Low-energy e-H_2 scattering: Separation of dissociative attachment and dissociation channels

Y. Xu

Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588-0111

A. K. Kazansky

Institute of Physics, University of St. Petersburg, St. Petersburg 198904, Russia

I. I. Fabrikant

Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588-0111

Electron impact dissociation and dissociative attachment (DA) via the $^2\Sigma_u^+$ shape resonance in e-H_2 collisions is treated by the quasiclassical version of the nonlocal resonance theory. Optical theorem is applied to analyze all the energetically accessible channels. Collisionally induced dissociation and dissociative attachment cross sections for vibrationally or rotationally excited H_2 molecule are presented in the electron energy range up to 5 eV. It is shown that the DA cross sections we published recently [Phys. Rev. A **61**, 052705 (2000)] in fact represent the sum of the cross sections for the DA and dissociation processes in the energy range above the dissociation threshold.

Inelastic processes in low-energy e-H_2 scattering are dominated by the $^2\Sigma_u^+$ shape resonance. While vibrational excitation of the H_2 molecule has been studied by a variety of theoretical methods [1–4], the breakup processes, i.e., the dissociative attachment (DA) and electron impact dissociation processes have been investigated mostly through resonance approaches [5–9]. In fact, the resonant contribution to the electron impact dissociation of H_2 was studied theoretically only by Atems and Wadehra [10], who employed a semiempirical local theory and discretization of the vibrational continuum. DA cross sections obtained from different theories are in general close to each other, and close to available experimental data, for collision processes involving the H_2 molecule in its ground state [4,7]. Regarding processes involving vibrationally or rotationally excited targets, however, our understanding is still quite limited both theoretically and experimentally [11].

In a recent paper [12], we calculated the DA cross section for vibrationally and rotationally excited H_2 and HF molecules in the energy range from 0 to 6 eV within the framework of the nonlocal resonance theory. Our calculation was based on *ab initio* description of the fixed nuclei resonance [13] and quasiclassical treatment of the nuclear dynamics [14]. Equations used in Ref. [12], when applied in the energy range above the dissociation threshold, gives only a sum of the dissociation and DA cross sections [12]. In this brief report we consider the breakup processes above the threshold in more detail and calculate the DA and dissociation cross sections separately.

The dissociative attachment cross section via a temporary negative ion resonance can be obtained by examining the asymptotic behavior of the negative ion wave function. Within the framework of the quasiclassical nonlocal resonance theory, Kalin and Kazansky derived the following expression for DA to an initial state v_i at total energy E [15]:

$$\sigma_{v_i}^{DA}(E) = \frac{\pi}{k_i^2 \sqrt{2M}} |\tilde{b}(D_0)|^2 \text{Re } \tau(D_0), \qquad (1)$$

here k_i^2 is the energy of the incident electron, $\tau(D_0)$ is the reduced time of nuclear vibration, and $\tilde{b}(D_0)$ is proportional to the expansion coefficient of the negative ion wave function over the rovibrational eigenstates of the neutral molecule $b(D_0)$. Explicit definition of $\tilde{b}(D_0)$, $b(D_0)$ and $\tau(D_0)$ can be found in Ref. [15]. For inclusion of rotational motion, these quantities should be evaluated with account of the centrifugal term in the energy functions of the molecule and ion [12]. The angular momentum for the nuclear motion is assumed to be a constant during the DA process.

Equation (1) was derived with the implicit assumption that all the flux associated with nuclear motion in the continuum goes into the dissociative attachment channel. This is indeed the case when the dissociation channel is energetically forbidden. When the energy is above the dissociation limit of the neutral molecule, however, the dissociation channel is open, and the fluxes in the dissociation and dissociation attachment channels need to be separated. Subsequently, the DA cross section should be calculated according to

$$\sigma_{v_i}^{DA} = \frac{\pi}{k_i^2 \sqrt{2M}} |\tilde{b}(E)|^2 \text{Re } \tau(E), \qquad (2)$$

where all the quantities are now taken at total energy E instead of the dissociation threshold D_0. Equation (1) includes the contribution from the dissociation reaction and thus gives the sum of the dissociation and dissociative attachment cross sections.

