Proton kinetic-energy distributions from dissociative photoionization of hydrogen*

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Measurement of proton kinetic-energy distributions from dissociative photoionization of H_2 is reported, for incident-photon energies up to 41 eV. Data are presented for transitions involving the $1s\sigma_g$ ground state and higher states of H_2^+. At a photon energy of 41 eV, direct ionization involving the $2p\sigma_u$ state accounts for approximately one-half of the dissociative ionization; other processes, autoionization or direct ionization involving states of higher energy than $2p\sigma_u$, account for the remainder.

INTRODUCTION

A number of studies of proton kinetic energy and angular distributions from dissociative ionization under electron impact have been reported in the literature.[1-11] Following Stevenson's observation[6] that the fast protons observed in the earlier data[1-5] did not agree with the predictions of the Franck-Condon distribution into the lowest energy repulsive curve of $H_2^+(2p\sigma_u)$, Dunn and Kieffer,[7] and later Kieffer and Dunn,[8] remeasured the proton energy distribution and compared the data with more accurate Franck-Condon calculations. Poor agreement was found, attributed to either the occurrence of autoionization from high-lying Rydberg states of neutral H_2 and/or the variation of the electronic transition moment across the transition range. Kieffer and Dunn's results were confirmed by Van Brunt and Kieffer.[9]

Crowe and McConkey[10] observed further structure in the proton energy distribution produced under electron impact attributed to autoionization, and also reported measurements of the abundances and angular distributions of protons from dissociative transitions involving the H_2^+ $1s\sigma_g$ ground state.

Very little data exist for dissociative photoionization of H_2. Browning and Fryar[12] have measured the H^+/H_2^+ ratio for photon induced dissociation through the H_2^+ $1s\sigma_g$ ground state, and Fryar and Browning[13] have reported the H^+/H_2^+ ratio for photon energies of 21.2 and 40.8 eV. Backx *et al.*,[14] using coincidence techniques with small angle scattering of 8-keV electrons, have recently measured oscillator strengths for ionization of H_2, including dissociative ionization, under conditions such that the data represent dipole transitions and can be compared to photoionization data. Samson[15] has reported a photoelectron spectrum of H_2 at an incident photon energy of 50.2 eV which shows transitions into the repulsive states of H_2^+. We wish to report here the measurement of kinetic-energy distributions of protons from dissociative photoionization of hydrogen. These results follow similar measurements in CO and N_2,[16] and O_2.[17]

EXPERIMENTAL

The experimental technique has been presented in detail elsewhere.[16] The ion energy spectra were recorded with a cylindrical mirror energy analyzer of measured transmission and whose response is independent of the angular distribution of the ejected ions.[16] The analyzer incorporates a lens such that spectra were recorded with constant resolution throughout the energy range (150-meV FWHM). The scanning voltage was obtained from a highly repeatable, linear, calibrated potentiometer driven by a stepping motor. No mass spectrometer was employed; the undissociated molecular ions appear in the spectra at low energy, following the Maxwell-Boltzmann distribution, and serve to calibrate the energy scale to within a few meV. The peak of the Maxwell-Boltzmann distribution for 300 K appears at an energy of 46 meV following convolution with a 150-meV Gaussian analyzer response.

Spectra were recorded using both dispersed and undispersed He and Ne discharges. The spectral content of the undispersed radiation was determined by recording photoelectron spectra of the rare gases. From the known analyzer transmission[18] and known photoionization cross sections,[19] the relative intensity of the various photon energies was determined; this information is discussed further below.

Franck-Condon distributions are included in the discussion of the spectra. All such results were obtained by numerically integrating the Schrödinger equation, using the hydrogen potential energy curves tabulated by Sharp,[20] and calculating the overlap of the radial continuum wavefunction at a given energy with that of the H_2^+ ${}^1\Sigma_g^+$ $(v=0)$ level. The Franck-Condon distribution represents an approximation used to calculate the distribution of proton energies in the center-of-mass (CM) frame.

The transformation to the laboratory frame produces appreciable broadening of each monoenergetic release in the CM frame.[21] All calculated distributions compared with the spectra have been transformed to the laboratory frame,[22] and further convoluted with the 150 meV response of the analyzer. This final convolution was more for aesthetic reasons than practical, as the effect was negligible following the transformation to the laboratory frame.

