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Cross sections for 14-eV e -H₂ resonant collisions: Dissociative electron attachment

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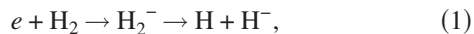
The dissociative electron attachment (DEA) process in electron-H₂ molecule collisions, involving the $^2\Sigma_g^+$ excited electronic Rydberg state of molecular hydrogen ion H₂⁻, is investigated theoretically. The DEA cross section has been calculated within the local complex potential approximation. The convoluted cross section, which presents a peak located at the incident energy of about 14 eV, compares favorably with available experimental data.

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I. INTRODUCTION

The process of dissociative electron attachment (DEA) to molecular hydrogen,



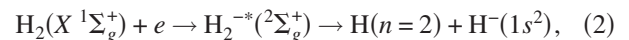
is quite important in the development of negative hydrogen ion beams and in the diagnostics of a hydrogen plasma. This process was first investigated, in classic experiments, by Schulz [1], and by Schulz and Asundi [2,3] who observed three distinct peaks in the cross section of DEA to molecular hydrogen in the electron energy range from 3 to 20 eV. These three peaks, around 3.75, 10, and 14 eV, in the DEA cross sections were also observed for the heavier isotopes of H₂ by Rapp *et al.* [4], and by Schulz and Asundi [2,3]. The 14 eV DEA peak appears to be the most pronounced one. Theoretically, the process of dissociative attachment is understood to proceed via the formation of an intermediate resonance state of H₂⁻ [5]. The two lowest resonant states of H₂⁻, namely, the $^2\Sigma_u^+$ and the $^2\Sigma_g^+$ states, are responsible for the lowest two peaks, around 3.75 and 10 eV, in the DEA cross sections. The third peak in the DEA cross section, around 14 eV, has not yet been investigated theoretically, primarily due to lack of data related to the higher resonances of H₂⁻. An important step forward, toward the clarification of the resonances involved in the 14 eV DEA peak, was made by the experimental observation of H₂⁻ resonances in e -H₂ collisions [6] for which the parent states are those H₂ molecular states that dissociate to H(1s) and H($n=2$) products. From a theoretical point of view, a further important progress toward the clarification of the resonances responsible for the 14 eV DEA peak was made by the recent highly accurate *ab initio* calculations of the parameters of these resonances [7] as a function of the internuclear distance R .

With the availability of this new theoretical information, it has now become possible to explore the cross sections of

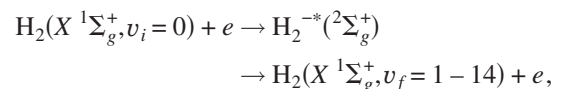
DEA to H₂ in the vicinity of 14 eV. In this paper we present the resonance mechanism responsible for the large 14 eV peak in the DEA cross section of H₂. We are also investigating the effect of initial rovibrational excitation of the molecule on the DEA cross sections for incident electron energies around 14 eV.

II. THEORETICAL MODEL

The excited $^2\Sigma_g^+$ state of H₂⁻, whose parent states have been identified as the $a^3\Sigma_g^+$, $E,F^1\Sigma_g^+$, $c^3\Pi_u$, and $C^1\Pi_u$ excited electronic states of the H₂ molecule [7], gives rise to a long-lived resonance, which, by electron emission, decays on the vibrational manifold of the ground state of the neutral molecule. The proximity of energy position of experimental 14 eV DEA peak with the energy parameters of this excited $^2\Sigma_g^+$ resonance suggests that this resonant state is also predominantly responsible for the DEA process



where the H₂ molecule is assumed initially to be in its lowest rovibrational state. While using this single resonance in our DEA cross-section calculations, we make two important observations. First, unlike the ground $^2\Sigma_u^+$ resonance of H₂⁻, which is primarily responsible for the peak around 3.75 eV in the DEA cross section, the excited Rydberg $^2\Sigma_g^+$ state of H₂⁻ is a sharp long-lived Feshbach resonance. Because of the Feshbach nature of this $^2\Sigma_g^+$ resonant state, it is quite appropriate to use the local complex potential (LCP) model [8]. This model can possibly break down for a broad shape resonance, such as the $^2\Sigma_u^+$ resonance [9,10], but is very reasonable for a long-lived Feshbach resonance characterized by a small width, such as the $^2\Sigma_g^+$ resonance used in the present work. The adequacy of this local complex potential model for description of the excited $^2\Sigma_g^+$ resonance has been further validated by our recent cross-section calculations [11] (referred to as I) for the resonant vibrational excitation (RVE) process