The differential in energy cross section for dissociation of state v_i with final energy of nuclear motion μ can be calculated quasiclassically as follows:

$$\frac{d\sigma_{v_i}^{diss}}{d\mu} = \frac{2\pi^3}{k_i^2} \Gamma(\mu) |b(\mu)|^2, \qquad (3)$$

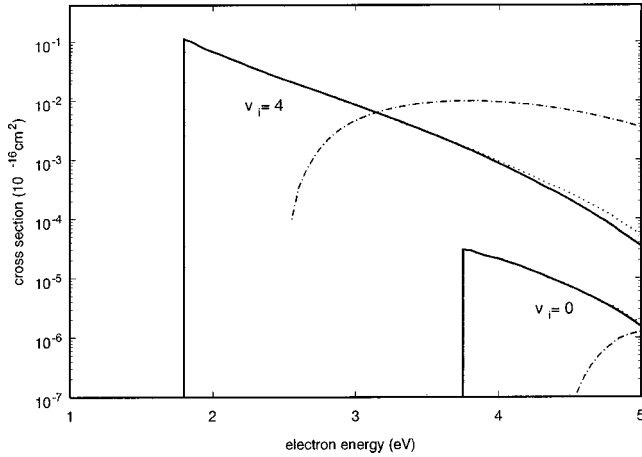where $\Gamma(\mu)$ is the partial resonance width at energy μ.

FIG. 1. Dissociative attachment cross sections from Eq. (1) (solid curves) and from the optical theorem (dotted curves). The dissociation cross sections are shown as dashed curves.

From the optical theorem, the following relation between the vibrational excitation, dissociative attachment and dissociation cross sections can be obtained [15]:

$$\sigma_{v_i}^{DA} + \sum_{v_f} \sigma_{v_i}^{VE}(v_f) + \sigma_{v_i}^{diss} = \frac{2\pi^2}{k_i^2} \text{Im} \; [b(\epsilon_{v_i}) V(E, v_i)],$$

(4)

in which ϵ_{v_i} is the vibrational energy for state v_i, $V(E, v_i)$ is the coupling amplitude between the diabatic state and the continuum state, $b(\epsilon_{v_i}) V(E, v_i)$ is the elastic scattering amplitude for initial state v_i as given by the quasiclassical non-local theory.

The DA cross section and dissociation cross section can thus be calculated in a consistent way through Eqs. (2) and (3). Upon calculation of the elastic scattering amplitude and all the vibrational excitation cross section for an given initial state, optical theorem in low energy e-H_2 scattering can be checked using Eq. (4).

Figure 1 compares the dissociative attachment cross sections given by Eq. (1) and by the optical theorem. In order to obtain the DA cross section from Eq. (4), we calculate the cross sections for dissociation and vibrationl excitation (and deexcitation for $v_i = 4$) to all the 16 vibrational states of H_2 and subtract them from the imaginary part of the elastic scattering amplitude. The resultant DA cross section agrees well with the DA cross section from Eq. (1) for $v_i = 0$. For $v_i = 4$, the agreement at higher energies is poorer. We should point out that in the electron energy range above 4 eV, the DA cross section for $v_i = 4$ is 5 or 6 orders of magnitude smaller than the elastic cross section, and actually is even much smaller than the dissociation cross section, as is seen from Fig. 1. Therefore evaluation of the DA cross section from Eq. (4) requires high accuracy in the calculation of the cross sections for all processes, especially in the numerical integration of the differential dissociation cross section. For highly excited states, the difference between the DA and the total dissociation cross sections at high energies is even bigger, and the present comparison becomes numerically infeasible.

Figure 2 gives the cross section spectral density for the $v_i = 4$ state at electron energy 4 eV. The continuum part of the spectral density (with energy of nuclear motion more than 4.75 eV) is the differential dissociation cross section, the discrete part of the spectral density is defined as the ratio of the vibrational excitation (or deexcitation) cross section to the energy interval occupied by this state [16]. The cross section spectral density joins smoothly in the vicinity of the dissociation threshold, which indicates the consistency between the treatment of the vibrational excitation and dissociation in the present theory.