RESULTS AND DISCUSSION

A. $1s\sigma_g$ dissociation

The data of Browning and Fryar,[12] and Franck-Condon calculations,[23] show that approximately 2% of ionization events into the H_2^+ $1s\sigma_g$ ground state are dissociative. The resulting atomic ions peak in intensity at zero energy and extend to approximately 1 eV, thus covering the same energy range as the H_2^+ undissociated ions. However, if two photon energies are chosen, one on either side of the H_2^+ $1s\sigma_g$ dissociation energy of 18.068 eV, the H_2^+ content in the ion spectra will follow the same Maxwell-Boltzmann distribution and differ only by the recoil energy required by conservation of momentum in the ejection of the photoelectron, whereas the spectrum recorded above the dissociation limit will contain both H_2^+ and H^+ ions.

Photons of energy 21.2 and 16.8 eV (dispersed He I and Ne I radiation, respectively) were used. The corresponding recoil energies (determined from the weighted mean photoelectron energy) are 1.4 and 0.2 meV, respectively. These energies are negligible when compared with the complete Maxwell-Boltzmann distribution (which has a half width of 64 meV at 300 K) and thus the H_2^+ distribution will be the same for the two photon energies. A photoion spectrum was recorded from the 21.2 eV photons and, without altering the scanning conditions, the photon energy was changed to 16.8 eV and the resulting spectrum was subtracted from the data accumulated until the low energy tail of the spectrum was reduced to zero.

The measured Maxwell-Boltzmann distribution extended to apparent negative energies as a result of the 150-meV instrument function and in addition exhibited a tail of scattered ions. As noted above, for practical purposes the shape of the H_2^+ spectrum is identical for the two photon energies. Since the H^+ content of the 21.2-eV spectrum is weak,[12] the criterion of stopping the subtraction when the low-energy tail was reduced to zero was chosen. It should be noted that some 20 data points of the scattered tail have been omitted from Fig. 1.

Figure 1 shows a plot of the complete 21.2-eV photoion spectrum, together with the difference spectrum. Poisson statistics applied to the differencing procedure yield a RMS error of ±2% in the integrated count in the difference spectrum compared with an estimated 10% error in choosing the end point of the subtraction. The dashed line of Fig. 1 is the result predicted from the Franck-Condon distribution over H_2^+ $1s\sigma_g$ above the dissociation limit, calculated as described above. The calculated distribution in the center-of-mass frame is in excellent agreement with that calculated by Ford and Docken.[24] The calculated distribution shown in Fig. 1 includes a transformation to the laboratory frame[22] and has been convoluted with the 150-meV (FWHM) response of the analyzer. Good agreement between the predicted curve and the difference spectrum is seen.

B. Dissociative ionization via higher repulsive potential energy curves

Photoion spectra were also recorded with undispered He and Ne discharges. The He radiation

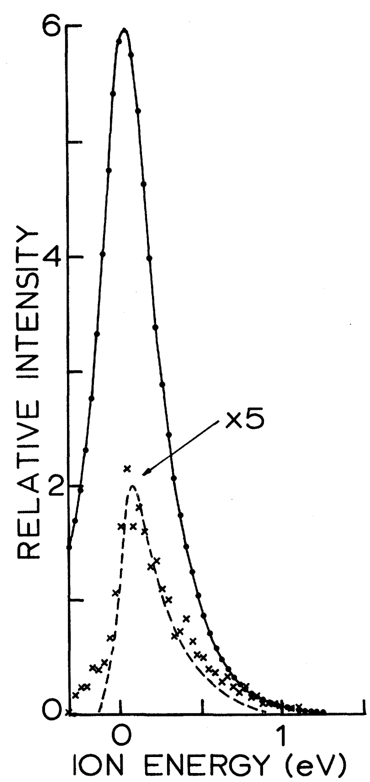

FIG. 1. Photoion kinetic energy spectra of H_2, corrected for the analyzer transmission. ●—Dispersed 21.2-eV photons. ×—Difference spectrum between 21.2 and 16.8-eV photons. The dashed line represents a calculated distribution for H_2^+ $1s\sigma_g$ in the laboratory frame, as explained in the text.

