Time-of-flight study of H(2S) and D(2S) produced by electron impact on H_2, D_2, and HD: Evidence for predissociation

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(Received 6 February 1979)

Time-of-flight spectra of H(2S) and D(2S) fragments from electron-bombardment-dissociated H_2, D_2, and HD have been observed. Structure in the kinetic-energy distributions below 1.3 eV is interpreted as arising from predissociation of bound vibrational levels. For H_2 and D_2 the primary predissociation process appears to be predissociation of the D state via the B' state. Predissociation structure for HD, although more prominent than for H_2 and D_2, is not as easily interpreted. Evidence for the direct dissociation of the B' state has also been obtained and the relative probabilities of direct dissociation and predissociation have been estimated.

I. INTRODUCTION

Metastable H(2S) fragments resulting from electron-bombardment-induced dissociation of H_2 have been reported by several investigators.[1-5] Leventhal, Robiscoe, and Lea[1] first examined the velocity distribution of the H(2S) fragments using a time-of-flight (TOF) technique. They found two distinct energy groups of H(2S) atoms present: a "fast" group with energies centered at about 5 eV, and a "slow" group with energies centered at about 0.3 eV.

The "fast"-group energy distribution is typical of that expected from excitation to a single repulsive excited state. Misakian and Zorn[4] concluded from measurements of the H(2S) angular distribution and excitation function that the state is a doubly excited $^1\Pi_u$ state that dissociates into H(2S)+H(2P). Hazi and Wiemers[6] have calculated H(2S) velocity distributions from theoretical potential-energy curves for this repulsive state and find reasonable agreement. The latter study, however, pointed out discrepancies among the several experimental results.

The "slow" group results in part from excitation from the Franck-Condon region of the ground state to the repulsive portion of bound excited electronic state energy curves which have separated-atom limits of H(1S)+H(2S). These excited states are $E\,^1\Sigma_g^+(2s\sigma)$, $a\,^3\Sigma_g^+(2s\sigma)$, $B'\,^1\Sigma_u^+(3p\sigma)$, and $e\,^3\Sigma_u^+(3p\sigma)$. According to calculations of Chung, Lin, and Lee,[7] at electron energies near 100 eV, which was the electron energy for the present study, the $B'\,^1\Sigma_u^+$ state is the principal contributor to this mode of dissociation.

Another process yielding slow H(2s) fragments is the predissociation of molecules in bound vibrational levels of excited electronic states whose potential curves merge at small internuclear distances with those of the dissociating states just listed. In this case the fragments have discrete energy groups corresponding to the various vibrational levels populated. This predissociation has been investigated by observation of Lyman-α radiation from quenched H(2S) atoms produced by photodissociation of H_2.[8-10] Czarnik and Fairchild[3] have reported partial resolution of some of these predissociation groups for H_2 in an electron-bombardment experiment using a TOF technique. The results of these experiments show that the principal predissociating levels are those with $v>3$ in the $D^1\Pi_u(3p\pi)$ electronic state, which are coupled to the repulsive portion of the B' electronic state.

There are other possible channels for H(2S) production that cannot be ruled out yet do not appear to account for more than a few percent of the observed metastable fragments. In this category are, for example, molecular dissociations into $H(n'L)+H(nP, n>2)$ followed by the decay $H(nP)\rightarrow H(2S)$. In addition there may be dissociations into $H(2S)+H^+$ or $H(2S)+H(n\geq 2)$. The existence of some of these channels can be inferred from experiments in which protons[11] and high-Rydberg ($n\gtrsim 15$) fragments[12,13] have been observed during electron bombardment of H_2.

The total cross section for H(2S) production by electron bombardment of H_2 has been measured by Vroom and de Heer[14] and by Mumma and Zipf.[15] Chung, Lin, and Lee[7] compared these measured cross sections with their calculations for direct dissociation and concluded that, over the range 50–1000-eV electron-bombarding energy, about two-thirds of the measured yield could be accounted for by direct dissociation via the B', e, and E states. It should be noted that the calculated cross sections exclude the "fast" H(2S) fragments that can contribute above their threshold electron-bombarding energy of 29 eV. Czarnik and Fairchild[3] conclude from their data

that at 30-eV bombarding energy predissociation is the dominant H(2S) production mode. In addition, Misakian and Zorn[4] have measured the angular distribution of the slow H(2S) fragments with 18.4-eV electron-bombarding energy and likewise conclude that predissociation is the "dominant but not exclusive process" since direct dissociation via the B' state should produce a $\cos^2\theta$ angular dependence near threshold in contrast to the observed isotropic distribution. It is somewhat surprising that the calculated cross section for direct dissociation can account for such a large portion of the H(2S) production rate when experiments (although done at lower-electron-bombarding energies) indicate that predissociation is the major contributor.

In this article we report the observation of predissociation peaks in the TOF and energy spectra of metastable 2S fragments from electron-bombardment-dissociated H_2, HD, and D_2. Evidence for predissociation from H_2 is much clearer in the present work than in the previously published data of Czarnik and Fairchild.[3] The predissociation peaks in HD and D_2 are the first reported observations of such in TOF work.

