

## Vibrational- and Rotational-State Dependence of Dissociative Attachment in $e$ - $H_2$ Collisions

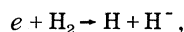
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(Received 21 September 1978)

Resonant scattering theory is applied to the calculation of  $e$ - $H_2$  dissociative attachment cross sections near threshold for several vibrational and rotational states of the  $H_2$  molecule. Typical values just above threshold are, in  $cm^2$ ,  $2.8 \times 10^{-21}$  for the ground state ( $v=0$ ,  $J=0$ ),  $8.3 \times 10^{-20}$  for (1,0),  $1.0 \times 10^{-18}$  for (2,0), and  $3.5 \times 10^{-20}$  for (0,10). The effect of rotational excitation is found to be significant, although it is not as large as suggested by Chen and Peacher.

The study of dissociative attachment in  $H_2$ ,



provided much of the motivation for the development of resonant scattering theory as applied to electron-molecule collisions.<sup>1-6</sup> The process is interpreted in terms of the formation and dissociation of unstable states of  $H_2^-$ . Demkov<sup>3</sup> pointed out that the competition between electron emission and dissociation in the molecular negative ion could lead to a strong dependence of the dissociative attachment cross section on the mass of the hydrogen nuclei and on the initial vibrational state of the neutral molecule. Furthermore, Chen and Peacher<sup>6</sup> argued that the cross section near threshold should be very sensitive to the rotational state of the  $H_2$  molecule.

Experimental verification of the isotope effect was obtained by Rapp, Sharp, and Briglia<sup>7</sup> and by Schulz and Asundi.<sup>8</sup> Spence and Schulz<sup>9</sup> examined the temperature dependence of dissociative attachment at 3.75 eV for temperatures up to 1300 K but could not discern any systematic variation in the cross section. Similar studies on  $O_2$  (Refs. 10 and 11) showed a significant increase in the attachment cross section as the temperature is raised which was analyzed in terms of the vibrational-state dependence of the cross section by O'Malley.<sup>12</sup>

Cross sections for dissociative attachment to excited  $H_2$  molecules are required for the analysis of  $H^-$  production in the negative-ion sources that are being developed for injection into controlled thermonuclear devices.<sup>13</sup> Recent advances in experimental design<sup>14</sup> have led to the possibility of measurements of the cross sections for specific vibrational and rotational states. The aim of these calculations is to provide theoretical estimates of these cross sections over a wide range of vibrational and rotational levels, including those that have been measured by Allan and Wong.<sup>14</sup> We will concentrate on the region near

threshold where the dominant contribution comes from the ground  $^2\Sigma_u$  state of  $H_2^-$ .

The basis of the resonance theory of electron-molecule collisions is the wave equation describing the motion of the nuclei during the lifetime of the temporary negative ion. This can be written<sup>2,4</sup> following the Born-Oppenheimer separation as

$$\left( -\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + \frac{J(J+1)}{2MR^2} + V(R) - \frac{1}{2}i\Gamma(R) - E \right) \xi_J(R) = \zeta_{v_i j_i}(R) \left( \frac{\Gamma(R)}{2\pi k(R)} \right)^{1/2} \quad (1)$$

in which  $M$  is the reduced mass of the nuclei,  $J$  and  $E$  give the total angular momentum and energy,  $V(R)$  and  $\Gamma(R)$  are the potential energy and width for the appropriate electronic state of the negative ion, and  $\zeta_{v_i j_i}(R)$  is the radial nuclear wave function corresponding to the initial vibrational and rotational state of the neutral molecule. The function  $k(R)$  gives the wave number of electrons that can be captured or emitted when the nuclei are at the separation  $R$  without change in the nuclear velocity. It is defined in terms of the potential energy of the neutral molecule,  $V_0(R)$ , by

