

Calculations of electron scattering from H_2^+

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We have extended the convergent close-coupling method to investigate electron scattering from the vibrationally excited molecular hydrogen ion H_2^+ , within the Born-Oppenheimer approximation. Results are presented for proton-production and dissociative-ionization cross sections. The comparison with experiment is excellent across the energy range from near threshold to 1 keV.

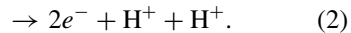
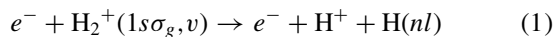
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I. INTRODUCTION

The *ab initio* convergent close-coupling (CCC) method has achieved considerable success in providing accurate collision data for electron and positron scattering from atoms and ions [1–5]. Our long-term goal is to do the same for molecular targets. We have already extended the CCC method to positron [6] and antiproton [7] scattering from molecular hydrogen, which produced results in good agreement with experiment over a broad energy range. Here we report the extension to electron scattering from the vibrationally excited molecular hydrogen ion H_2^+ .

The H_2^+ molecule is of fundamental interest to experimentalists and theorists in the study of electron-molecule scattering. It is a unique target; practically all electronic excitations lead to a dissociative process. Electron scattering from the electronic ground state $1s\sigma_g$ of H_2^+ in a vibrational state v is described by the following direct dissociative reactions:



Dissociative excitation (DE) (1) and dissociative ionization (DI) (2) are expected to be the major processes in the intermediate- and high-energy regions. Recently Chakrabarti *et al.* [8] used the multichannel quantum-defect theory to investigate indirect resonant electron attachment processes (dissociative excitation, recombination, and ion-pair production), which are important at low energies (≤ 10 eV). Here we consider the direct processes only and concentrate on impact energies above 10 eV.

The direct dissociative reactions (1) and (2) lead to proton-production (PP) cross sections $\sigma_{\text{PP}} = \sigma_{\text{DE}} + 2\sigma_{\text{DI}}$, where σ_{DE} and σ_{DI} are the DE and DI cross sections, respectively. It is worth noting that the DI cross sections [9,10] are an order of magnitude lower than the PP cross sections and are smaller than the experimental error bars of σ_{PP} [10–13].

Experimentally H_2^+ is produced by electron- or photon-impact ionization of H_2 . Almost all experimental measurements [9–13] have been taken with H_2^+ populated across a range of its 20 bound vibrational states [14]. The initial vibration population is well described by the Franck-Condon (FC) factors [15]. Peart and Dolder [9] suggested to use

the experimentally determined distribution of von Busch and Dunn [14], which better describes the experimental conditions. The von Busch–Dunn (BD) distribution is smooth, close to the FC factors and was produced by a least-squares fit of vibrationally resolved photodissociation cross sections of H_2^+ . The most recent measurements of El Ghazaly *et al.* [10] determined the ion-beam-source vibrational level distribution via resolution of the kinetic energy release spectrum of the protons. This showed good agreement with the FC and BD distributions. Dissociative excitation experiments have also been conducted with laser-controlled ion beams at the Aarhus Storage Ring Denmark, which produced HD^+ in $v = 0$ and H_2^+ in $v = 0$ and 1 vibrational states [16].

To date, theoretical investigations into electron scattering from vibrationally excited H_2^+ have been conducted only by first-order approaches. Born-Oppenheimer calculations of the electron- H_2^+ system within the first Born [17,18] and Bethe-Born [18] approximations found that the DE cross sections have a strong dependence on v and increase dramatically as v becomes larger. Liu [19] used the Bethe theory combined with the reflection approximation to calculate PP, DI, and DE cross sections assuming the BD and FC distribution. These methods compared well with experimental PP and DI data at high energies. Peek and Green [20] validated closure methods (summing cross sections over final rotational-vibrational states) in the Born approximation for H_2^+ .

