

Disociative Electron Attachment (DEA) to H_2 molecules

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Results of collaboration of

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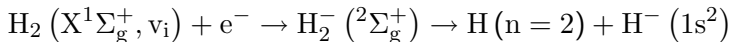
J. Tennyson - London, UK

Published in

- ▶ R Celiberto, R K Janev, J M Wadehra and J Tennyson
Dissociative electron attachment to vibrationally excited H_2
molecules involving the $^2\Sigma_g^+$ resonant Rydberg electronic state
Chemical Physics **398**,206-213,(2012)

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Dissociative electron attachment to vibrationally excited H_2
molecules involving the $^2\Sigma_g^+$ resonant Rydberg electronic state
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- ▶ the process studied is:



Local Complex Method

A molecular resonant state is described as an overlap of

- ▶ a discrete state formed by the captured extra electron, $\Phi_d(\vec{r}_i; R)$
- ▶ continuum states of the electron as an unbound particle, $\psi_\varepsilon(\vec{r}_i; R)$

The scattering wave function in the Born-Oppenheimer approximation is:

$$\Phi_d(\vec{r}_i; R) + \sum_{vJ} \int_0^\infty d\varepsilon f_{vJ}(\varepsilon) \psi_\varepsilon(\vec{r}_i; R) \chi_{vJ}(\vec{R}) \quad (1)$$

$\chi_{vJ}(\vec{R})$ is the rovibrational wave function of the target molecule

Schrödinger equation transforms to nonlocal integral equation

$$\left[-\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + \frac{\hbar^2 J_i (J_i + 1)}{2MR^2} + V^-(R) - E \right] \xi_i(R) - f(\varepsilon_i) F_i(R) \chi_{v_i J_i}(R) - \sum_{vJ} F(R) \chi_{vJ}(R) \times \int_0^\infty dR' \chi_{vJ}^*(R') F^*(R') \xi_i(R')$$

the coupling matrix has been factorized into $V(\varepsilon, R) = f(\varepsilon) \cdot F(R)$

$V(\varepsilon_i, R) = f(\varepsilon_i) \cdot F_i(R)$ is the entry amplitude: describes the capture of the incoming electron with kinetic energy ε_i

$\xi_i(R)$ is the resonant nuclear wave function; i corresponds to the initial rotational state J_i

$V^-(R)$ is the adiabatic potential of the resonant state

$\chi_{vJ}(R)$ is the radial rovibrational target wave function

The coefficients c_{vJ_i} are given by

$$c_{vJ_i} = P \int_0^\infty d\varepsilon \frac{|f(\varepsilon)|^2}{\varepsilon_{vJ_i} - \varepsilon} - i\pi |f(\varepsilon_{vJ_i})|^2$$

- ▶ P is the principal value of the integral
- ▶ $\varepsilon_{vJ_i} = E - E_{vJ_i}$, E is the total energy, E_{vJ_i} are the molecular energy eigenvalues

Procedure:

- ▶ The Schrödinger equation has been solved by assuming the local resonance width, $\Gamma(R) = 2\pi|F(R)|^2$, the partial width $\Gamma_X(R) = 2\pi|F_i(R)|^2$ and the resonance potential $V^-(R)$ in the interval $R = 1.1 - 4.0a_0$ are the same as those used in previous publications of this group and are taken from [1]
- ▶ $f(\varepsilon)$ have been put to 1, consistent with narrow width
- ▶ The bound vibrational wave functions $\chi_{vJ_i}(R)$ were obtained by solving the nuclear Schrödinger equation for the H_2 molecule using the potential curve of [2]
- ▶ $J_i = 0$, i.e. no rotational transitions are considered.

[1] D.T.Stibbe, J.Tennyson, J.Phys.B31(1998)815

[2] W.Kolos, L.Wolniewicz, J.Chem.Phys.43(1965)2429

- ▶ Finally, the DEA cross sections are calculated from:

$$\sigma(\varepsilon_i) = 2\pi^2 \frac{m}{M} \frac{K}{k_i} \lim_{R \rightarrow \infty} |\xi_i(R)|^2 \quad (2)$$

- ▶ m and M are the electron and reduced nuclear masses
- ▶ K is the relative atom-negative-ion outgoing momentum
- ▶ k_i is the initial momentum corresponding to the incident electron kinetic energy ε_i .