II. EXPERIMENTAL

In all previous TOF observations of the H(2S) velocity spectra from dissociating H_2, except that by Czarnik and Fairchild,[3] the sharp energy groups from predissociating vibrational levels were not resolved from the gross structure of the "slow" energy peak because of the random thermal motion of the H_2 molecules in the interaction region. Since these vibrational levels are separated by about 0.1 eV, source-gas temperatures of 50 K are required to resolve these peaks. Czarnik and Fairchild[3] made special efforts to cool the source gas and succeeded in partially resolving this structure.

In this experiment we have used a room-temperature (300 K) multicapillary array to produce a collimated beam of H_2 molecules perpendicular to both the intersecting electron beam and the flight path of the H(2S) fragments (see Fig. 1). This collimation reduces the thermal velocity components along the line of the flight path and results in improved energy resolution. The multicapillary array contained 5- μm-diam capillaries and was 1 mm in length. A ribbon beam 1 cm $\times$ 1.5 mm was produced with an estimated density of 10^{13} molecules/cm^3 and an estimated[16] angular divergence of 0.5° FWHM.

The electron gun used a 0.25 mm thoriated-tungsten wire filament and various apertures and lenses to produce a ribbon beam of electrons

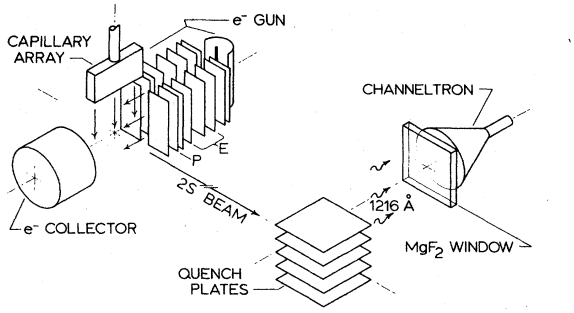

FIG. 1. Schematic apparatus diagram. The pulsed grid in the electron gun, consisting of a fine mesh covering a vertical slit, is labeled P; a three-element einzel lens is labeled E. The vertical molecular beam is shown intersecting the horizontal electron beam. The quench plates are described in Ref. 17.

approximately 1 cm $\times$ 2 mm with a typical dc current of 0.5 mA. The electron beam was pulsed by applying a positive voltage step of typically 0.2 μsec width to a mesh grid normally held at a voltage negative relative to the filament. The electron energy was determined by the potential of the filament relative to the interaction region, which was held at ground potential. Due to the voltage drop in the directly heated filament the energy spread of the electron beam was about ± 2 eV. The electron beam was pulsed at rates between 5 and 10 kHz depending on the flight-path length and the maximum time span to be measured. During pulsed operation, typical average electron currents were 0.5 to 1 μA.

A 17.8-cm flight path was used for the measurements reported here; however, as a check on our results, some H_2 data was taken with a 42.1-cm flight path. The H(2S) atoms were quenched by an electric field at the end of the flight path and the resulting Lyman-α radiation (1216 Å) was detected by a channel electron multiplier (CEM) looking in a direction perpendicular to the flight path. The CEM was enclosed in a box with a 2-mm-thick MgF_2 window for viewing the radiation from the quenched metastables. A 50-μg/cm^2 coating of KI on the CEM input cone was found to increase the detection efficiency for Lyman α by a factor of about 5. The detector has been described in detail in a previous article.[17] The molecular-beam–electron-beam interaction region was not separately pumped and the entire vacuum chamber was operated at a pressure of 8×10^{-6} Torr. The chamber pressure with no gas admitted was 2×10^{-8} Torr.

Time spectra were taken with a Nuclear Data Corp. Model No. 541 time-of-flight module and Model No. ND660 pulse-height analyzer system. Normally 256 or 512 channels with a time dispersion of 0.25 μsec/channel were used. The

start signal was taken from the pulser used to pulse the electron gun, and the stop signal was obtained from the CEM Lyman-α detector. Count rates varied from 1 to 50 counts/sec depending on electron energy.

III. RESULTS

TOF spectra for $2S$ metastable fragments from H_2, D_2, and HD using an electron-bombarding energy (E_b) of 100 eV are shown in Fig. 2. A sharp peak at the left-hand side of each spectrum is caused by photons created during the electron pulse and serves to define time zero for the TOF axis. Counts received before the gun pulse provide a measurement of the constant background rate. It should be noted that, in the case of HD, H($2S$) and $D(2S)$ fragments both contribute to the TOF distribution and cannot be detected separately with the present apparatus. The peaks labeled f in the spectra are due to "fast" (>3 eV) metastables and will be discussed in detail in a separate publication. The remaining data features in Fig. 2 occur at kinetic energies less than 1.3 eV and will be discussed next.

In order to compare our data with the results of other workers, it is convenient to have the energy distributions of the metastables. These can be obtained from the time distributions by a straightforward numerical conversion once the constant background is subtracted from the raw TOF data. The energy spectra derived from the data of Fig. 2 are shown in Figs. 3–5.