The distorted-wave method of Robicheaux [21] utilized the fixed-nuclei approximation to calculate DI cross sections. Robicheaux [21] used a fixed-nuclei distance of $R = 2.15a_0$, which is the average distance of H_2^+ according to the BD vibrational distribution [14]. Recently the fixed-nuclei ($R = 2.0a_0$) approximation was utilized in the time-dependent close-coupling (TDCC) method [22] and configuration-average distorted-wave (CADW) method [23] to calculate DI cross sections. Though these calculations [21–23] compared well with the experiment of Peart and Dolder [9], they did not take into account the initial vibrational distribution of molecular states. In the present paper it is shown that account of the initial vibrational distribution leads to a substantial increase in the DI cross sections.

Here we present an *ab initio* approach to electron scattering on H_2^+ in the electronic ground, arbitrary initial vibrational state. We start by formulating the scattering problem within the fixed-nuclei approximation. The account of initial vibrational levels is performed as postprocessing of fixed-nuclei scattering results and requires scattering calculations to be conducted at a (large) number of internuclear distances.

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II. METHOD

The Hamiltonian of the H_2^+ molecule within the fixed-nuclei approximation describes an electron in the Coulomb potential of two protons that are fixed at distance R (atomic units are used throughout the paper),

$$H_T = K(\mathbf{r}) - \frac{1}{|\mathbf{r} + \frac{\mathbf{R}}{2}|} - \frac{1}{|\mathbf{r} - \frac{\mathbf{R}}{2}|} + \frac{1}{R}. \quad (3)$$

We have adopted a single-center approach to calculate the H_2^+ structure. The spherical body-frame coordinate system is chosen with the origin at the midpoint between two nuclei and the z axis along the internuclear axis \mathbf{R} . Wave functions of the H_2^+ molecule are characterized by the angular momentum projection m on the z axis and parity π . For each combination of (m, π) the electron wave function of the H_2^+ molecule is obtained by a diagonalization of the Hamiltonian (3) in a Sturmian (Laguerre) basis [24]. This leads to a set of target states $\Phi_n^{m\pi}$ with energy ε_n that satisfy

$$\langle \Phi_{n'}^{m\pi} | H_T | \Phi_n^{m\pi} \rangle = \varepsilon_n \delta_{n',n}. \quad (4)$$

The multicenter nature of the H_2^+ system leads to a slow convergence rate of the calculated wave functions with respect to the orbital angular momentum l of the Laguerre functions, in particular for the $1s\sigma_g$ ground state and $2p\sigma_u$ excited state. In order to improve accuracy and save on computational resources we have performed structure calculations in two steps. First, we produced an accurate $1s\sigma_g$ orbital of H_2^+ using a large Laguerre basis with exponential falloff $\alpha_l = 1.4$, $l_{\max} = 8$, and the number of functions N_l taken to convergence. Second, we produced a Laguerre basis with the same values of exponential falloffs, $l_{\max} = 4$, and $N_l = 15 - l$. Then we replaced the $1s$ orbital of this basis with the $1s\sigma_g$ orbital calculated in the first step. Such a structure results in a total energy of -0.601 for the $1s\sigma_g$ state and -0.155 for the $2p\sigma_u$ state at $R = 2.0$, which compares well with the accurate values of -0.603 and -0.168 , respectively [25]. For the H_2^+ ground-state static dipole polarizability we obtained $\alpha_{\parallel} = 4.950$ and $\alpha_{\perp} = 1.767$, which compare well with the accurate values of $\alpha_{\parallel} = 5.078$ and $\alpha_{\perp} = 1.758$ [26].

In the present calculations diagonalization of the target Hamiltonian leads to $N = 289$ states. These states are used to perform a multichannel expansion of the total wave function of the scattering problem. In the CCC method, we transform the body-frame electronic Schrödinger equation of the scattering system (for a fixed internuclear distance R) into the coupled Lippmann-Schwinger equations for the T matrix [6],

$$\begin{aligned} \langle \mathbf{k}_f \Phi_f | T_S | \Phi_i \mathbf{k}_i \rangle &= \langle \mathbf{k}_f \Phi_f | V_S | \Phi_i \mathbf{k}_i \rangle \\ &+ \sum_{n=1}^N \sum_k \frac{\langle \mathbf{k}_f \Phi_f | V_S | \Phi_n \mathbf{k} \rangle \langle \mathbf{k} \Phi_n | T_S | \Phi_i \mathbf{k}_i \rangle}{E^{(+)} - \varepsilon_k - \varepsilon_n}. \end{aligned} \quad (5)$$