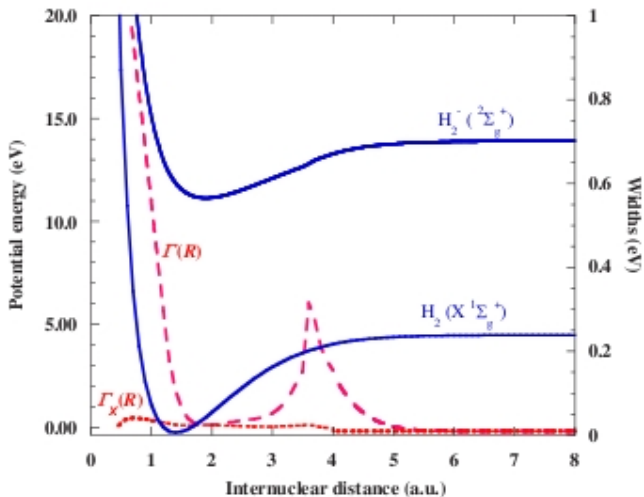
The nonlocal Schrödinger equation can be cast in local form by applying the degenerate state approximation and assuming that the coefficient c_{vJ_i} is almost constant; so,

$$\left[-\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + \frac{\hbar^2 J_i (J_i + 1)}{2MR^2} + V^-(R) + \Delta(R) - E \right] \xi_i(R) = -F_i(R) \chi_{v_i J_i}(R)$$

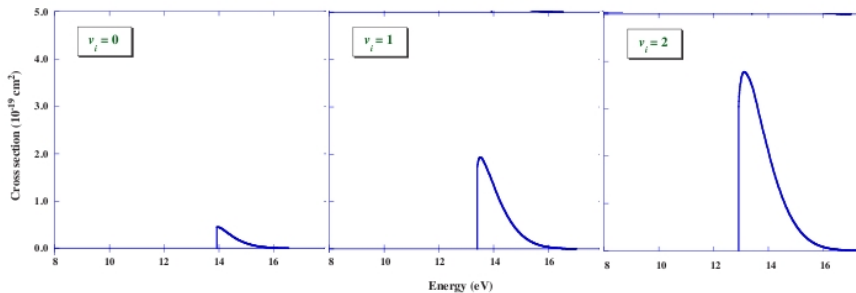
where the level shift, $\Delta(R)$ is given by

$$\Delta(R) = |F(R)|^2 \cdot P \int_0^\infty d\varepsilon \frac{|f(\varepsilon)|^2}{\varepsilon \bar{\nu}_{J_i} - \varepsilon}$$

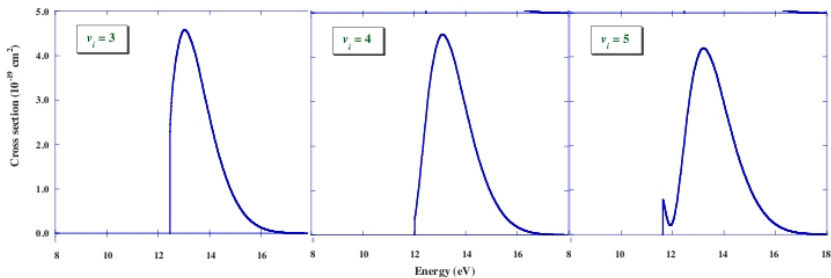
and $f(\varepsilon) = 1$; $\bar{\nu}$, J_i indicate a selected rovibrational state, representative of the whole manifold of the rovibrational levels.
 ! The local form was used to check some particular results - otherwise the authors used nonlocal form of the Schrödinger eq.



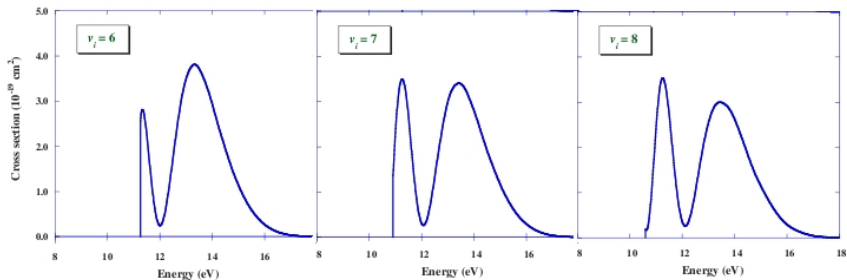
Full: H_2 electronic ground state (lower) and H_2^- resonant state (upper curve); total $\Gamma(R)$ (long dashed) and partial $\Gamma_X(R)$ (short dashed) resonance widths.



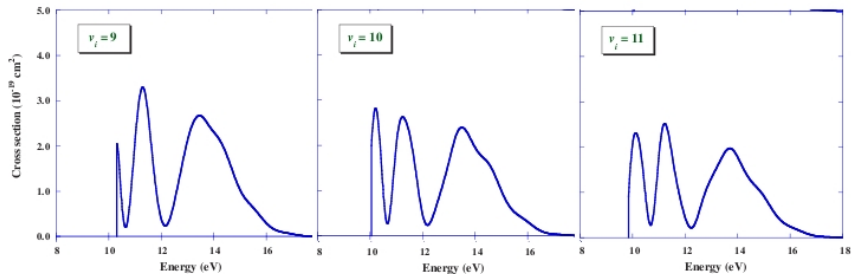
Cross sections for the DEA proces for H₂ starting from the level v_i shown in the figure