In Fig. 3 and Fig. 4, we present the DA cross sections for vibrational states of H_2 up to $v_i = 9$ and several rotationally excited states of the vibrational ground state. The cross sections do not show any plateau type structure of Fig. 1 and Fig. 4 of Ref. [12] and their dependence on energy is close to exponential decrease. From comparison between Eqs. (1) and (2), it can be seen that the structure in Ref. [12] is simply
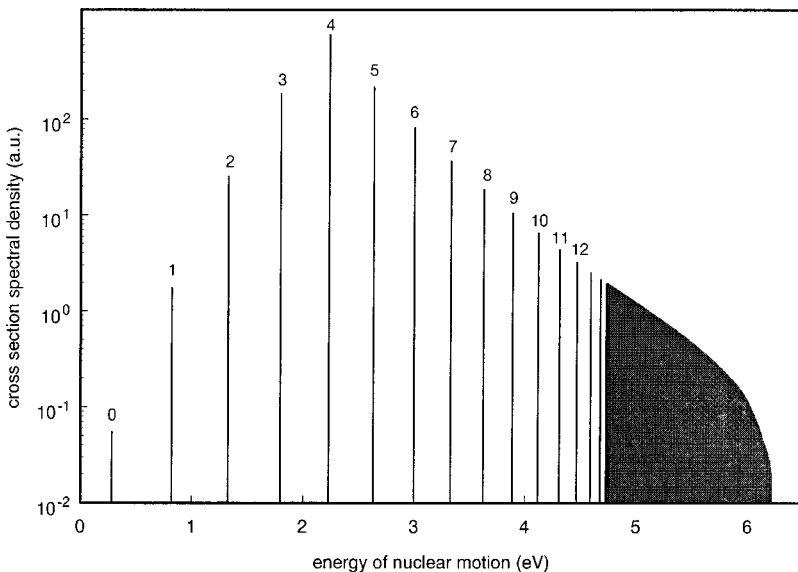

FIG. 2. Cross section spectral density for the $v_i = 4$ initial state and incident electron energy 4 eV.
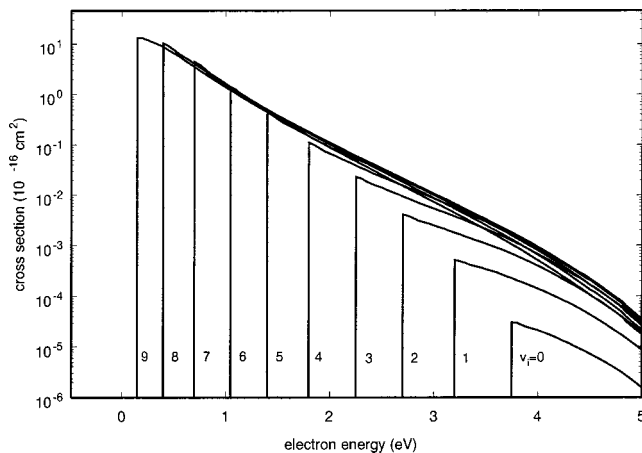
FIG. 3. Dissociative attachment cross sections for various vibrational states of H_2.

FIG. 5. Dissociation cross sections for various vibrational states of H_2.

the effect of the contribution from the dissociation cross section. The cross sections in [12] for the HF molecule do not exhibit this type of structure because the dissociation cross section for the states studied were all negligible in the whole energy range. Therefore, although the state selected cross sections for H_2 presented in [12] should be separated into DA and dissociation components, the results for HF represent basically the DA cross sections. By the same reasoning, the temperature averaged DA cross section for H_2 calculated in Ref. [12] was almost unaffected by the dissociation channel, since at the temperature studied ($T = 1400$ K) the main contribution to the cross section is from the low-lying vibrational states, for which the dissociation cross section is relatively small.

Figure 5 gives the electron impact dissociation cross section for different vibrational states of H_2 through the $^2\Sigma_u^+$ shape resonance. Our cross sections for the vibrationally excited states $v_i = 3,6,9$ all agree quite well with the results of Atems and Wadehra [10] in both the shape and the magnitude. For the ground state, however, our cross section is about one order of magnitude larger than that of Atems and Wadehra, which probably is another indication that the local
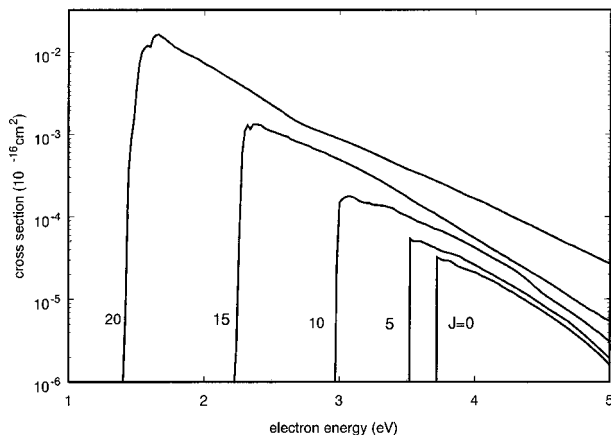
theory works well for excited states but fails for the ground states [17,18].