Here $|\mathbf{k}\rangle$ are Coulomb waves describing the incident electron. The potential V_S describes Coulomb interactions of the incident electron with the H_2^+ ion for a given spin channel S (singlet $S = 0$ and triplet $S = 1$). The Lippmann-Schwinger equations (5) are solved by performing a partial-wave expansion of the incident electron Coulomb waves $|\mathbf{k}\rangle$ to obtain T -matrix elements per partial wave of total angular momentum projection M , parity Π , and spin S . The body-frame T -matrix

elements are used to obtain body-frame scattering amplitudes $F_{fi}^{(B)}$, which are then averaged over all orientations using standard procedures [27] to obtain integrated cross sections σ_{fi} for electronic transitions.

We have performed 289-state CCC calculations over the energy range from 10 to 1000 eV for several values of R . Calculations were performed with projectile partial waves up to a total angular momentum $L_{\max} = 8$ and its projection $M = 8$, for singlet and triplet spin S and odd and even parity Π . We have used an orientation-averaged analytic Born subtraction method to speed up convergence of the partial-wave expansion [27].

The single-center formulation requires large expansions to obtain accurate ground-state $1s\sigma_g$ and $2p\sigma_u$ energies at large values of R ; other states are hydrogenic and are sufficiently accurate in the current formalism. Due to this, we chose to use the accurate Born-Oppenheimer potential curve $\varepsilon_1(R)$ provided to us by Wolniewicz and Poll [28,29] in the calculation of the electronic ground-state nuclear wave functions $\Phi_{1\nu J}^{(\text{nuc})}(\mathbf{R})$. We form the Born-Oppenheimer Hamiltonian

$$H_1^{(\text{BO})} = -\frac{1}{2M_1} \nabla_1^2 - \frac{1}{2M_2} \nabla_2^2 + \varepsilon_1(R) \quad (6)$$

of the molecule and calculate the nuclear wave functions via diagonalization of each nuclear state symmetry of rotation J . Here $M_i = 1836.152$ is the mass for a proton. For the current study we assume a nonrotating molecule, taking $J = 0$ and dropping the dependence on J . The vibrational states calculated were checked against the energies and FC factors of [15].

Following from Lane [30], we write electronic and vibrationally resolved cross sections for the transition $i v_i \rightarrow f v_f$ as

$$\sigma_{f v_f, i v_i} = 4\pi^3 \frac{k_f}{k_i} \sum_{\substack{L_f, L_i \\ M_f, M_i}} |\langle \Phi_{f v_f}^{(\text{nuc})} | T_{L_f, L_i}^{(fi)} | \Phi_{i v_i}^{(\text{nuc})} \rangle|^2. \quad (7)$$

Due to the completeness of the vibrational basis, we utilize the closure property to sum over all final vibrational state transitions to obtain

$$\sigma_{f, i v_i} = \sum_{v_f} \sigma_{f v_f, i v_i} = \int dR |\Phi_{i v_i}^{(\text{nuc})}(R)|^2 \sigma_{fi}(R), \quad (8)$$

where $\sigma_{f, i v_i}$ are cross sections resolved for an initial electronic, vibrational state transition to a final electronic state. Expression (8) averages the cross sections over the initial vibrational wave function of the molecule but does not retain energy conservation between vibrational state transitions. This has been shown to be accurate outside the low-energy region for H_2^+ [20]. To compare with experiment we weight cross sections of the bound H_2^+ vibrational levels via

$$\tilde{\sigma}_{f, i} = \sum_{v=0}^{17} p_v \sigma_{f, i v} / \left(\sum_{v=0}^{17} p_v \right), \quad (9)$$

where p_v are the FC factors or BD distribution weights. We averaged cross sections over all the bound H_2^+ vibrational states (up to $v = 17$ in the Born-Oppenheimer approximation [15]).

