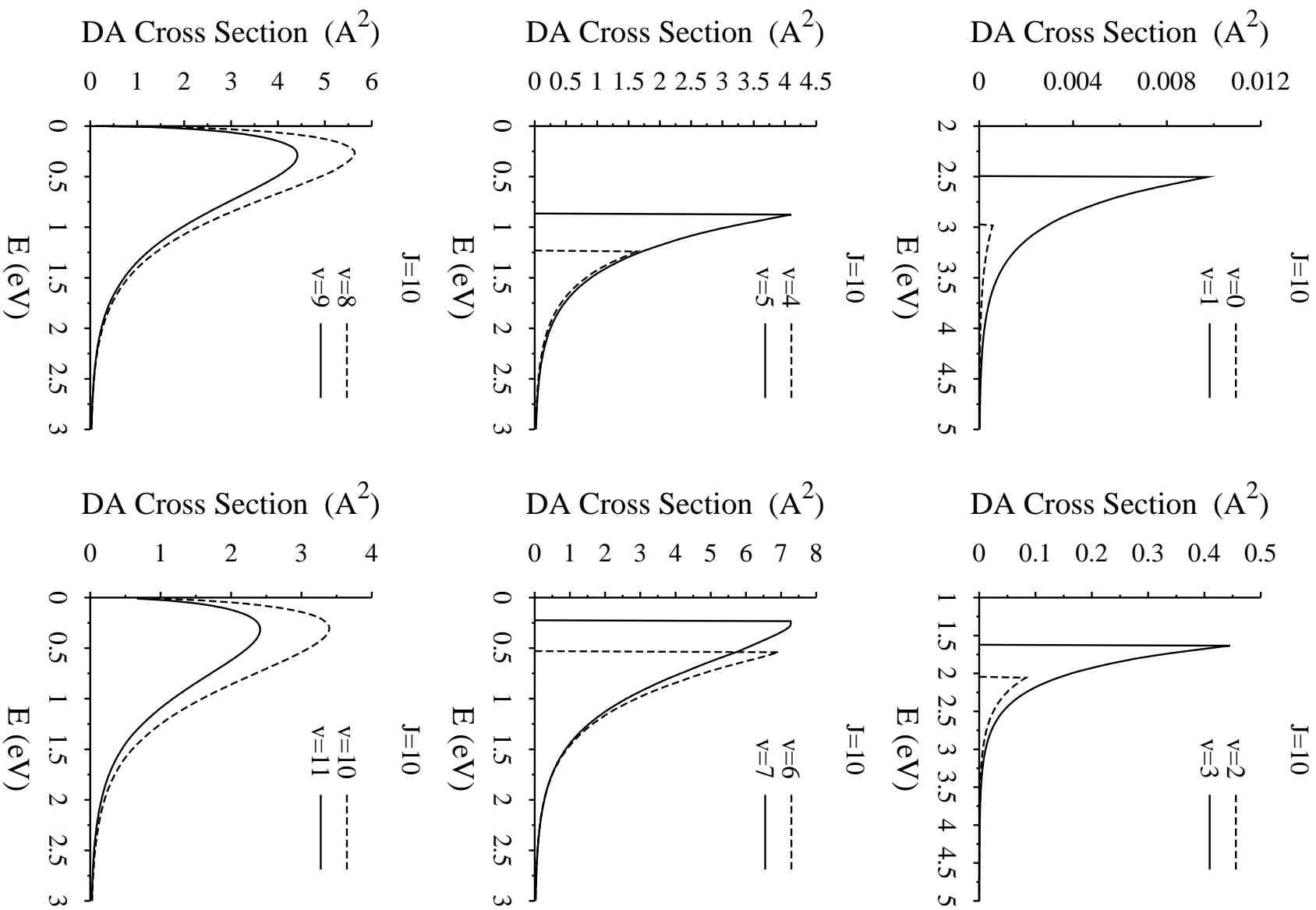


Figure 2: DA cross section for initial vibrational target states $v=0,1,\dots, 11$ for rotating hydrogen molecule. The rotational state was $J=10$.