consisted of photon energies 21.2 eV (He I), 23.0 eV (He I), 40.8 eV (He II) and 48.4 eV (He II) in the intensity ratio 6.4:0.2:1.0:0.1, respectively, with the remaining lines negligible by comparison. These intensities were determined by photoelectron spectroscopy for our hollow cathode lamp under our particular operating conditions. Thus the He discharge is seen to primarily produce the resonance lines of He I and He II at 21.2 and 40.8 eV. The ion energy spectrum obtained with the He discharge is plotted in Fig. 2; the data have been corrected for the analyzer transmission. Ion energies peaking about 7.8 eV and extending to 12 eV were expected from dissociative ionization involving the H_2^+ $2p\sigma_u$ level. In fact, the data show an intensity maximum near 5.5 eV and the spectrum is very similar in appearance to the spectra recorded by Lozier under electron impact.[2]

The spectra of Figs. 1 and 2 have been corrected for the transmission of the energy analyzer,[16] but not for the relative response of the detector to H^+ and H_2^+ ions. A Be-Cu surface has been shown to favor H^+ over H_2^+ in a ratio of $\simeq 2:1$ at the energies employed here (2 keV).[25] By comparing the relative intensities of the difference and total spectra of Fig. 1 with the H^+/H_2^+ ratio measured by Browning and Fryar,[12] the relative response of the present detector for H^+:H_2^+ was determined to be 3.2:1. Then combining the measured spectral distribution of the undispersed He discharge with the relevant photoionization cross sections[26] leads to an estimate that the H^+/H_2^+ ratio for photoionization at 40.8 eV is 12%. This ratio is in excellent agreement with that measured by Fryar and Browning[13] and by Backx *et al.*[14]

Figure 3 shows a plot of the hydrogen potential energy curves, together with some calculated Franck-Condon overlaps for direct ionization from the H_2^+ $X\,^1\Sigma_g^+$ ($v=0$) level. A number of discussions of autoionization through repulsive curves of the neutral H_2 have recently appeared in the literature.[11,14,27-29] Autoionization under photon impact is a resonance process, that is, the photon energy must lie within the Franck-Condon region of the neutral curve for autoionization to occur with any measurable probability. The 40.8-eV photon responsible for the energetic ions in Fig. 2 clearly will have little probability of causing autoionization through Rydberg states leading up to H_2^+ $2p\sigma_u$. The effect of such terms can be seen in the data of Browning and Fryar,[12] Backx *et al.*,[14] and Crowe and McConkey,[11] and is the subject of calculations by Hazi,[27] Bottcher and Docken,[28] and Bottcher.[29] Figure 3 shows that direct ionization to, or autoionization through, neutral terms leading to the H_2^+ $2p\pi_u$ and $2s\sigma_g$ states of H_2^+ may be appreciably populated with 40.8-eV photons. Direct ionization into these levels above $2p\sigma_u$ cannot produce ion energies in the laboratory frame above 9 eV with a photon energy of 40.8 eV. Thus, the ion energy distribution expected in the laboratory frame for direct dissociative ionization via the H_2^+ $2p\sigma_u$ state was normalized to the data at 10 eV and is plotted in Fig. 2. This process provides good agreement with the data at proton

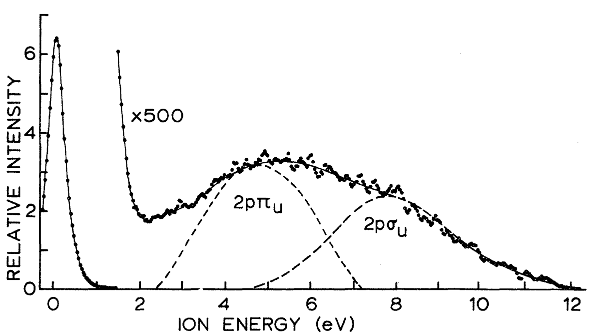

FIG. 2. Photoion kinetic energy spectrum of H_2, corrected for the analyzer transmission, recorded with an undispersed He discharge. The dashed curves are calculated distributions in the laboratory frame for dissociation of the indicated H_2^+ states, as explained in the text.