III. RESULTS

Scattering calculations were conducted over a R grid of 15 points within the interval $1.15 \leq R \leq 5.5$. Resulting $\sigma_{\text{PP}}(R)$ and $\sigma_{\text{DI}}(R)$ cross sections were found to be smooth functions with respect to the internuclear distance R . These cross sections were interpolated and extrapolated over the grid $1.0 \leq R \leq 12.0$ (extent of the $v = 17$ state). Extrapolation of cross sections outside the region $1.15 \leq R \leq 5.5$ introduces uncertainty in the vibrationally weighted cross sections. We have investigated the stability of the final results with respect to different extrapolation techniques and estimate that the weighted cross sections have a maximum error of 5%.

In Fig. 1 we present our results for FC and BD vibrationally weighted calculations for PP cross sections, compared with our fixed-nuclear $R = 2.0$ results, calculations of Peek [18] and measurements of El Ghazaly *et al.* [10], Dunn *et al.* [11,12], and Dance *et al.* [13]. We also present DE cross sections for HD^+ in the vibrational ground state and compare with the DE measurements of Andersen *et al.* [16]. In the latter case we find good agreement with experiment for energies above the $2p\sigma_u$ excitation threshold. Considering that the current formulation neglects indirect (resonant) channels, this agreement indicates the dominance of the direct processes. The fixed-nuclear PP cross sections have little difference from the $\text{HD}^+(v=0)$ results in the intermediate- and high-energy regions; only near threshold is a difference evident. Comparing the fixed-nuclear and vibrationally weighted results, we note the importance of accounting for the vibrational distribution, which has a 225% larger cross section at lower energies. In the low- (10–20 eV) and intermediate-energy regions (20–100 eV) the vibrationally weighted CCC results clearly favor the most recent experimental data of El Ghazaly *et al.* [10]. The large

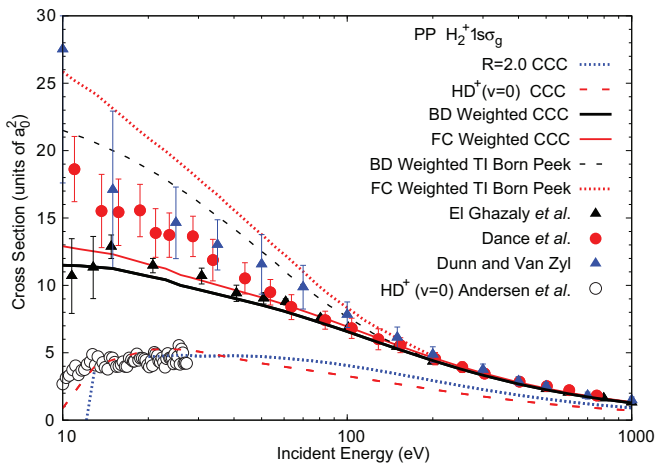


FIG. 1. (Color online) Franck-Condon (FC) and von Busch–Dunn (BD) [14] weighted proton-production (PP) cross sections for electron scattering from the electronic ground, vibrationally excited states of H_2^+ . The present calculations are compared with experiments of El Ghazaly *et al.* [10], Dunn *et al.* [11,12], and Dance *et al.* [13]; fixed-nuclei ($R = 2.0$) results obtained in the present method; and total inelastic (TI) Born calculations of Peek [18]. Calculations of dissociative excitation cross sections for HD^+ in the vibrational ground state are compared with the experiment of Andersen *et al.* [16].

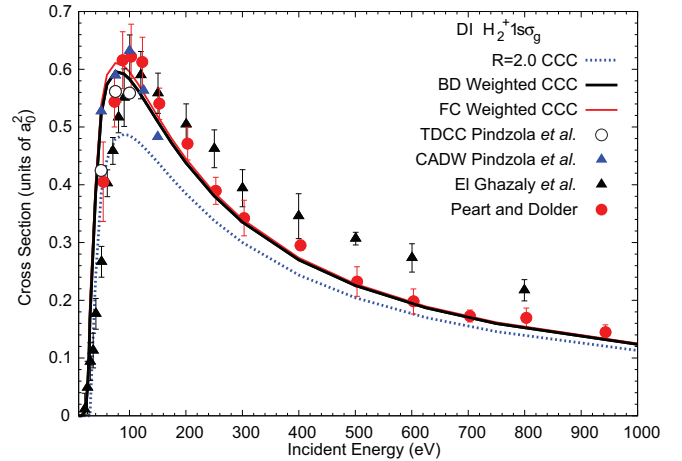


FIG. 2. (Color online) Franck-Condon and von Busch–Dunn [14] weighted dissociative ionization (DI) cross sections for electron scattering from the electronic ground, vibrationally excited states of H_2^+ . The present calculations are compared with measurements of Peart and Dolder [9] and El Ghazaly *et al.* [10] and fixed-nuclei ($R = 2.0$) results obtained in the present method, the configuration-average distorted-wave (CADW) method [23], and the time-dependent close-coupling (TDCC) method [22].