$$\frac{\hbar^2}{2m_e} k^2(R) = V(R) - V_0(R). \quad (2)$$

In using Eq. (1) we have assumed that the decay by electron emission can be described by the addition of a local imaginary part to the potential. The significance of this assumption has been discussed by Fiquet-Fayard.<sup>15</sup> In calculating the inhomogeneous term, which represents the formation of the resonance through electron capture, it has been assumed that the wave function describing the incident electron beam is normalized to a  $\delta$  function in energy and direction. The dissociative attachment cross section can then be

obtained by examining the flux of dissociating negative ions, giving<sup>2, 4, 15</sup>

$$\sigma_{DA} = \frac{2\pi^2}{k_0} \frac{K}{M} \lim_{R \rightarrow \infty} |\xi(R)|^2, \quad (3)$$

where  $k_0$  and  $K$  are the wave numbers describing the incident electronic motion and the outgoing ion motion (in the center-of-mass frame).

The potential energy  $V(R)$  and width  $\Gamma(R)$  for the ground state of  $H_2^-$  were constructed to give qualitative agreement with the only available *ab initio* calculations,<sup>4</sup> with adjustable parameters that were chosen on the basis of experimental data on collisions of electrons with ground-state  $H_2$  and  $D_2$  molecules. The potential  $V(R)$  is taken as

$$V(R) = V_0(R) - A + B \exp(-\beta R^2). \quad (4)$$

The parameter  $A$  was set to equal the affinity of H ( $\sim 0.754$  eV) and  $B$  and  $\beta$  were constrained so that the stabilization point, at which  $V(R)$  equals  $V_0(R)$ , is  $3.0a_0$ . The width  $\Gamma(R)$  was taken to be

$$\Gamma(R) = Ck^3(R),$$

reflecting the  $p$ -wave nature of this  $^2\Sigma_u$  resonance. The experimental data that were considered in the fitting of the two remaining parameters were (a) the magnitude and energy dependence of the cross sections for excitation of the  $v = 1, 2,$  and  $3$  levels of  $H_2$ ,<sup>16</sup> (b) the magnitude of the dissociative attachment cross section for ground-state  $H_2$  near  $3.75$  eV,<sup>8</sup> and (c) the isotope effect in dissociative attachment at  $3.75$  eV.<sup>8</sup> We found that the data (a) and (b) can be fitted using either of the two values suggested by Schulz and Asundi for the threshold attachment cross section ( $1.6 \times 10^{-21}$  or  $2.8 \times 10^{-21}$  cm<sup>2</sup>). However, the isotope effect could not be fitted simultaneously with both of the other data sets. Because of the difficulty of measuring the extremely small cross sections for dissociative attachment in  $D_2$  we deemed it appropriate to give least weight to these data. In order to reduce the discrepancy in the isotope ratio (to about 40%) we used the higher value of  $2.8 \times 10^{-21}$  cm<sup>2</sup> for the attachment cross section in  $H_2$ . The selected parameter values,  $B = 0.2152$ ,  $\beta = 0.2276$ , and  $C = 2.65$  (all in a.u.) lead to a resonant state which at the equilibrium internuclear distance of  $H_2$  (1.4 a.u.) occurs at 3 eV with a width of 5.4 eV. Further details of this fitting procedure will be presented later.

Equation (1) was solved numerically, both by

direct integration of the inhomogeneous equation and through the evaluation of the appropriate Green's function. After the two procedures were checked for consistency, the Green's-function method was used.

The dependence of the attachment cross section upon the initial vibrational state arises simply from the change in the inhomogeneous term in Eq. (1). The rotational state enters in two ways. First, the initial radial wave function is modified due to centrifugal stretching in the neutral molecule. Second, an increase in the total angular momentum  $J$  will lead to faster dissociation of the  $H_2^-$  ion and reduced competition from electron emission. Because of the absence of spherical symmetry several values of  $J$  can be formed in resonant collisions with molecules with each specific value of initial angular momentum  $J_i$ . However, assuming that electron capture is dominated by the  $p$ -wave contribution, we find that little error is made by assuming an average value for  $J$ , namely  $J = J_i$ .