for which a very satisfactory agreement of calculated cross

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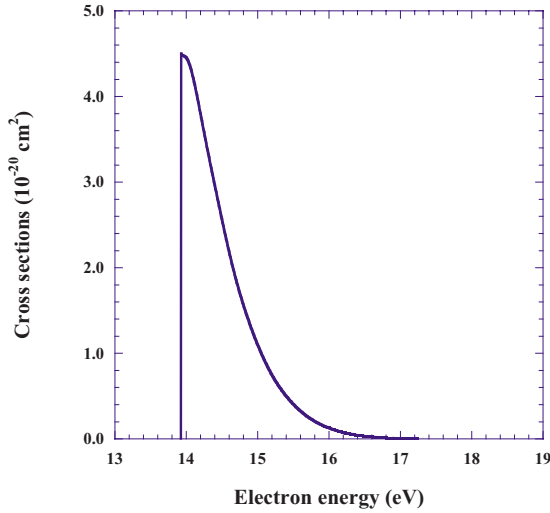


FIG. 1. (Color online) Dissociative electron attachment cross sections as a function of the incident electron energy, for the process: $H_2(X^1\Sigma_g^+, v_i=J=0) + e \rightarrow H_2^{-*}(^2\Sigma_g^+) \rightarrow H(n=2) + H^-(1s^2)$.

sections with the measurements of Ref. [6] was obtained. The second observation concerns the resonant states, among those identified in Ref. [7], which could in principle contribute to the DEA process. These states, however, as reported in Ref. [7], show inaccurate and fragmented widths that could be expected to generate numerical problems and consequent unreliable results. The inaccuracy affecting these widths comes from the impossibility to fit confidently the time delay of these resonances near their parent state threshold.

The cross section of the above DEA process can be calculated within the local potential model following the standard procedure [5,8,12] and by assuming the same input data (resonant potential and level widths) as adopted in the vibrational excitation calculations in I (see I for details). The only change in the input data, used here, is in the extrapolation of the total level width $\Gamma(R)$ for large bond lengths ($R > 4.0$ a.u.), as will be discussed later in more detail. The DEA cross section can be written as [12]

$$\sigma(E) = 2\pi^2 \frac{mK}{M k_i R} \lim_{R \rightarrow \infty} |\xi(R)|^2, \quad (3)$$

where $\xi(R)$ is the local nuclear wave function for the resonant state obtained by using the Green's function technique to solve the radial equation [11]. In addition, $k_i = \sqrt{2mE}/\hbar$ is the incident electron momentum, m is the electron mass, M is the reduced mass of the nuclei, and K is the outgoing negative-ion momentum.

III. RESULTS AND DISCUSSION

The results of our calculations of DEA cross sections for H_2 in the electron energy range around 14 eV are shown in various figures. Figure 1 shows the DEA cross sections as a function of the incident electron energy when the molecule H_2 is in the lowest rovibrational state. The cross section exhibits the characteristic onset behavior at the threshold of 13.922 eV, where it reaches the maximum value of

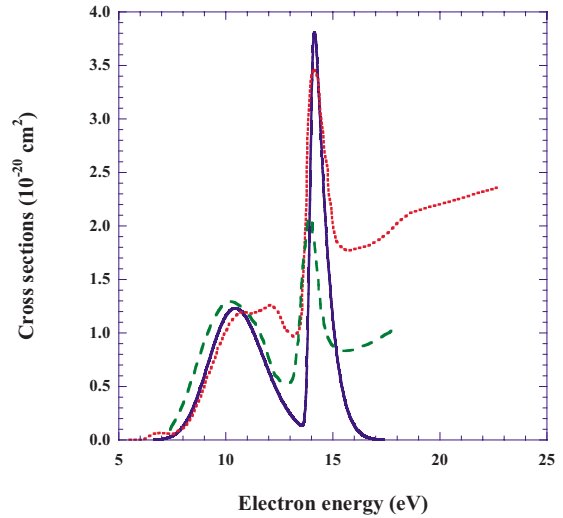


FIG. 2. (Color online) Comparison of calculated (full curve) and measured DEA cross section of Rapp *et al.* [4] (dashed curve) and Schulz [1] (dotted curve), as a function of the incident electron energy, for the process $H_2(X^1\Sigma_g^+, v_i=J=0) + e \rightarrow H_2^- \rightarrow H + H^-$. The theoretical cross sections have been convoluted at the resolution energy of 300 meV (see text).

