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LETTER TO THE EDITOR

DISSOCIATIVE IONIZATION OF H_2 AND D_2 BY ELECTRON IMPACT NEAR THRESHOLD

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We have studied the dissociative ionization of H_2 and D_2 by electron impact. It is found that in the vicinity of the $^2\Sigma_g^+$ dissociation threshold of H_2^+ (18.08 eV) a significant fraction of the produced protons originates from the process $e + H_2 \rightarrow H^- + H^+ + e$ (threshold at 17.34 eV). Similar results are found for D_2.

1. Introduction

Dissociative ionization of simple diatomic molecules (in particular H_2) by electron impact has been studied by many investigators. Dunn and Kieffer [1], Kieffer and Dunn [2] and Van Brunt and Kieffer [3] measured the energy distribution of protons originating from dissociative ionization of H_2 for electron impact energies larger than 29 eV. In these experiments the dissociation most probably takes place via the repulsive $^2\Sigma_u^+$ state of H_2^+. Crowe and McConkey [4] performed similar measurements at a lower energy of about 25 eV. At this energy the $^2\Sigma_u^+$ state of H_2^+ is not accessible within the Franck–Condon region. They also measured the cross section for production of protons, originating from dissociative ionization via the $^2\Sigma_g^+$ state of H_2^+ in the energy region starting from the $^2\Sigma_g^+$ dissociation threshold (18.08 eV) to a few eV above. Köllmann [5] studied the dissociative ionization of H_2 for impact energies above 17 eV. He measured the proton production efficiency curves at different proton energies and emission angles.

In this paper we present measurements on the dissociative ionization of H_2 and D_2 at energies just below and above the $^2\Sigma_g^+$-state dissociation limit at 18.08 eV (H_2) and 18.16 eV (D_2), respectively. Additional evidence is found that dissociation of H_2 and D_2 via an intermediate state into a positive and a negative ion gives an important contribution to the number of produced ions in the energy region just above and below the $^2\Sigma_g^+$-state dissociation limit.

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2. Experimental set-up

The experimental set-up has been described extensively before by Boesten [6]; we will only give a short outline here. The gas under investigation, for instance molecular hydrogen, is introduced into the collision chamber via a narrow tube. A stationary pressure is maintained by continuously pumping. Under working conditions the gas pressure can be varied from 10^{-6} to 10^{-5} mbar. An electron beam (10^{-7} to 10^{-6} A) is directed through the collision chamber. The ions formed are extracted from the collision region, accelerated, analyzed in a quadrupole mass spectrometer and detected with a multiplier. The current pulses at the anode of the multiplier are amplified, discriminated and finally stored in a PDP 11-05 computer. The half width of the energy distribution in the electron beam is about 0.28 eV. In the analysis of our experiment we use the E.D.D. unfolding technique (Winters et al. [7], Vriens et al. [8]) in order to diminish the effective electron energy spread. The remaining energy spread in the corrected dissociation curves may be estimated to be about 0.12 eV.

3. Results

3.1. Hydrogen

The measured data obtained for dissociative ionization of H_2 by electron impact are presented in fig. 1. Due to the finite resolution of the quadrupole mass spectrometer not only the produced H^+-ions are detected but also a background of H_2^+-ions. In fig. 1 the signal between 15.5 and 17 eV is solely due to this background. Both the raw and the unfolded data are given in the figure. The E.E.D.-method has been used twice (Vriens et al. [8]); the energy scale has been calibrated with help of the background H_2^+-signal. The intersection of the linear part of the ionization curve with the energy axis was shifted to 15.54 eV (Rapp and Englander-Golden [9]).

At 17.35 eV we find a sudden increase in the number of detected H^+-ions, which exceeds the linear rise of the H_2^+-background. The observed onset at 17.35 eV suggests that the increase is due to the process $e + H_2 \rightarrow H^+ + H^-(1s^2) + e$. The energy needed to produce $H^+ + H^-$ is 17.34 eV, the difference between the dissociative ionization energy (18.08 eV) of H_2 and the formation energy (0.74 eV) of $H^-(1s^2)$. Further support for this is provided by the photoionization results of Chupka et al. [10]. They observed a strong H^- peak at 714.20 Å ($\simeq$ 17.36 eV) in the efficiency curve for photo-dissociation of H_2 into $H^+ + H^-$. The increase in H^+ ions above 17 eV has also been observed by Köllmann [5], who measured the production of H^+ due to dissociative ionization of H_2 by electron impact. However, from his measurements an accurate determination of the onset cannot be made as his curve exhibits a gradual increase in signal between 17 and 18 eV.