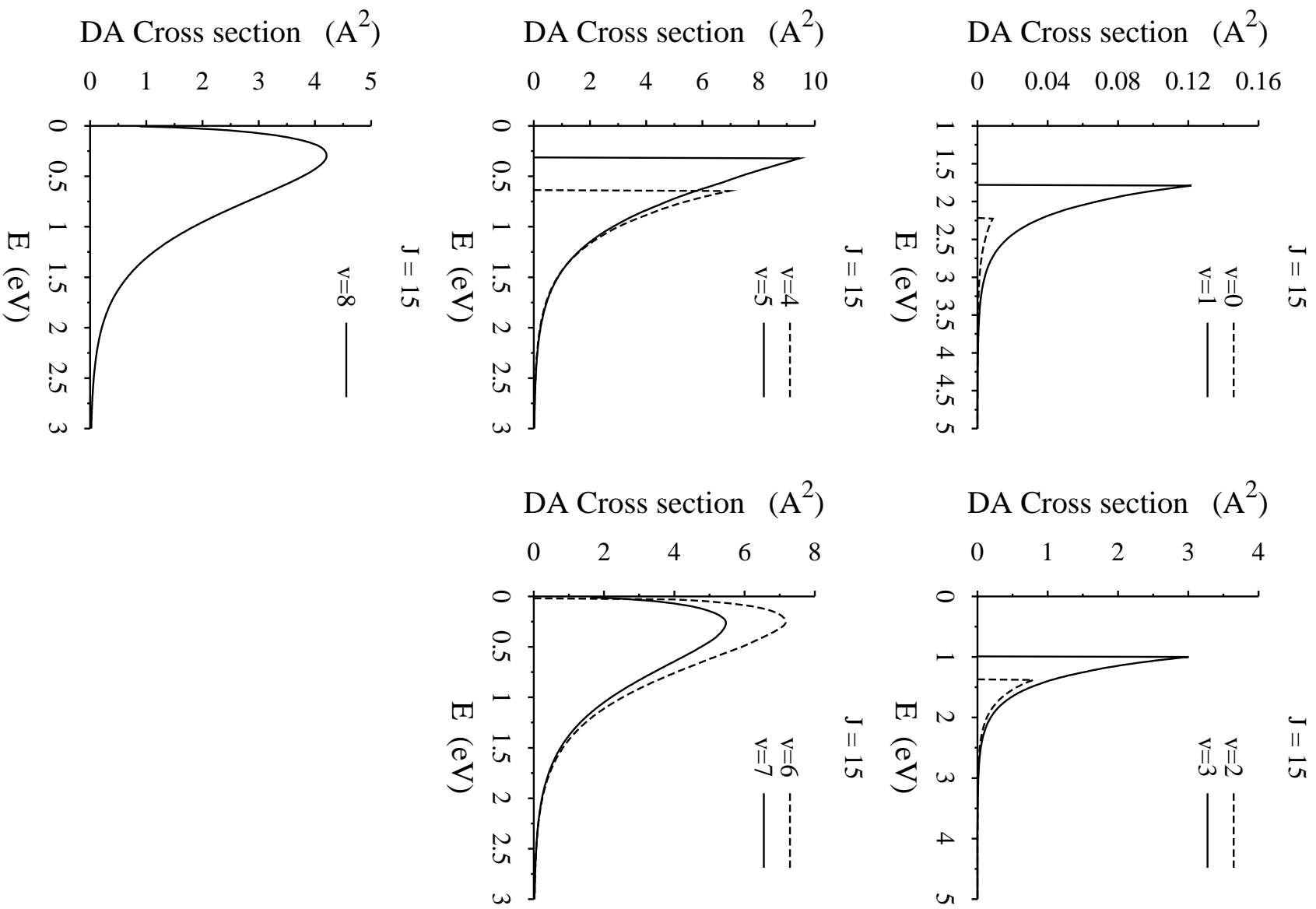


Figure 3: The same as for Figure 2 but for a higher rotational state, $J=15$.

