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Dissociative ionization of H_2 and D_2 produced by bombardment with fast He^+ ions

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H^+ and D^+ energy spectra have been obtained using the time-energy spectroscopy technique. Spectra are presented for He^+ bombarding energies of 0.5, 1, 2, 3, and 4 MeV. The reflection approximation is used to analyze the spectra and determine the relative contribution to the H^+ and D^+ yields of the $1s\sigma_g$, $2p\sigma_u$, $2p\pi_u$, $2s\sigma_g$, and double-ionization potential curves of the target molecules. Yield observed in the 2- to 4-eV range suggests that states of H_2 and D_2 which autoionize to the dissociative continuum of the ground $1s\sigma_g$ state of H_2^+ and D_2^+ contribute to the spectra. The yield is dominated by the excitation of the $2p\sigma_u$, $2p\pi_u$, and double-ionization potential curves.

INTRODUCTION

Several investigators have studied the dissociative ionization of H_2 by electrons. Dunn and Kieffer[1] used the reflection approximation to predict the H^+ kinetic energy spectrum from the $2p\sigma_u$ dissociative state of H_2^+ but found poor agreement with their experimental results. In a later report[2] they suggested that the discrepancies may be due in part to the presence of autoionizing states of H_2 contributing to the production of H^+ ions. However, they found no evidence of autoionizing potential curves lying in the region between the $1s\sigma_g$ and the $2p\sigma_u$ curves of H_2^+. These results were verified by Van Brunt and Kieffer[3] and, for the case of D_2, by Stockdale *et al.*[4] The predictions of Dunn and Kieffer did not include the $2p\pi_u$ and the $2s\sigma_g$ dissociative states or the H^+H^+ potential curve. These are expected to be only weakly excited by electron excitation.

Pronounced structure at 2 and 4 eV in the H^+ kinetic energy spectrum is reported by Crowe and McConkey.[5] Along with the new peaks, appearance potential measurements indicate potential curves existing in the region between the $1s\sigma_g$ and the $2p\sigma_u$ H_2^+ curves. These potential curves are believed to be autoionizing states of H_2 which are responsible for the 2- and 4-eV structure. Several autoionizing states have now been calculated by Bottcher and Docken,[6] Bottcher,[7] and Hazi[8] and a mechanism for decay of these states into the dissociative continuum of the ground $1s\sigma_g$ state of H_2^+ has been presented by Hazi.[9,10]

We report measurements of dissociative ionization of H_2 and D_2 by fast He^+ ion impact. The time-energy spectroscopy (TES) technique[11] is used to measure the kinetic energy spectra of the H^+ (D^+) fragments. It is necessary to use TES in order to separate the desired H^+ (D^+) fragments from H_2^+ (D_2^+) as well as N^+ and O^+ contaminants. The reflection approximation is used to predict the H^+ (D^+) intensities from six different potential curves which are in turn fitted to the experimental measurements by a least-squares fitting program. The potential curves of the $1s\sigma_g$, $2p\sigma_u$, $2p\pi_u$, $2s\sigma_g$ states, the doubly ionized state, and one autoionizing state were required to obtain good fits to the data. The position of the potential curve for this autoionizing state relative to the ground state H_2^+ curve has not been determined in this experiment. The energy of the autoionized electron must be measured to determine if the potential curve lies between the $1s\sigma_g$ and the $2p\sigma_u$ potentials.

EXPERIMENTAL PROCEDURE

H^+ (D^+) energy spectra were obtained by simultaneously measuring the kinetic energy and time of flight (TOF) of positive ions produced by the bombardment of H_2 and D_2 gas with a pulsed beam of He^+ ions. The experimental procedure and method of data reduction have been described in detail elsewhere,[11] and only a few points need to be discussed here.

A consequence of the measurement of energy and TOF is that the H^+ (D^+) ions can be separated from H_2^+ (D_2^+) ions or N^+ and O^+ ions which are present as impurities. The method therefore permits isolation of H^+ (D^+) ions and the determination of a kinetic energy distribution free of contaminants.