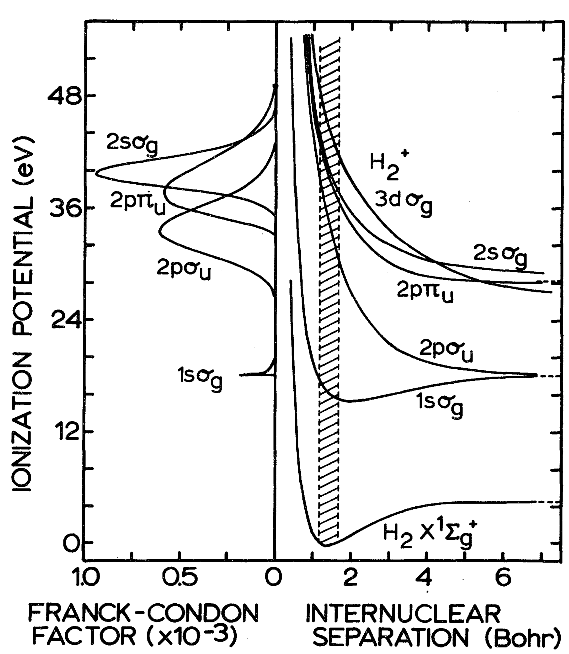

FIG. 3. Potential energy curves for some of the hydrogen states, from Ref. 20. The shaded region represents the Franck-Condon region from the neutral H_2 ground state ($v=0$). On the left are calculated Franck-Condon overlaps for the direct dissociative ionization processes indicated.

energies above 8 eV, although ions of these energies may also be present from autoionization through neutral processes near 40 eV which then dissociate to the $H^+ + H(1s)$ limit at 18.068 eV. The calculated distribution also ignores the variation of the electronic transition moment across the Franck-Condon region. Backx *et al.*[14] have shown that this variation is significant for ionization to the $1s\sigma_g$ state.

Also shown in Fig. 2 is the calculated ion energy distribution in the laboratory frame for direct dissociative ionization of the $2p\pi_u$ state with a maximum transition energy of 40.8 eV. In fact, the two direct ionization processes, $2p\sigma_u$ and $2p\pi_u$ alone, in an intensity ratio of 0.8:1, provide a good explanation of the data. However, the electron impact data[8-10] do not support such a high population of the $2p\pi_u$ state. The onset of the $2p\pi_u$ state is shown in the cross section for formation of H^+, measured by Backx *et al.*[14] However, they caution that autoionization is most likely taking place near this onset also. Such autoionization must be via Rydberg states converging to the $2p\pi_u$ or higher states of H_2^+ to lie within the Franck-Condon overlap region with the neutral ground state.

The low-energy region of the ion spectrum could also contain ions from direct dissociative ionization into the $2s\sigma_g$ or higher states of H_2^+. These ions, having a maximum energy of 6.3 eV in the center-of-mass frame, would be difficult to distinguish from the $2p\pi_u$ distribution shown.

A photoion spectrum was also recorded with undispersed Ne radiation, containing photon energies at 16.8, 26.9, 27.8 and 30.5 eV with relative intensities 12.0, 1.0, 0.2 and 0.15, respectively (determined from photoelectron spectra of the rare gases). The theoretical predictions of autoionizing states leading to $2p\sigma_u$ suggest that some energetic ions should be seen for photon energies in the 26–30 eV range, and an increase in the H^+ yield in this range has been observed.[12,14] No ions beyond those of the undissociated H_2^+ range could be detected in the spectrum recorded with the undispersed Ne radiation. We estimate that if 1% of the signal from 26.9 eV photons had produced energetic ions (i.e., at energies above the tail of the Maxwell-Boltzmann distribution), they would have been detectable. Thus either little autoionization occurs at this photon energy, or those ions that are produced appear at energies below 1.5 eV. Backx *et al.*[14] show a minimum in the H^+ signal near 27 eV. The intensities of the two higher photon energies, 27.8 and 30.5 eV, are too weak compared with the 26.9-eV photons for conclusive comments on the ion energies produced via autoionization at these energies.

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