4.5×10^{-20} cm². This value is about 30 times larger than that of the DEA cross sections around 3.75 eV for the process involving the ground $^2\Sigma_u^+$ resonant state of the H_2^- molecular ion [8], implying a more effective production of negative ions through DEA from Rydberg states. This circumstance is of significant importance in the laboratory plasmas where DEA plays a critical role [13].

In order to compare directly with the experimental cross sections, which are measured with a finite resolution of the instruments, it is necessary to convolute the calculated cross sections with an assumed Gaussian energy distribution in the electron beam. The convoluted cross sections are compared with the experimental results in Fig. 2, together with the 10 eV DEA peak produced by electron capture to the lowest $^2\Sigma_g^+$ resonant state and leading to H^- and $H(1s)$ products. The dotted and dashed lines reproduce the experimental measurements by Schulz [1] and Rapp *et al.* [4], respectively. These measured cross sections are, to the best of our knowledge, the only available experimental data in literature for the 10 and 14 eV DEA peaks. As can be seen in the figure, their most striking feature is the different magnitude shown by the cross section of the two measurements, which at the peak reaches a ratio of about 1.7. In the same figure the theoretical cross sections are represented by the full curve. This curve is the result of two separate calculations referring to two different resonances. The cross sections in the region from the threshold to approximately 12 eV, in which the curve shows the first maximum at 10 eV, have, in fact, been calculated in Ref. [14] in the frame of the local potential approximation for the DEA process involving the $B^2\Sigma_g^+$ resonant states. These cross sections were added to the present calculations for the DEA process occurring through the Rydberg $^2\Sigma_g^+$ resonant state, which is responsible for the 14 eV peak. The resulting cross sections have been finally convoluted at the resolution of 300 meV, used by Rapp *et al.* in their experi-

ments. The theoretical curve of Fig. 2 does not reproduce the features between the two peaks. Different resolution energies have also been tried (400 and 500 eV) but the cross sections showed only a slight decrease, with respect to the curve shown in Fig. 2, in the energy range contained within 15% of the peak. The theoretical cross sections become vanishingly small for high energies while the experimental curves show an increasing tail beyond 17 eV, probably due to the opening of the pure polar dissociative channel, leading to $H^+ + H^-$ production [4]. This process has not been considered in the present work.

Let us now turn to the main feature of the comparison in Fig. 2, represented by the satisfactory agreement of the theoretical cross sections with the measurements of Schulz. Before drawing any definitive conclusion from this agreement, we have to point out a relevant aspect of our calculations. From a theoretical point of view, the DEA cross section depends on the behavior of the complex nuclear wave function $\xi(R)$ for large R [see Eq. (3)]. This requires the accurate knowledge of the potential-energy curves and of the level width $\Gamma(R)$ for large values of internuclear separation R . In the present work, as well as for the RVE cross-section calculations of I, we have adopted for the ion $V^-(R)$ potential and for the level width $\Gamma(R)$ the calculated values of Stibbe and Tennyson [7], which cover the interval $1.0 \leq R(\text{a.u.}) \leq 4.0$ only. The lack of data beyond 4.0 a.u., which results in the truncation of both $V^-(R)$ and $\Gamma(R)$ before they show any asymptotic trend, requires adopting of an adequate extrapolation of the above quantities. The same situation was met also in the cross-section calculations for the RVE process. There, however, the uncertainty arising in the potential curve and width, for large R , is mitigated by the fact that the vibrational wave functions are appreciably different from zero only inside the Franck-Condon region so that the cross-section results are quite insensitive to different extrapolations outside the above interval of calculated bond lengths (see paper I). In the present DEA calculations we have adopted for the potential curve $V^-(R > 4.0 \text{ a.u.})$ the same function as used in I [15], based on a standard mathematical form, and, in order to have a more reliable extrapolation for the total width, we extrapolated $\Gamma(R)$ by fitting the last five calculated points from Ref. [7] (instead of three points considered in I), and have used the following expression [9]:

$$\begin{aligned} \Gamma(R > 4.0 \text{ a.u.}) = & 0.087684e^{-0.45317(R-3.66)^2} \\ & + 0.040081e^{-149.04(R-3.66)^2} \\ & + 0.16628e^{-2.8271(R-3.66)}. \end{aligned} \quad (4)$$