Because of the inefficiency of the momentum transfer from the incident electron to the nuclei one would not expect the dissociative ionization $e + H_2 \rightarrow H^+ + H^- + e$ to proceed in a direct way. Therefore, as suggested before by Crowe and McConkey [4], it is more probable that the temporary formation of an intermediate H_2^- state precedes the dissociation process. These suggestions are supported by the results of Schowengerdt and Golden [11] and Sanche and Schulz [12]. They found evidence for H_2^- states with energies ranging up to 16.90 eV.

An alternative suggestion is offered by Hazi [13],

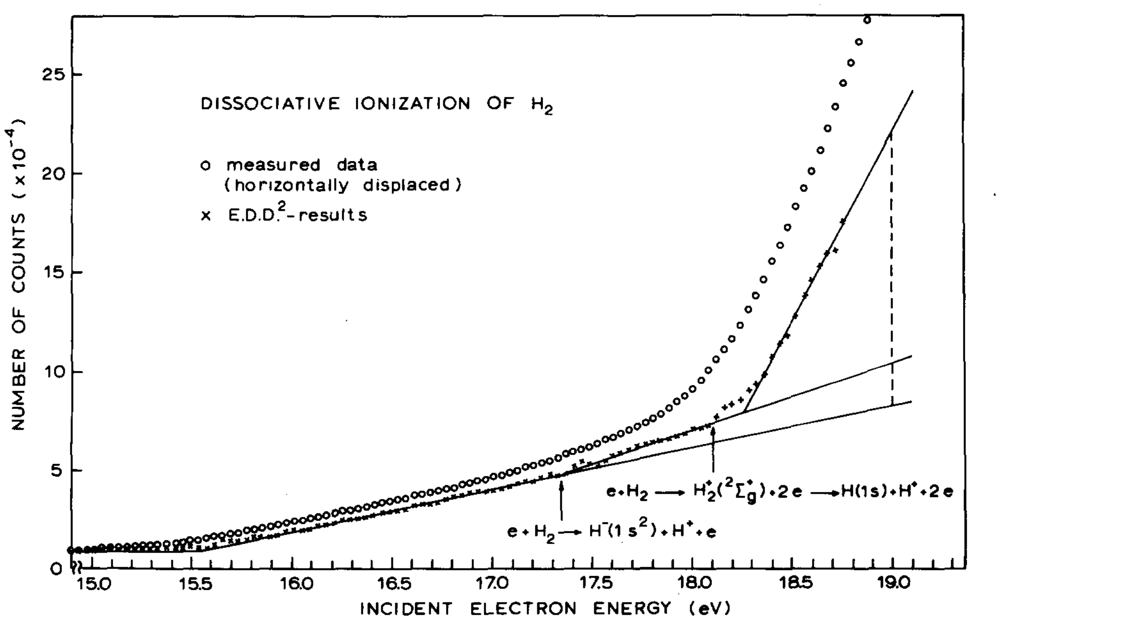

Fig. 1. Dissociative ionization of H_2 by electron impact. The linear rise between 15.5 and 17.3 eV is due to the background of H_2^+ ions (see text). The arrows indicate the thresholds of two different dissociation processes.

who states that in the energy range concerned a doubly excited state of H_2 ($^1\Sigma_g(2p\sigma_u^2)$) exists, which preferentially dissociates into $H^+ + H^-$. It is possible that this state is responsible for the strong H^--peak at 714.20 Å in the photo-ionization spectrum of Chupka et al. [10]. In our experiment both negative ions and doubly excited states can be formed and we are unable to distinguish between the two possible indirect mechanisms.

If the production of H^+ ions in the energy region just above 17.4 eV indeed proceeds via the above mechanisms, then there must be an accompanying increase in the formation of H^- above that energy. Schulz [14] measured the cross section for H^- formation in e + H_2 collisions. A slight change in slope may be present near 17.5 eV, which is close to the observed value in our experiment. The measured increase above 17.35 eV in our experiment is nearly linear until a second onset at about 18.10 eV. Here we find a sharp increase of the number of detected H^+-ions. These H^+-ions are caused by the dissociation of the $^2\Sigma_g^+$-state of H_2^+ into H(1s) and H^+. The non-linear behaviour just above 18.10 eV in the E.D.D.-curve cannot be fully explained by the effective energy spread of the electron beam. It may at least partly be caused by resonances or by electron correlation effects similar to those that give rise to specific threshold laws for electron impact ionization of atoms (Wannier [15], Fano [16]).