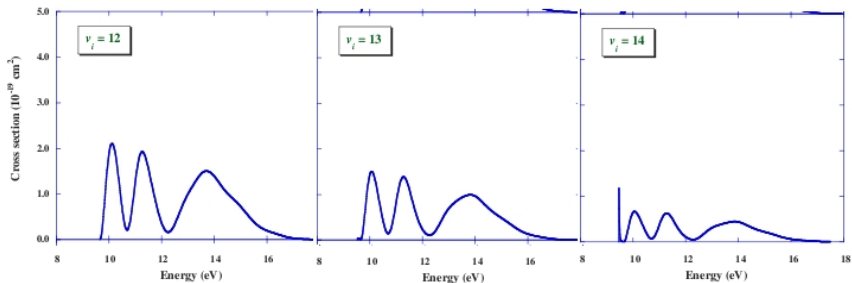
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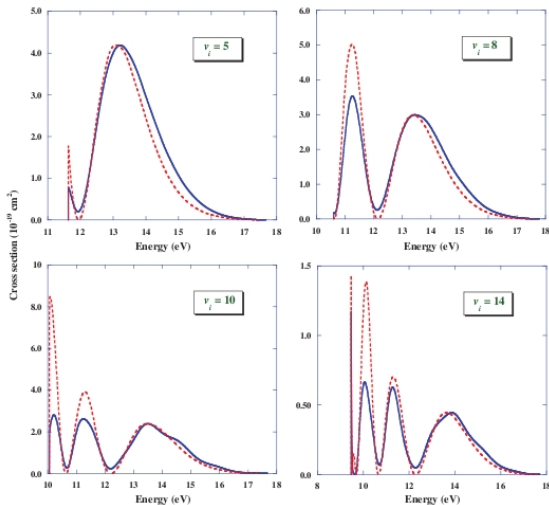
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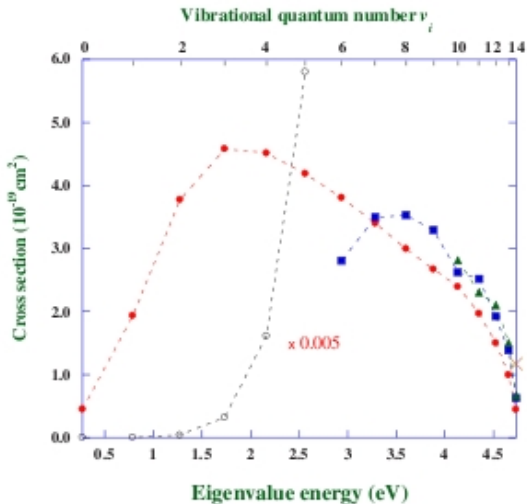
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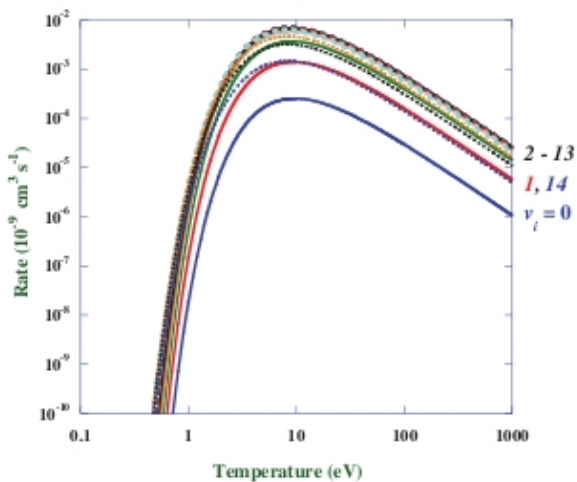
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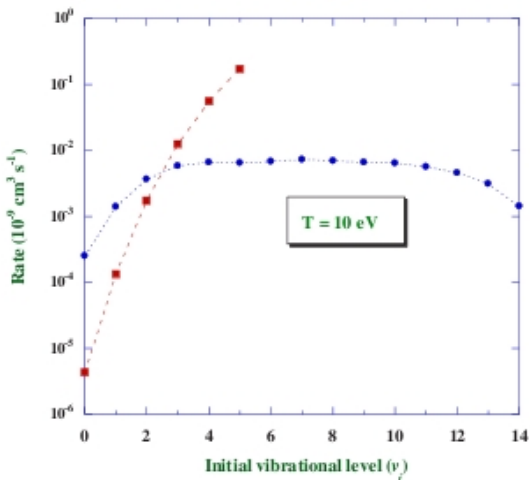
Squared bound-continuum wave function overlap, Q_{v_i} (dotted) normalized to the highest-energy peak of the calculated DEA cross sections (full) starting from the various levels v_i



Peak cross sections vs. the internal energy of H_2 (lower), and v_i (upper). Four series can be identified; open circles: $X^2\Sigma_u^+$ shape resonance cross sections reduced by a factor $1/200$



Rate coefficients as a function of the electron temperature for the DEA processes starting from the v_i -th vibrational level of H₂



Rate coefficients; Circles: $^2\Sigma_g^+$ Rydberg resonance; squares: $X^2\Sigma_u^+$ shape resonance