In Fig. 6, we show the dissociation cross section for different rotational states of the vibrational ground state of H_2. It is interesting to note that for the $v_i = 0$, $J = 20$ state, the dissociation cross section is about one order of magnitude smaller than that for the $v_i = 5$, $J = 0$ state, which has about the same internal energy. As was observed for the DA cross sections [12,19], the enhancement of the dissociation cross sections is smaller due to rotational motion than due to vibrational motion at the same internal energy.

The drastic enhancement of the threshold DA cross section with higher initial energy of the target molecule can be

FIG. 4. Dissociative attachment cross sections for various rotational states of H_2 with $v_i = 0$. From bottom to top the curves correspond to $J = 0$, 5, 10, 15, and 20.
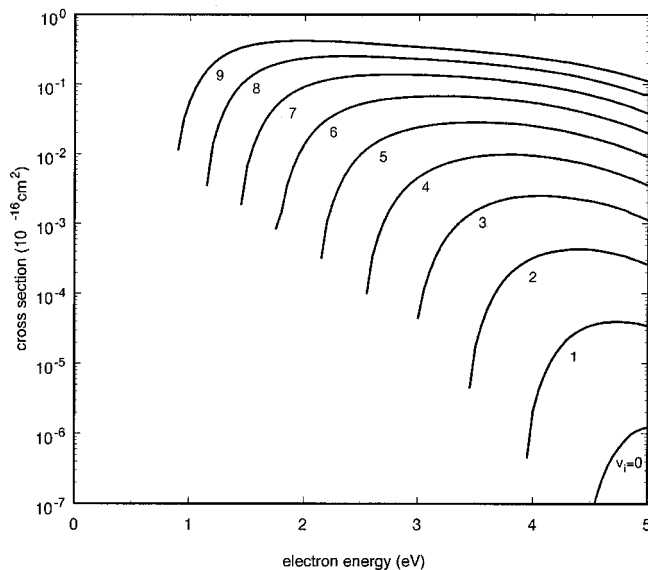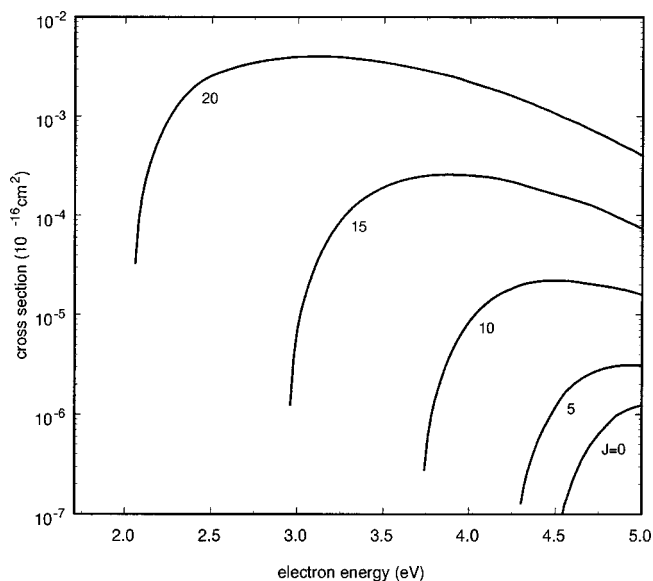

FIG. 6. Dissociation cross sections for various rotational states of H_2 with $v_i = 0$. From bottom to top the curves correspond to $J = 0$, 5, 10, 15, and 20.

attributed to the increase in the negative-ion survival probability [20,21], which affects the cross sections exponentially for dissociating processes governed by a short-lived resonance. Quasiclassically, the negative ion survival probability is determined by the velocity of relative nuclear motion and also the distance between the Franck-Condon point and the stabilization point. With increasing v_i, the Franck-Condon point indeed moves toward the stabilization point for a given total energy [13]. Although the rotational excitation shifts the Franck-Condon point equally for the same internal energy, it is less efficient in enhancing the DA cross section because the relative motion of the nuclei is slowed down by the rotational barrier [21]. The same behavior of the state dependence of the resonant dissociation cross section is expected since the dissociation process is also affected by a negative ion survival probability with the only difference that the negative ion should survive until the point at which the electron autodetachment with formation of the dissociating state occurs.