To test the reproducibility we repeated the experiment after a period of several months under somewhat different experimental circumstances. The results, in particular the onsets at 17.35 eV and 18.10 eV, appeared to be the same. In the latter experiments the measurements were extended to larger impact energies. From 18.4 up to 20 eV a linear behaviour was found, in agreement with the results of Köllmann. The different circumstances, however, lead to larger energy spread in the incident electron beam, so the unfolded results showed more spread. We may conclude from our measurements that dissociative ionization of H_2 via an intermediate state leading to formation of H^+ and H^- gives a significant contribution to the proton production in the energy region around 18 eV.

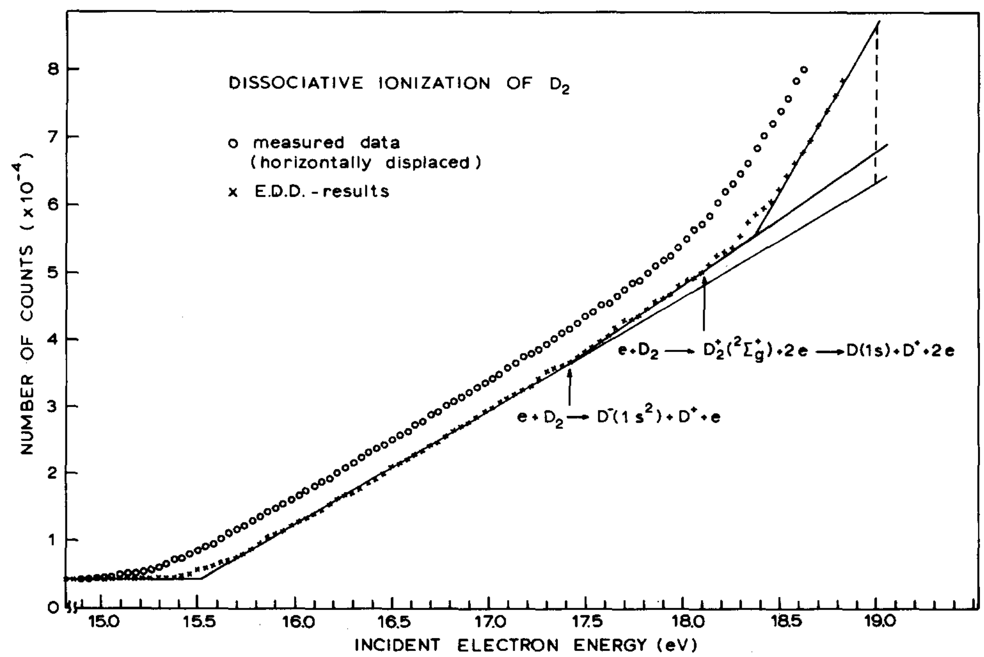

Fig. 2. The same as fig. 1, but for D_2.

3.2. Deuterium

We have also studied the dissociative ionization of D_2 by electron impact. The measured data are given in fig. 2. The background signal in this case is much larger than in the corresponding H^+ measurement (fig. 1). This is due to ionization of the background H_2 molecules (background pressure $\simeq 10^{-9}$ mbar), which have the same mass as the D^+-ions. Due to the rather poor signal to background ratio it was not meaningful to apply the E.D.D. method twice to the measured curve. The remaining energy spread in the corrected experimental results is about 0.2 eV. The energy scale of the corrected curve has been calibrated using the ionization results of Rapp and Englander–Golden [9]. The linear part of their D_2-ionization curve intersects the energy axis at 15.51 eV. Again we find, although less pronounced than in the H^+-case an increase in the D^+ production starting at about 17.45 eV. This increase is most probably due to the process $e + D_2 \rightarrow D_2^-$ (or D_2^{**}) $\rightarrow D^+ + D^- + e$. For D_2 the electron energy needed to produce $D^+ + D^-$ is equal to 17.43 eV, the difference between the dissociative ionization energy (18.16 eV) of D_2 and the formation energy (0.73 eV) of D^-.

The only recent data on D^+ production in $e - D_2$ collisions are those obtained by Stockdale et al. [17]. However, due to the poor signal to noise ratio, a comparison between their and our results in the energy region between 17.5 and 18 eV is not meaningful. Again the observed onset at 17.45 eV is consistent with photodissociation results of Chupka et al. [10], who find a strong D^--peak at 709.99 Å ($\simeq$ 17.46 eV). As expected, a second increase of the number of detected D^+-ions, due to dissociation via the $^2\Sigma_g^+$-state, is observed at about 18.20 eV. Similarly, as in the case of H_2, this increase becomes linear after a few tenths of an eV.

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