For $R < 1.1 \text{ a.u.}$ both $\Gamma(R)$ and $V^-(R)$ have been obtained in the same manner as in paper I. Above the stabilization point, placed at $R = 8.8 \text{ a.u.}$, the width $\Gamma(R) = 0$. The stabilization point is located at the crossing of the extrapolated potential curve of the $2^2\Sigma_g^+$ state with the asymptotic parts of the curves of the two overlapping target states $B^1\Sigma_u^+$ and $E, F^1\Sigma_g^+$. Here the total width takes a small value of $\Gamma(8.8 \text{ a.u.}) = 6.35 \times 10^{-7} \text{ eV}$, calculated by Eq. (4). The B and E, F states, along with the ground $X^1\Sigma_g^+$ and repulsive $b^3\Sigma_u^+$ states of H₂ molecule, represent, according to Ref. [7], the decaying

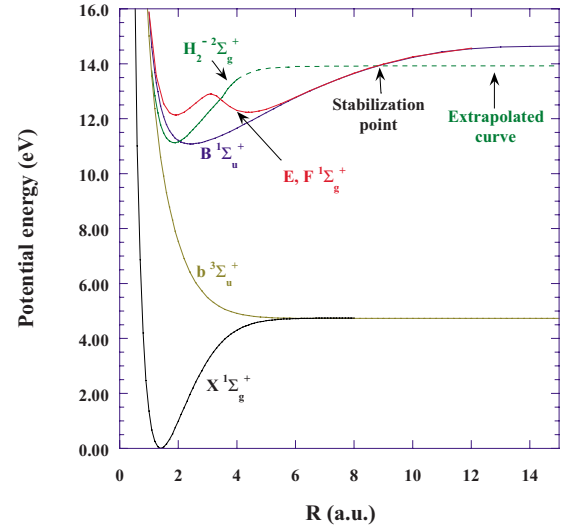


FIG. 3. (Color online) Potential energy curves of the $H_2^- 2^2\Sigma_g^+$ resonant state and its possible H_2 decay channels [7]. In the figure is shown the stabilization point located at 8.8 a.u.

channels of the $H_2^- 2^2\Sigma_g^+$ resonance before the stabilization point ($R < 8.8 \text{ a.u.}$). Figure 3 shows the corresponding potential energies while the partial width, for each channel, is given in Ref. [7].

In order to test the sensitivity of the cross sections to the chosen extrapolation, we have altered $\Gamma(R)$ of Eq. (4) by $\pm 10\%$, observing a corresponding variation in the cross-section maximum less than 10% with respect to the theoretical values of Fig. 2. Slight variations in the width, and the corresponding variation in the position of the stabilization point, do not affect substantially the magnitude of the cross section.

Another aspect of the problem is represented by the strong vertical onset of the cross sections at the threshold (Fig. 1). A time-dependent analysis [16] of DEA process, occurring through the short-lived $X^2\Sigma_u^- H_2^-$ shape resonance, shows that the strong behavior of the cross section at threshold may have a fundamental role in determining the correct shape and value of the DEA cross sections. This effect, as shown in Ref. [16], is not properly accounted for by the LCP model. It appears that, in the case of the broad shape resonance, the effect of the vertical onset of DEA cross sections at threshold cumulates with the effect of the large width in affecting the reliability of the LCP approximation. This is confirmed by the fact that, in the case of shape resonance, LCP approximation also fails for the RVE cross sections where the vertical onset at threshold is completely missing. However, in the present DEA process around 14 eV, the small width of the Rydberg resonance could prevail in maintaining the validity of the LCP approximation. The adequacy of the use of LCP approximation in the present calculations is further justified by the high energy of the Feshbach resonance [11].

We merely observe that the calculated cross sections follow closely, in shape and magnitude, the Schulz experimental curve around 14 eV, while in the range of 11–13 eV, the theory qualitatively reproduces the behavior of the Rapp *et al.* results. The experimental cross sections in the energy

range of 7–11 eV, due to the $^2\Sigma_g^+$ repulsive state of the molecular ion, are well described by the theoretical curve. In this energy region the cross section is generated mainly by the semiempirical calculations of Wadehra [14], as the contribution coming from the excited $^2\Sigma_g^+$ Rydberg state vanishes rapidly below 13 eV.

It is worth mentioning that a multichannel formalism for calculating the DEA cross section in the energy region around 14 eV, which includes all the possible resonances with parent states that correlates to the $H(1s)+H(n=2)$ asymptotic states, would certainly provide a more complete description of the underlying dynamics. However, as discussed in Sec. II, the presently available information on the parameters of these resonances [7] is inadequate (both in terms of accuracy and bond distances) to implement such calculations. On the other hand, the observed fair agreement of present DEA cross-section calculations with the available experimental data, as well as the agreement of theoretical RVE results [11,17] based on the same single-resonance model used here, with the experimental observations [6], provide a strong evidence that the $^2\Sigma_g^+$ resonant state of H_2^- gives the main contribution to the cross sections of both processes in the energy region under consideration.