Pulses of He^+ ions from a Van de Graaff accelerator pass through a differentially pumped collision chamber containing the target gas. The fragments formed in the dissociative processes and ejected at 90° from the beam direction are focused onto the entrance slit of a parallel-plate electrostatic analyzer. A channeltron detector is positioned at the exit of the analyzer. The energy resolution of the analyzer is approximately 0.5%, and all fragments are preaccelerated to be ana-

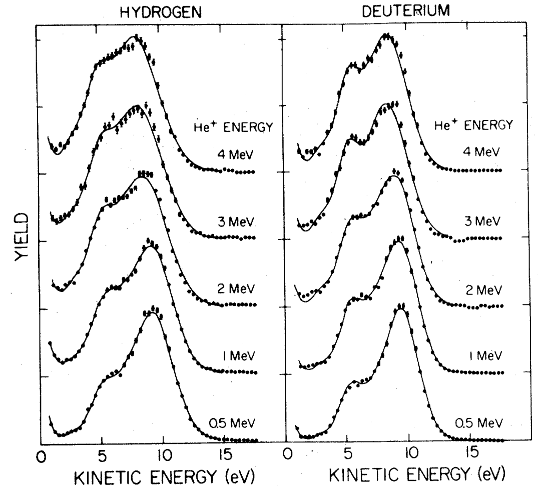

FIG. 1. H^+ and D^+ yield as function of kinetic energy for 0.5–4-MeV He^+ incident on H_2 and D_2. The spectra are normalized to the same height, and the error flags indicate purely statistical uncertainties. The solid curves are calculated fits to the data and are described in the text.

lyzed at 50 eV. Analyses at 40 and 60 eV yield the same energy spectra as is obtained at 50 eV. The target gas pressure is fixed at 1 mTorr. Measurements at 0.5 mTorr produce identical results.

RESULTS AND DISCUSSION

The kinetic-energy spectra obtained in this experiment are shown in Fig. 1. The H^+ yield is plotted with a variable ordinate so that all spectra have identical heights. The error bars indicate purely statistical uncertainties. The solid curves through the data points are calculated least-squares fits which are described in the following paragraphs.

The energy spectra have the appearance of being a superposition of several peaks including broad, possibly composite peaks at H^+ kinetic energies of 6 and 9 eV. Each of the peaks is due to the excitation of an H_2 molecule to an autoionizing state of H_2, a dissociative state of H_2^+, or doubly ionized H_2. Potential curves for the accessible states are shown in Fig. 2. The curves for H_2^+ and H_2 are taken from Bates *et al.*[12] and Sharp.[13] The H_2^{++} curve is a simple Coulomb potential of the form k/r.

The shape of the H^+ spectrum produced by excitation to one of the potential curves in Fig. 2 and subsequent dissociation can be computed by the reflection approximation.[1,14] The method predicts an energy distribution function $N(E)$ given by

$$N(E)=\overline{M}^2(x[E])S^2\chi^2(x[E]). \qquad (1)$$

In Eq. (1), $\overline{M}(x[E])$ is the electronic transition moment, S is a normalization factor for the repulsive state,[14] $\chi(x[E])$ is the normalized eigenfunction for the H_2 or D_2 ground state, and x is the displacement from the equilibrium separation of the ground-state molecule.

The relationship between E and x is established by the shape of the potential curve to which excitation takes place. The ground-state wave functions for H_2 and D_2 were represented by

$$\chi(x)=(\alpha/\pi)^{1/4}e^{-\alpha x^2/2}. \qquad (2)$$

Parameters given by Stoicheff[15] were used to calculate the value of α for the H_2 ground state. Parameters given by Herzberg[16] were used to calculate the value of α for D_2. The values were 63.52 and 91.05 $Å^{-2}$ for H_2 and D_2, respectively. The value of the equilibrium separation is 0.741 Å.[15]

The factor $\overline{M}$ is assumed to be constant in the calculation. The factor S is a slowly varying function of energy. Let the value of S at the kinetic energy E_0 corresponding to a value of $x=0$ in Eqs. (1) and (2) be S_0. The relative value of S at energy E is then[14]

$$S=S_0\left(\frac{E-E_\infty}{E_0-E_\infty}\right)^{1/4}, \qquad (3)$$

where E_∞ is the kinetic energy of the positive ion when infinitely separated from the other atom of the parent molecule. Since the analysis of this work concerns only spectral shapes and not absolute cross sections, the value of S_0 was taken

