IONIZATION OF THE HYDROGEN MOLECULE BY ELECTRON IMPACT NEAR THRESHOLD

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In this Letter, new data are presented on the ionization of the hydrogen molecule by electron impact near threshold. It is found that within the limitations of a finite energy spread, the cross section is essentially a linear function of the electron energy excess above threshold. These results indicate that a direct-ionization model does not correctly predict the threshold law, and that some other model such as autoionization or intermediate negative-ion formation may possibly provide a better description of the ionization process.

In order to properly measure an ionization cross section as a function of electron energy, the number of ions formed in a fixed path length per electron must be determined, and the ion collection efficiency must be independent of electron energy. The method of Bleakney[1] and Tate and Smith[2] provides just such an arrangement. We have studied ionization of H_2 near threshold in a Tate-Smith apparatus[2,3] using (a) the full energy spread from an indirectly heated cathode, (b) the reduced energy spread obtained by removing the slow electrons in the distribution, and (c) the greatly reduced spread obtained with an ac-modulated, double phase-sensitive detection variation of the R.P.D. method.[4] The cross sections obtained in each case are essentially identical. The cross section obtained by method (c) is shown in Fig. 1 along with the measured electron energy distribution. An ion collection field sufficient to collect all ions formed in a given path length was used in these experiments. The absolute energy scale was obtained by each of three methods which agree within ±0.05 eV. In one method the electrons were retarded in the ionization region and the absolute potential difference with respect to the cathode obtained. In another, the observed H^- cross-section peak was chosen as the standard at 14.0 eV.[5] Finally a "total-collection mass-spectrometer" variation[6] of the Bleakney, Tate, and Smith method has been used with helium as calibrating gas (appearance potential of He^+ taken as 24.56 eV). It was shown by energy analysis of the electrons that the energy scale was linear over the region of interest. Within the limitations of the finite electron-energy spread the cross section for formation of H_2^+ is essentially a straight line with onset 15.4 eV.[7]

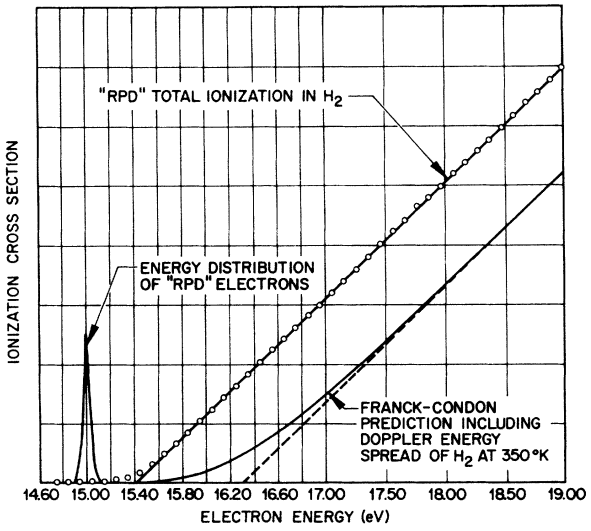

FIG. 1. Experimental and theoretical electron-impact ionization cross sections in H_2. The circles are experimental values obtained with electrons characterized by an energy distribution possessing a full width at half-height of ~0.06 eV. The solid line is a composite Franck-Condon ionization cross section, assuming linear threshold behavior for each vibrational state of H_2^+, whose relative contribution is given by vibrational overlap integrals, the whole being broadened by an assumed 350°K Doppler effect from the H_2. The dashed curve is the extrapolated straight line tangent to the Franck-Condon ionization cross section assuming a linear threshold law. Although a slight amount of structure is observed in the experimental curve, a "best straight line" has been drawn to determine the linearly extrapolated appearance potential.

If only direct ionization of H_2 of H_2^+ is considered (the possibility of autoionization being neglected), the Franck-Condon principle leads to the prediction that the probability of formation of H_2^+ in any vibrational level v is proportional to the square of the overlap integral between the wave function of the initial state of H_2 and the vth vibrational wave function of H_2^+. If one assumes in addition that the probability of formation of each vibrational state of H_2^+ is proportional to the electron-energy excess above its threshold, one obtains a predicted total ionization cross section consisting of a

series of straight-line segments.[8] Inclusion of the Doppler spread due to the vector addition of the thermal velocity of the H_2 molecules produces curvature at the corners in the theoretical ionization cross section for monoenergetic electrons as shown in Fig. 1. According to this model, the population of vibrational states of H_2^+ at moderately high electron energies (>30 eV) should be independent of electron energy and proportional to the squares of the overlap integrals. The linearly extrapolated onset for H_2^+ is 16.3 eV according to this model. It is evident that the model fails to predict the observed cross section for H_2^+ formation near threshold. The distribution of vibrational states in H_2^+ is very important to a number of related experiments.[9-14] The failure of the direct-ionization model to predict the correct threshold law for H_2^+ implies that the distribution of vibrational states in H_2^+ cannot be predicted by simple Franck-Condon overlap considerations.[15]

Our results are quite similar to those reported previously by Stevenson[16] and Bleakney.[1] They are in poor agreement with the work done with electrostatic energy selectors.[17-19] Because of the 100% collection-efficiency feature of the total ionization tube, we believe the correct threshold-ionization law has been measured in the present work.