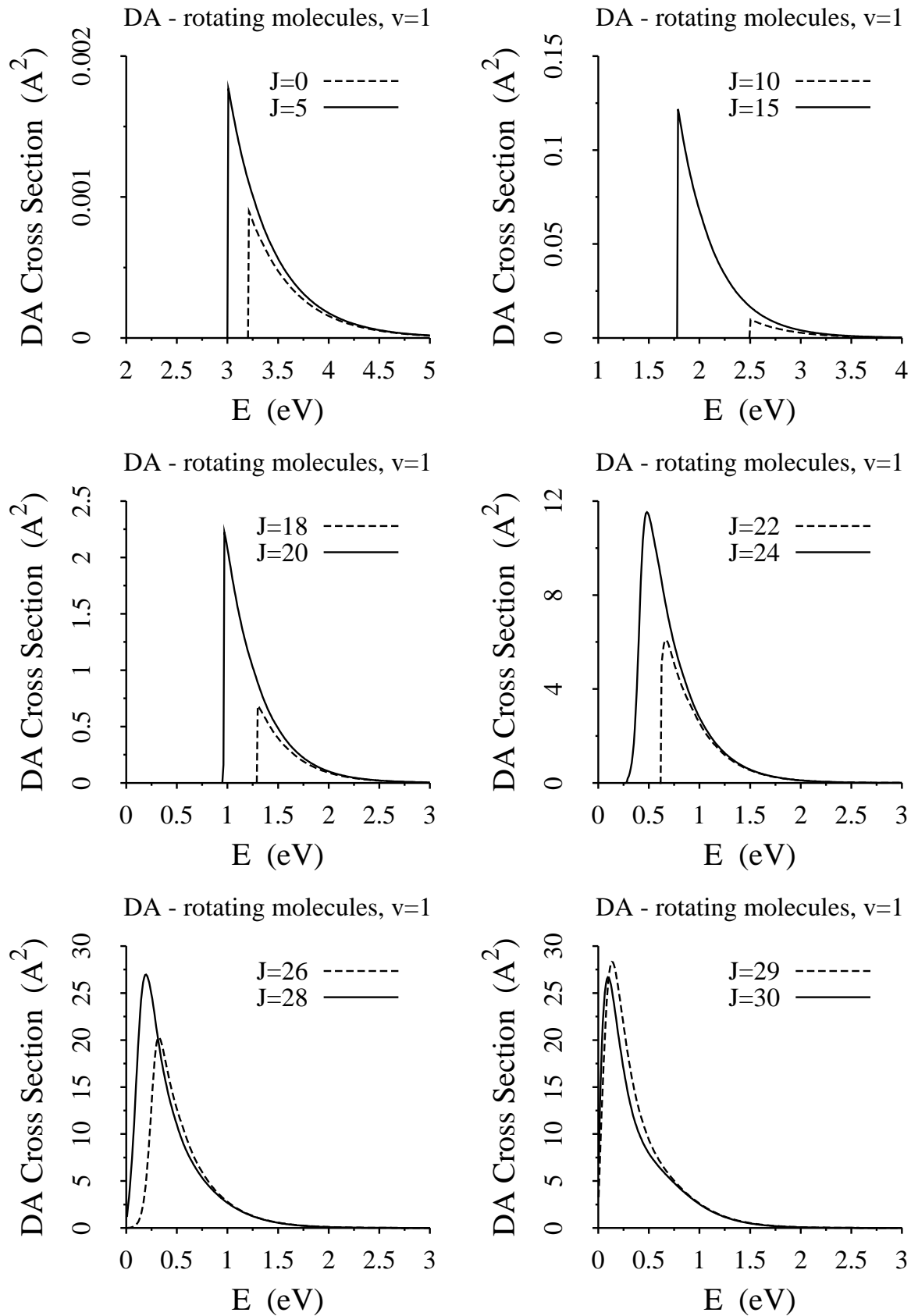


Figure 4: DA cross section for rotating hydrogen molecules, $J=1, \dots, 30$ assuming excited vibrational state $v = 1$ of the target.