In order to investigate the role played by initial rovibrational excitation of the molecule H_2 in enhancing the DEA cross section, we have repeated the calculations for the initial rovibrational levels $(v,J)=(1,0)$ and $(v,J)=(0,8)$. These levels of H_2 have approximately the same total rovibrational energy. Figure 4 shows three different DEA cross sections, occurring through the $^2\Sigma_g^+$ excited Rydberg state of H_2^- , corresponding to (v,J) values of (0,0), (1,0), and (0,8). It is observed that, for a fixed internal excitation energy, a pure vibrational excitation of H_2 is more efficient in enhancing the DEA cross section than a pure rotational excitation. The peak value of the DEA cross section increases by a factor of 4.3 when H_2 is initially vibrationally excited to (1,0) level but it increases by a factor of 1.2 only when H_2 is initially rotationally excited to (0,8) level. For comparison, we have also shown in Fig. 4 the DEA cross sections, of Horáček *et al.* [10], corresponding to the 3.75 eV peak that occur through the lowest resonant $^2\Sigma_u^+$ state of H_2^- . It is worth noting that, for a given initial rovibrational excitation of the molecule H_2 , the DEA cross section proceeding through the $^2\Sigma_g^+$ excited Rydberg state is consistently larger than the DEA cross section proceeding through the lowest $^2\Sigma_u^+$ resonance. It leads to the conclusion that the DEA cross section around 14 eV peak may be as important in the production of negative ions as the cross section around the 3.75 eV peak.

The good agreement between the theory and the Schulz experiment found in the present work is indirectly confirmed by the nonlocal calculations of Horáček *et al.* for the $^2\Sigma_u^+$ state [10]. For this cross section, in fact, they obtained the peak value of 2.85×10^{-21} cm², which favorably compares with the value of 2.8×10^{-21} cm² evaluated from the 14 eV

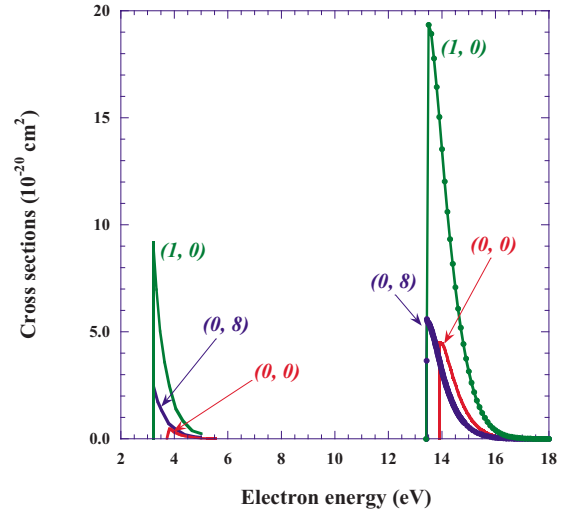


FIG. 4. (Color online) Cross sections, shown on the right side, for dissociative electron attachment to rovibrationally (v,J) excited H_2 occurring through the resonant $^2\Sigma_g^+$ excited Rydberg state of H_2^- , as a function of incident electron energy. The corresponding cross sections, shown on the left side, occurring through the lowest resonant $^2\Sigma_u^+$ state of H_2^- , are taken from Ref. [10].

peak of Schulz by using the ratio between the two peaks measured in Ref. [2]. In comparison, the cross sections obtained by the same procedure from the Rapp *et al.* measurements give the lower value of 1.6×10^{-21} cm² (see Refs. [2,4,10] for details).

IV. CONCLUSION

In conclusion, in the present paper we have calculated the contribution to dissociative attachment cross sections coming from the $H_2^{-*} ^2\Sigma_g^+$ excited state. The good agreement with the Schulz experimental data, in the energy region around 14 eV, demonstrates the adequacy of local approximation for description of the DEA process involving this Feshbach-type resonant state. The present calculations can be improved by adopting nonlocal or multiresonance models. Such possibility, however, will be amenable only when new input nonlocal parameters become available in literature. We have also shown that the initial rovibrational excitation of H_2 molecule leads to drastic enhancement of the DEA cross sections involving this resonant state. This circumstance has important implications for the kinetics in negative-ion sources [13].

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