Our calculated cross sections are shown in Figs. 1 and 2. Rotational and vibrational excita-

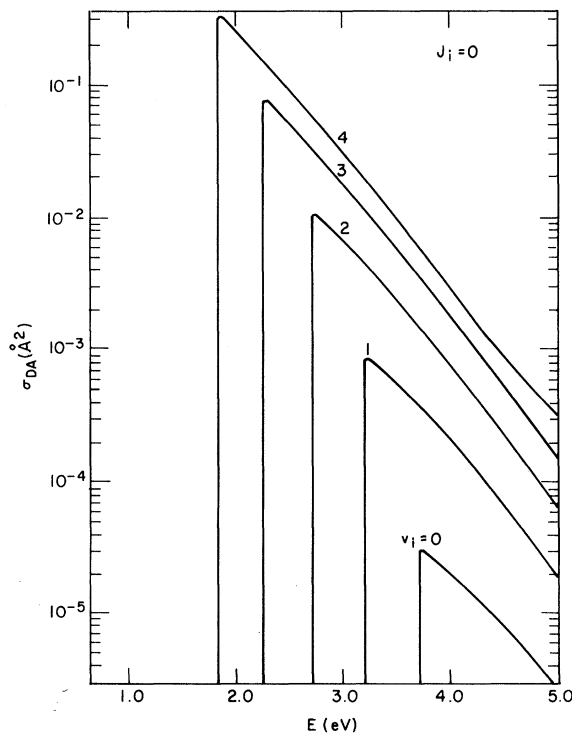


FIG. 1. Dissociative attachment cross section for various vibrational states of  $H_2$ , each in the rotational state  $J = 0$ .

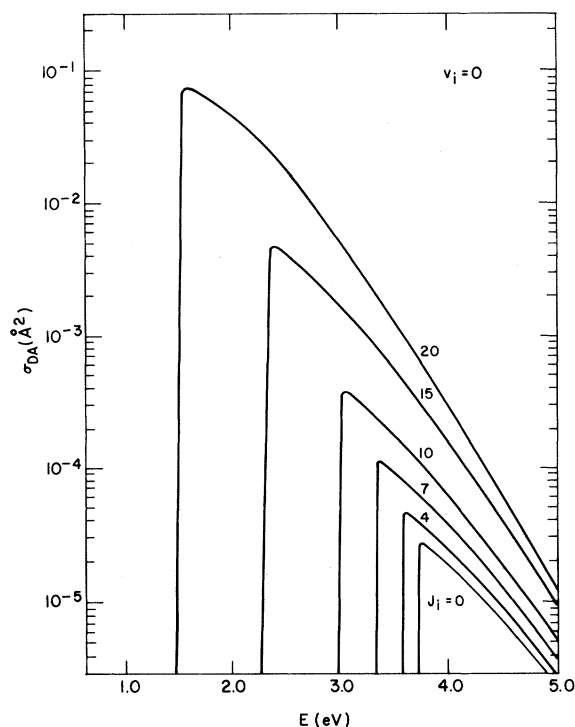


FIG. 2. Dissociative attachment cross section for various rotational levels of the ground vibrational state of  $H_2$ .

tion both lead to increased attachment cross sections at each electron energy and the lowering of the threshold energies results in further increases in the threshold cross section. The effect is most obvious for vibrational excitation and in Table I we show the attachment cross section for each initial vibrational state at an energy 0.028 eV above threshold. In each entry the total energy is equal to that of a 3.75-eV electron scattered by an  $H_2$  molecule in the ground state.