The main conclusion to be drawn is that near threshold, ionization of H_2 occurs primarily through nondirect processes, and the distribution of vibrational states of H_2^+ is very uncertain at this time.

Note added in proof.—Recently, other work has been reported which leads to the same conclusion, namely that autoionization appears to dominate the direct "Franck-Condon" process in the ionization of H_2 near threshold. Measurements of the photoionization efficiency in H_2 by Dibeler, Reese, and Kraus[20] show considerable autoionization at threshold. However, our results may also include contributions from autoionizing states which can not be populated by photon impact. Thus, a one-to-one correspondence between photon- and electron-impact results is not to be expected in general, especially if several triplet states of H_2 can autoionize. The recent results of Dunn[14] on photodissociation of H_2^+ are also relevant here. The poor agreement between experiment and theory may be due to the assumption that the vibrational population of H_2^+ is that given by the "Franck-Condon" model.

The present results also indicate that it will not be possible to achieve the population inversion among vibrational states of HD^+ which, it has been proposed,[22] will be adequate to support infrared maser action. The failure to observe such maser action[22] may also be interpreted as evidence that the vibrational population in HD^+ is non-"Franck-Condon."

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[6]This method consists of increasing the magnetic field to collect only the heavy ion, the lighter ions drifting out the side of the ionization region. One can therefore collect either He^+ or $(H_2^+ + He^+)$ with 100% collection efficiency. Further work on this method for absolute mass-analyzed ionization cross sections will be reported at a later date.

[7]Recently, W. H. Hamill and C. E. Melton [J. Chem. Phys. 41, 546 (1964)] have found similar results. Recent work in our laboratory with an ion source and quadrupole mass spectrometer using He-H_2 mixtures have led again to 15.4 eV as the linearly extrapolated appearance potential of H_2^+.

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[15]Note added in proof: Recently, a related inadequacy of a direct ionization model in O_2 has been reported [J. W. McGowan, E. M. Clarke, H. P. Hanson, and R. F. Stebbings, Phys. Rev. Letters 13, 620 (1964)].
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CHARGE-STATE CORRELATIONS IN Ar^+-Ar COLLISIONS

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Single collisions of Ar^+ on Ar, at 25 to 150 keV, have been studied using a coincidence scattering apparatus. For the reaction

$$Ar^+ + Ar \rightarrow Ar^{m+} + Ar^{n+} + (m+n-1)e, \qquad (1)$$

the charge states m and n of both particles from the same large-angle collision are determined. The experiment finds the probabilities of seeing m and n in coincidence. In addition, simultaneous measurements of the two scattering angles θ and φ determine the inelastic energy loss Q_{mn} for the (m,n) reaction.

The first such coincidence measurements were reported recently by Afrosimov, Gordeev, Panov, and Fedorenko,[1] who studied the above reaction at 12.5 and 50 keV. Our apparatus and procedure, while different from theirs, are functionally similar, and our 50-keV data for Q_{mn} agree with theirs. However, our correlation measurements suggest a new interpretation for the phenomena.

We find no correlation between m and n. Figure 1 shows a typical case, using 50-keV, $\theta = 15°$ data. Each curve is for a specified charge state m of the scattered incident particle and shows the percentage distributions P_n for the recoil particle. Within the scatter of the data, these distributions are the same. A similar diagram results when the roles of m and n are interchanged, again showing that the distribution among the charge states of one particle is independent of the charge state of the other particle. Other data sets at 25, 100, and 150 keV confirm this lack of correlation. This result, at first sight, appears to disagree with the previous work,[1] which plots the relative

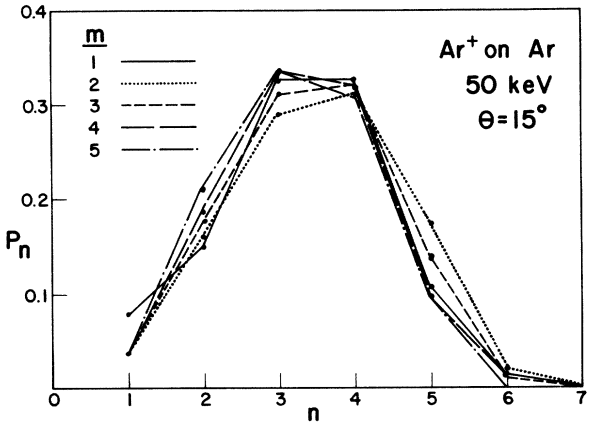

FIG. 1. Charge-state correlation diagram for Ar^+-on-Ar collisions at 50 keV, $\theta = 15°$.

number of particles for constant $m+n-1$ vs $m-n$ and obtains curves of universal shape, suggesting a form of correlation. However, detailed examination would show that their result comes about because the distributions P_m and P_n, although uncorrelated, are the same for either particle.

This absence of correlation is consistent with the Russek[2] statistical theory of multiple ionization. He assumes that the inelastic energy transferred to each atom is statistically distributed among the outer electrons in an autoionizing transition. In his model each atom gets half the inelastic energy, and the transitions occur after the atoms have separated, hence no correlation.

Inelastic energy-loss data will illustrate both the previous[1] and the present interpretation. In Fig. 2, Q_{mn} is plotted versus $\sum U_i(m,n)$,