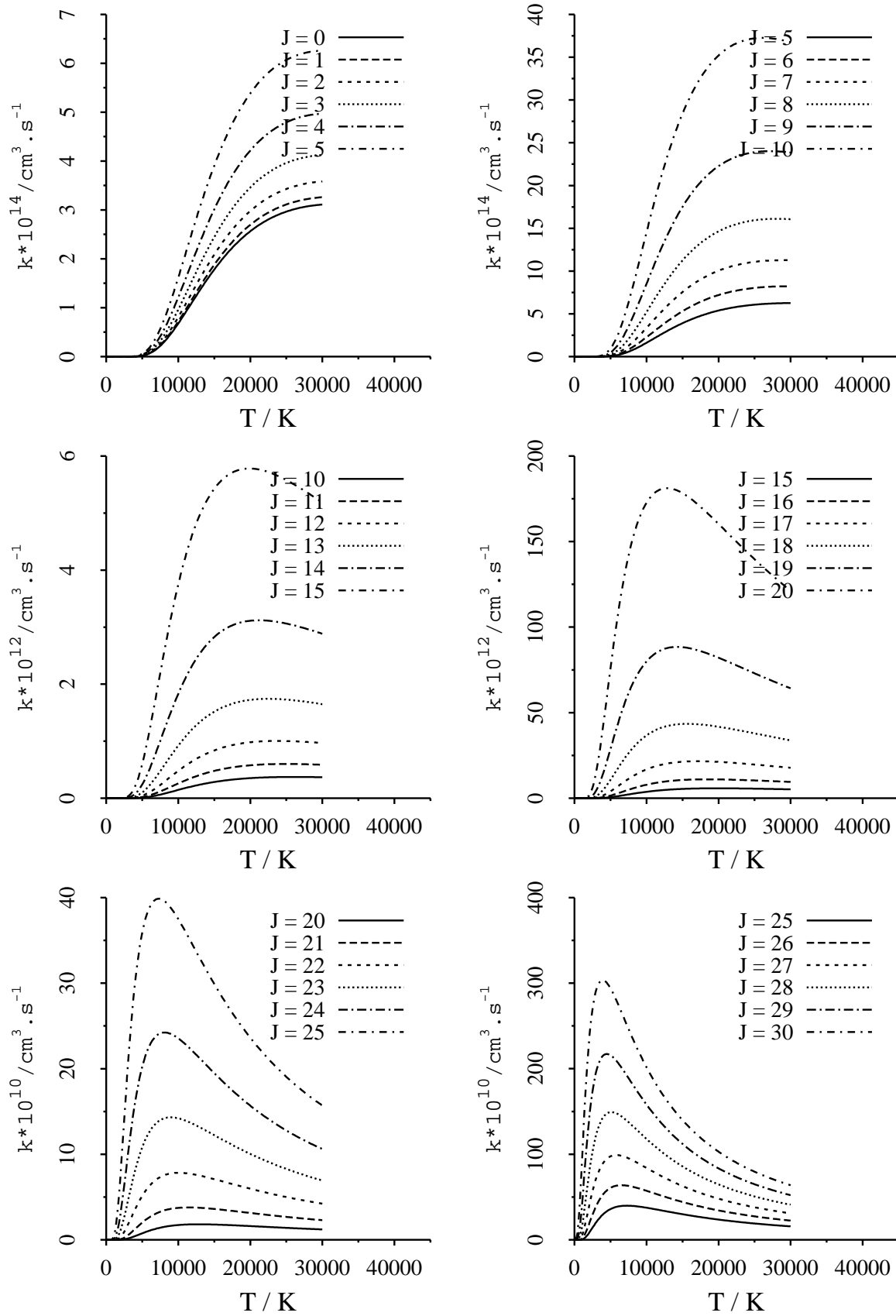


Figure 5: DA rates for ground vibrational state $v=0$ and various rotational states J .