The enhancement that we find due to rotational enhancement is less than that calculated by Chen and Peacher. A direct comparison of our threshold cross sections, for both  $H_2$  and  $D_2$ , is provided in the accompanying paper by Allan and Wong.<sup>14</sup> With hindsight it appears that better agreement would have been obtained by assuming the alternative value of  $1.6 \times 10^{-21}$  for the  $\sigma_{DA}$  for ground state  $H_2$  at 3.75 eV.

The formation of the level  $v = 0, J = 8$  and the level  $v = 1, J = 0$  each involve about 0.5 eV excitation energy. For electrons with energy 3.75 eV the attachment cross section is enhanced by less than threefold as a result of such rotational excitation and is enhanced by a factor of  $\sim 11$  as a result of vibrational excitation. Thus heating of the

TABLE I. Attachment cross sections near threshold for several vibrational levels.

$v$	$E$ (eV)	$\sigma_{DA}$ ( $cm^2$ )
0	3.75	$2.8 \times 10^{-21}$
1	3.23	$8.3 \times 10^{-20}$
2	2.75	$1.0 \times 10^{-18}$
3	2.29	$7.5 \times 10^{-18}$
4	1.86	$3.8 \times 10^{-17}$
5	1.46	$1.2 \times 10^{-16}$
6	1.08	$2.9 \times 10^{-16}$
7	0.74	$4.3 \times 10^{-16}$
8	0.42	$3.2 \times 10^{-16}$
9	0.14	$4.3 \times 10^{-16}$

$H_2$  molecules is most effective in increasing the dissociative attachment rates through vibrational excitation, provided that the vibrational threshold is reached. On the other hand, for Boltzmann distributions at moderate temperatures rotational excitation can be more important because of its lower threshold energy. At a temperature of 1300 K, corresponding to the upper limit in the experiment by Spence and Schulz,<sup>9</sup> the cross section should be enhanced by approximately 30% as a result of rotational excitation and 10% as a result of vibrational excitation. The combined effect appears to be near the edge of the resolution of the experiment of Spence and Schulz.<sup>9</sup>

In their analysis of  $H^-$  production in a low-pressure hydrogen plasma Nicolopoulou, Bacal, and Doucet<sup>13</sup> assume the dissociative attachment rate to be  $\sim 2 \times 10^{-15} cm^3 s^{-1}$  for an electron temperature of  $\sim 1$  eV. Our calculation shows that this rate could be considerably higher if the  $H_2$  molecules are heated. Indeed if the neutral molecules were in thermal equilibrium at this temperature a rate of  $\sim 10^{-10} cm^3 s^{-1}$  would be obtained. Although this latter situation is unlikely it is clear that even a modest amount of neutral heating would lead to significantly higher  $H^-$  production.

The width of the lowest  $^2\Sigma_u$  resonance in  $H_2^-$  is so large that one should be concerned about the accuracy of resonant scattering theory applied to reactions that proceed through this resonance. Further comparisons of this type between theory and experiment will help to determine the scope of the resonant scattering theories for electron-molecule collisions.

This work has been supported by the National Science Foundation, through Grant No. PHY76-21456. The authors are grateful to Martha Bacal and Arvid Herzenberg for suggesting this problem.

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<sup>1</sup>T. Holstein, Phys. Rev. 84, 1073 (1951).

<sup>2</sup>J. N. Bardsley, A. Herzenberg, and F. Mandl, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland, Amsterdam, 1964), p. 415.

<sup>3</sup>Yu. N. Demkov, Phys. Lett. 15, 235 (1965).

<sup>4</sup>J. N. Bardsley, A. Herzenberg, and F. Mandl. Proc. Phys. Soc., London 89, 305, 321 (1966).

<sup>5</sup>T. F. O'Malley, Phys. Rev. 150, 14 (1966), and 156, 230 (1967).

<sup>6</sup>J. C. Y. Chen and J. L. Peacher, Phys. Rev. 163, 103 (1967).

<sup>7</sup>D. Rapp, T. E. Sharp, and D. D. Briglia, Phys. Rev. Lett. 14, 533 (1965).