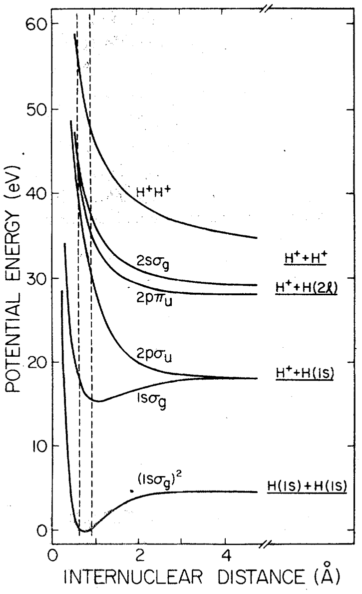

FIG. 2. Potential curves for selected states of H_2, H_2^+, and H_2^{++}.

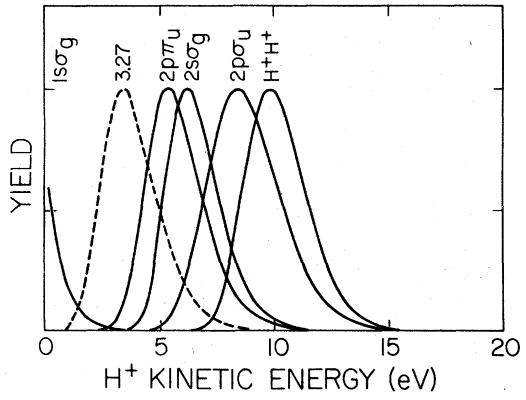

FIG. 3. Reflection approximation prediction of the shapes of the energy spectra produced by excitation and subsequent dissociation of the states shown in Fig. 2. The dashed curve is described in the text.

to be unity.

Equation (1) does not include the effect of the thermal motion of the parent molecules on the energy distributions of the dissociated atoms. Misakian and Zorn[17] followed the method of Chantry and Schulz[18] and found the energy distributions of H atoms produced by the $H_2 + e \rightarrow H(2s) + H + e$ process were broadened by thermal effects. The same method is followed in the present work where it is found that the full width at half maximum of a typical energy distribution predicted by Eq. (1) is increased by 4%.

The predicted H^+ energy distributions for the excitation to the potential curves in Fig. 2 and subsequent dissociation are shown in Fig. 3. All spectra have been normalized to the same height, and all spectra include thermal broadening effects. Only a portion of the $1s\sigma_g$ curve can contribute H^+ ions to the spectra, so that instead of a peak one observes an exponentially decreasing tail of low-energy H^+ ions.

Computer programs written by Bevington[19] were modified to perform a linear least-squares fit to the measured energy spectra. Initially the five solid curves in Fig. 3 were employed as the fitting functions and the contribution to the data of each of the functions was computed. The fits were not good in the 2–5-eV energy range. All observed spectra showed yield in excess of what could be accounted for by the five spectral shapes used. When plotted as a function of energy, the excess yield showed a peaked distribution similar in shape to one of the solid curves in Fig. 3. The energy of the peak was in all cases found to be very nearly 3.27 eV.

In order to make an estimate of the extent of the yield due to the 3.27-eV peak, two assumptions are made: (1) The yield is due to a single potential curve of an autoionizing state of H_2. (2) The H^+ (D^+) energy distributions from this state would have the same shape as that of the $2p\pi_u$ curve shown in Fig. 3.

The first assumption clearly represents a rather crude approximation since Crowe and McConkey[5] observe two prominent peaks in their data, one at 2 eV, and the other at 4 eV. In the present work it is likely that a superposition of these two distributions is being observed. The second assumption is an arbitrary selection. Figure 3 indicates that the shape of the energy distribution functions are quite similar despite the differences in the shapes of the corresponding potential curves.