We should point out now that the present study treats only the $^2\Sigma_u^+$ resonance in the electron energy range up to 5 eV.

For higher incident energies, the effect of the $^2\Sigma_g^+$ resonance on the DA and dissociation cross sections becomes more important [10,22]. When the electron energy exceeds 10 eV, the dissociation process proceeds predominantly via direct excitation of the $^3\Sigma_u^+$ electronic state of H_2 rather than any temporary negative ion states [10,23].

In conclusion, we have performed an *ab initio* calculation of the elastic and inelastic processes in low energy e-H_2 scattering via the $^2\Sigma_u^+$ shape resonance using the quasiclassical approximation for nuclear dynamics. We have shown that the cross sections presented in Ref. [12] are in fact the sum of the cross sections for dissociative attachment and dissociation. The DA and dissociation cross section we present here for excited H_2 molecule is consistent with the optical theorem and analysis of the dependence of the cross section on the final state energy of the nuclear motion.

[1] R.J.W. Henry, Phys. Rev. A **2**, 1349 (1970).

[2] B.I. Schneider, M. Le Dourneuf, and P.G. Burke, J. Phys. B **12**, L365 (1979).

[3] M.A. Morrison, A.N. Feldt, and D. Austin, Phys. Rev. A **29**, 2518 (1984).

[4] S. Mazevet, M.A. Morrison, and R.K. Nesbet, J. Phys. B **31**, 4437 (1998).

[5] T.F. O'Malley, Phys. Rev. **150**, 14 (1966).

[6] J.N. Bardsley, J. Phys. B **1**, 365 (1968).

[7] C. Mündel, M. Berman, and W. Domcke, Phys. Rev. A **32**, 181 (1985).

[8] J.M. Wadehra and J.N. Bardsley, Phys. Rev. Lett. **41**, 1795 (1978).

[9] A.P. Hickman, Phys. Rev. A **43**, 3495 (1991).

[10] D.E. Atems and J.M. Wadehra, J. Phys. B **26**, L759 (1993).

[11] M. Capitelli and R. Celiberto, in *Novel Aspects of Electron-Molecule Collisions*, edited by K.H. Becker (World Scientific, Singapore, 1998).

[12] Y. Xu, G.A. Gallup, and I.I. Fabrikant, Phys. Rev. A **61**, 052705 (2000).

[13] G.A. Gallup, Y. Xu, and I.I. Fabrikant, Phys. Rev. A **57**, 2596 (1998).

[14] I.S. Yelets and A.K. Kazansky, Zh. Éksp. Teor. Fiz. **80**, 982 (1981) [Sov. Phys. JETP **53**, 499 (1981)]; A.K. Kazansky and I.S. Yelets, J. Phys. B **17**, 4767 (1984).

[15] S.A. Kalin and A.K. Kazansky, J. Phys. B **23**, 4377 (1990).

[16] I.I. Fabrikant, S.A. Kalin, and A.K. Kazansky, J. Chem. Phys. **95**, 4966 (1991).

[17] M. Čížek, J. Horáček, and W. Domcke, J. Phys. B **31**, 2571 (1998).

[18] W. Domcke (private communication).

[19] J.N. Bardsley and J.M. Wadehra, Phys. Rev. A **20**, 1398 (1979).

[20] R. N. Compton and J. N. Bardsley, in *Electron-Molecule Collisions*, edited by I. Shimamura and K. Takayanagi (Plenum, New York, 1984).

[21] J.P. Gauyacq, J. Phys. B **18**, 1859 (1985).

[22] J.M. Wadehra, Appl. Phys. Lett. **35**, 917 (1979).

[23] T.N. Rescigno and B.I. Schneider, J. Phys. B **21**, L691 (1988).