<sup>8</sup>G. J. Schulz and R. K. Asundi, Phys. Rev. 158, 25

(1967).

<sup>9</sup>D. Spence and G. J. Schulz, J. Chem. Phys. 54, 5424 (1971).

<sup>10</sup>W. R. Henderson, W. L. Fite, and R. T. Brackmann, Phys. Rev. 183, 157 (1969).

<sup>11</sup>D. Spence and G. J. Schulz, Phys. Rev. 188, 280 (1969).

<sup>12</sup>T. F. O'Malley, Phys. Rev. 155, 59 (1967).

<sup>13</sup>E. Nicolopoulou, M. Bacal, and H. J. Doucet, J. Phys. (Paris) 38, 1399 (1977).

<sup>14</sup>M. Allan and S. F. Wong, preceding Letter [Phys. Rev. Lett. 41, 1791 (1978)].

<sup>15</sup>F. Fiquet-Fayard, Vacuum 24, 533 (1974).

<sup>16</sup>H. Ehrhardt, L. Laughans, F. Linder, and H. S. Taylor, Phys. Rev. 173, 222 (1968).

## Nonlinear Stability of Envelope Solitons

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(Received 22 September 1978)

The instability of plane envelope Langmuir solitons subject to transverse perturbations is reconsidered for the cubic nonlinear Schrödinger equation as well as the coupled set of high- and low-frequency equations in the case of nonadiabatic ion response. The nonlinear investigation demonstrates instability with a cutoff in all cases and predicts a drastic lowering of the instability growth rates when nonadiabatic ion motion is allowed for. Our analytical results agree with recent numerical computations.

The problem of perpendicular instability of plane solitons is of much interest in different areas of physics.<sup>1</sup> For Langmuir solitons, many authors<sup>2-8</sup> considered this problem but unfortunately the results are often contradictory: The previous investigations<sup>2-7</sup> predicting instability in the long-wavelength limit have been criticized by Infeld and Rowlands,<sup>8</sup> who demonstrated stability. Furthermore, the situation for short-wavelength perturbations is also quite unclear, although numerical<sup>9</sup> and analytical<sup>10</sup> studies suggest stability in the short-wavelength region.

In this Letter, we reconsider this problem and resolve the discord within a nonlinear calculation. Guided by the criticism of Infeld and Rowlands,<sup>8</sup> namely that the unstable modes violate the linearization procedure, the investigation necessarily has to be nonlinear. However, our results (i) justify the general linear conclusions of instability in the long-wavelength limit, (ii) correct some previous values for the growth rates and regions of instability, (iii) give at the first time the necessary and sufficient conditions for instability, i.e., the unstable  $k$  range limited by a cutoff  $k_c$ , and (iv) predict a drastic lowering of the known

values of growth rates because of nonadiabatic ion response.

In the following, we treat the scalar and vectorial cubic nonlinear Schrödinger equation (NSE) as well as their generalizations for nonadiabatic ion response. We now demonstrate the main procedure for the case of the scalar NSE,

$$i \partial f / \partial t + \nabla^2 f + f^2 f^* = 0, \quad (1)$$

and first derive a sufficient criterion for instability of the stationary solution

$$g = G(x - x_0) \exp(i\eta_0^2 t), \quad (2)$$

where  $G(x) = \sqrt{2}\eta_0 \operatorname{sech}(\eta_0 x)$ . Here, we restrict ourselves to standing solitons and we shall discuss the effect of a finite velocity at the end. Assuming periodic boundary conditions in the transverse direction, we write the perturbed state  $f$  in the form<sup>11</sup>

$$f = [G(x - x_0 - \xi) + a + ib] \exp[i\eta_0^2(t - \tau)]. \quad (3)$$

Furthermore, for deriving a sufficient condition for instability we only take perturbations which have the same values for the first three invariants as the unperturbed solution. From Eq. (1)