Presumably, the 3.27-eV structure is due to one or more autoionizing states of H_2. Potential curves, possibly contributing to the yield, have been calculated by Bottcher and Docken,[6] Hazi,[8] and O'Malley.[20] Bottcher[7] calculated the shape of the H^+ spectra for the $H_2 + e \rightarrow H_2^{**} + e \rightarrow H_2^+ + e + e$ process as observed by Crowe and McConkey, but with only qualitative success. The reflection approximation is not expected to accurately predict the energy distribution which should depend on the shape of the H_2^{**} state as well as the dissociative state of H_2^+ to which autoionization takes place. In the absence of a reliable method for the accurate prediction of the H^+ energy distribution, the dashed curve in Fig. 3 was used in the analysis of this work.

Using all six of the energy distribution functions shown in Fig. 3, least-squares fits to the observed spectra were performed again. The resulting fits are shown as the solid curves in Fig. 1. Because the quality of the fits was good, excitation to potential curves lying higher in energy than the $2s\sigma_g$ curve was neglected. Support for this decision is found in the relative proportions of the contributions to the $2p\sigma_u$, $2p\pi_u$, and $2s\sigma_g$ curves as discussed below.

The fits to the data permit the calculation of the fraction of the total yield due to each of the six modes of dissociative ionization indicated in Fig. 3. The computed fractions for hydrogen are presented in Table I. The computed fractions for deuterium are presented in Table II. In both tables the entries are the fractions of the total yield of H^+ or D^+ with energies above 1.25 eV.

Estimates of uncertainties are included for the fractions computed for 1-MeV He^+ incident on H_2. The uncertainties were computed using three independent measurements of H^+ spectra made during the course of the experiment. The three fractions for a given excitation mode resulting from the three runs were averaged, and the uncertainty taken to be the maximum deviation from the mean.

TABLE I. Fractions of the total H$^+$ yield above 1.25 eV due to excitation of the states indicated in the first column.

State	He$^+$ bombarding energy (MeV) 0.5	1.0	2.0	3.0	4.0
$1s\sigma_g$	0.013	0.031± 0.016	0.023	0.022	0.022
3.27	0.057	0.071± 0.009	0.103	0.116	0.141
$2p\sigma_u$	0.413	0.343± 0.034	0.456	0.480	0.505
$2p\pi_u$	0.208	0.192± 0.025	0.265	0.265	0.287
$2s\sigma_g$	0.011	0.075± 0.023	0.026	0.045	0.021
H$^+$H$^+$	0.283	0.275± 0.062	0.112	0.060	0.018

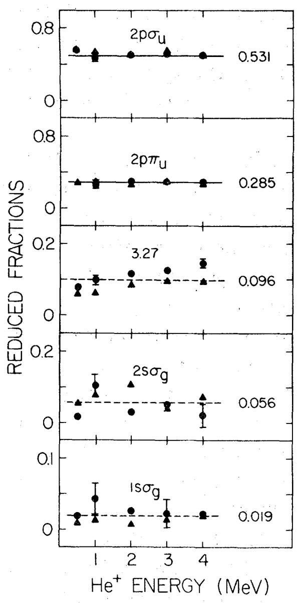

FIG. 4. Plots of the fraction of the reduced yield due to excitation and dissociation of the states shown in Fig. 2. The reduced yield is the total yield minus the yield calculated to be due to double ionization. All fractions were obtained by fitting the data of Fig. 1 with the spectral shapes of Fig. 3. The solid and dashed lines are simple averages which are described in the text.

Statistical uncertainties in the fractions calculated by the fitting programs were smaller than the estimates contained in the table by a factor of approximately 3. The most likely cause of error is an energy shift in the measured kinetic energy spectra. A shift of approximately 0.15 eV (0.5 channel in Fig. 1) produces changes in the deduced fractions comparable to the uncertainties listed in Table I. During the course of the experiment the energy scale was recalibrated several times. The changes observed corresponded to shifts of less than 0.07 eV for a channel at approximately 10-eV H$^+$ energy.

Examination of the tables shows that by far the most marked variation as a function of energy is observed for excitation to the double ionization states of H_2 and D_2. It is this factor that accounts for the major part of the bombarding energy dependence of the shape of the spectra shown in Fig. 1. The basic spectral shape is that of a superposition of two broad peaks. The contribution of the peak at higher energy decreases relative to the contribution of the peak at lower energy as the He$^+$ bombarding energy increases. This is consistent with the observed rapid decrease in the relative contribution of the double ionization process to positive ion production. (See Tables I and II).