variation in experimental data in the low-energy region could be due to the production of different vibrational populations in the presented experiments. Our vibrationally weighted results are in good agreement with all experiments in the high-energy region (100–1000 eV). We also agree with the vibrationally weighted Born total inelastic cross sections $\sigma_{\text{TI}} = \sigma_{\text{DE}} + \sigma_{\text{DI}}$ of Peek [18] in the high-energy region, which gives us confidence in our results. Like Peek [17] we have found that the PP cross sections can differ as much as two orders of magnitude when scattering from the individual $v = 0$ and 17 states. The difference in results using the BD and FC distributions is only evident for the lowest presented energies, where vibrational dependence is extremely important (in particular the account of high-lying vibrational levels).

Results for DI cross sections are presented in Fig. 2. We compare the CCC FC and BD weighted results with the CCC fixed-nuclei $R = 2.0$ results, the fixed-nuclei $R = 2.0$ TDCC [22] and CADW [23] results, and the measurements of Peart and Dolder [9] and El Ghazaly *et al.* [10]. The CCC fixed-nuclei DI cross sections are lower than the corresponding fixed-nuclei TDCC results [22]; at the peak of the cross section (95 eV) the difference is about 15%. The CADW results [23] are even higher at the cross-section peak; this is expected low-energy behavior for a first-order method. We find that CCC fixed-nuclei results are lower than the vibrationally weighted results by about 25% at the peak of the cross section and about 10% at larger energies. The dependence on the initial vibrational level distribution (FC or BD) is minor and only visible at the cross-section peak. Although not shown, the vibrationally weighted CCC results are in good agreement with the first-order Bethe weighted reflection method of Liu [19] at energies above 1 keV. Vibrationally weighted FC and BD results are in excellent agreement with the experiment of Peart and Dolder [9] across the entire energy range. Vibrationally weighted CCC results do not agree with the measurements of

El Ghazaly *et al.* [10], in particular at high energies. El Ghazaly *et al.* [10] differentiated protons from DI and DE processes by analyzing the kinetic energy release spectrum of the ions. In their analysis they assumed that the DI cross section are not dependent upon R , i.e., constant $\sigma_{DI}(R)$. This allowed the DI measurements to be extracted from the tail of the kinetic energy release spectrum. El Ghazaly *et al.* [10] expected that such a procedure would produce inaccurate results only for lower energies, however, we see that the disagreement between CCC results persists to high energies. The agreement between the CCC results and the experiment of Peart and Dolder [9] is most encouraging considering the fact that they differentiated the DI cross section from the DE cross section by measuring protons arriving at detectors in coincidence.

IV. CONCLUSION

In conclusion, we have solved the Lipmann-Schwinger equation for electron scattering from the molecular hydrogen ion in the fixed-nuclei approximation using the CCC method. Utilizing the closure property, we averaged cross sections over the initial vibrational wave functions of H_2^+ and weighted according to the FC and BD distributions. The results here indicate the critical dependence of accounting for the initial

vibration population for both PP and DI cross sections. We find excellent agreement with available experimental PP and DI cross sections.

Although we have shown excellent agreement with experiment, this method is by no means complete. A spheroidal or multicenter expansion will be required to eliminate the inaccuracies of our structure at large values of R . In the near future we plan to extend the CCC method to heavier diatomic molecules that can be described by one or two electrons above an inert core, for example, Li_2 . A general scattering code for polyatomic molecules will also be formulated in a single-center approach and applied to molecules such as H_3^+ , CH_4 , and H_2O , where a single-center expansion has proved to be sufficiently accurate [31–33].

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