To examine the bombarding energy dependence of the spectral shape in more detail, the yield due to double ionization determined by the fitting procedure discussed above was subtracted from the raw data. The fractions of the remaining yield due to each of the curves of Fig. 3 other than the double ionization curve were then computed. These are called reduced fractions and are shown in Fig. 4.

TABLE II. Fractions of the total D$^+$ yield above 1.25 eV due to excitation of the states indicated in the first column.

State	He$^+$ bombarding energy (MeV) 0.5	1.0	2.0	3.0	4.0
$1s\sigma_g$	0.005	0.009	0.004	0.013	0.018
3.27	0.038	0.044	0.067	0.087	0.086
$2p\sigma_u$	0.366	0.385	0.435	0.506	0.483
$2p\pi_u$	0.188	0.206	0.214	0.269	0.250
$2s\sigma_g$	0.035	0.055	0.073	0.036	0.065
D$^+$D$^+$	0.362	0.295	0.197	0.087	0.092

The errors shown for the 1-MeV He$^+$ on H_2 data were calculated using the uncertainties contained in Table I. The error bars for the other fractions are the same in absolute size as the bars at the 1-MeV point. The horizontal lines are simple averages of all of the reduced fractions of a single kind.

Figure 4 indicates that the relative uncertainty is smallest for the reduced fractions which are the largest. The reduced fractions for the $1s\sigma_g$ excitation mode are the least certain, in part because only a small portion of the $1s\sigma_g$ contribution to the H$^+$ spectrum falls above 1.25 eV. The lower limit for the energy distribution measured in this work is 1.25 eV and as a consequence the yield in only a few channels is all that serves to determine the $1s\sigma_g$ fraction.

The $2p\sigma_u$ and $2p\pi_u$ excitation modes dominate the yield and corresponding reduced fractions can be seen to be constant within the estimated uncertainties. Thus the contribution of the $2p\sigma_u$ relative to that of the $2p\pi_u$ state is independent of He^+ bombarding energy in the 0.5 to 4 MeV range.

The reduced fractions for the $2s\sigma_g$ state are consistent with a constant value, but relative uncertainties are large enough so that a definite statement that the reduced fraction is independent of He^+ energy is not possible.

The assumption of a single peak at 3.27 eV, with the shape determined as described earlier, leads to the conclusion that approximately 5–10% of the total H^+ yield is due to excitation of this mode of dissociation. Detailed conclusions concerning the H^+ yield in the neighborhood of 3.27 eV cannot be drawn on the basis of this work because of the simplifying assumptions that were made in order to perform the analysis. However, it can be seen in Fig. 4 that the reduced fractions for the production of the 3.27-eV peak are not constant within uncertainties, but show a trend of increasing with increasing bombarding energy. In addition, the reduced fractions for H_2 are consistently larger than the reduced fractions for D_2. The behavior of the 3.27-eV H^+ ions may reflect a difference in the mechanisms of excitation to a state of H_2^+ (D_2^+) and excitation to an autoionizing state of H_2 (D_2).

If the description of autoionization to the dissociative continuum of the ground $1s\sigma_g$ state of H_2^+ as proposed by Hazi[9,10] is applied, then it may be possible to see an isotope effect. Assuming the autoionizing state is dissociative with a lifetime which is independent of the internuclear separation, the internuclear separation of the H_2 molecule at autoionization will be larger than that of the corresponding D_2 molecule. Therefore, the H^+ ion produced by autoionization will have a higher energy than the D^+ ion. Using a classical picture of the molecular potential energy changing to kinetic energy, and using the ${}^1\Pi_u$ state of Hazi,[8] an autoionizing lifetime of 1.2×10^{-15} sec is required to produce an H^+ ion at 3.27 eV. With this lifetime the D_2 molecule would only separate far enough to produce D^+ ions of about 1.8 eV. This effect may explain the small excess of measured ions as compared to the fit as seen at the low energies in the D^+ spectra of Fig. 1. In order to detect an isotope effect exactly or to place the autoionizing potential curve between the $1s\sigma_g$ and $2p\sigma_u$ curves, it would be necessary to do a coincidence measurement with the autoionized electron and the H^+ (D^+) fragment.

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