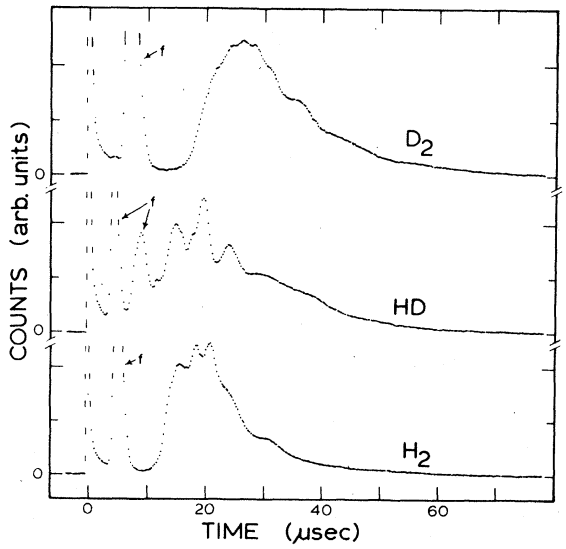

FIG. 2. TOF distributions of H($2S$) fragments from H_2, D ($2S$) fragments from D_2, and H ($2S$) and D ($2S$) fragments for HD. The electron-bombarding energy was 100 eV and the flight path was 17.8 cm.

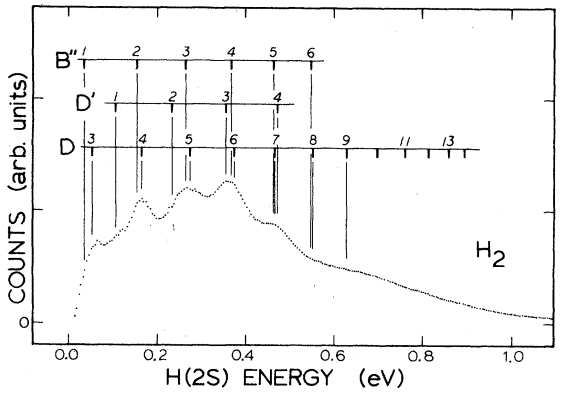

FIG. 3. Energy distribution of H($2S$) fragments from H_2. Predicted positions of predissociation (via the B' state) peaks are shown for several vibrational levels of the D, D', and B'' states of H_2.

The following formula for converting time to energy (for a 17.8-cm flight path) is useful for examining corresponding features in the time and energy spectra:

$$E = 165.7M/T^2, \tag{1}$$

where E is the energy in eV, M the metastable mass number, and T the time-of-flight in μsec. The case of HD again requires special mention.

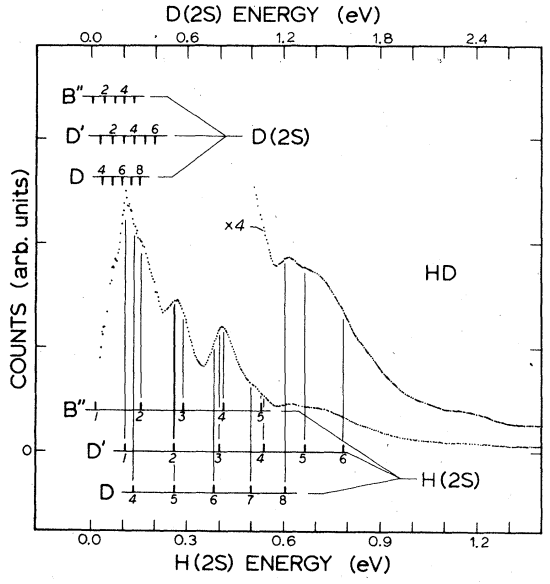

FIG. 4. Energy distribution of metastable $2S$ fragments from HD. Both H($2S$) and D($2S$) fragments are observed and are indistinguishable to our detector. If a feature in the data arises from H($2S$) fragments [D($2S$) fragments] its energy is given by the bottom (top) scale. Predicted positions of predissociation (via the B' state) peaks are shown for both fragments for several vibrational levels of the D, D', and B'' states of HD.

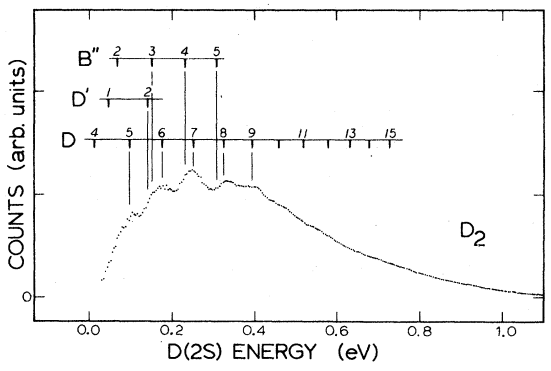

FIG. 5. Energy distribution of D(2S) fragments from D_2. Predicted positions of predissociation (via the B' state) peaks are shown for several vibrational levels of the D, D', and B'' state of D_2.

Since it is not known whether H(2S) or D(2S) metastables are responsible for any given peak in the energy distribution, two energy scales are given in Fig. 4, The lower scale assumes an H(2S) or mass-1 fragment, while the upper scale assumes a D(2S) or mass-2 fragment. We expect that the following effects determine our energy resolution: (i) the spread in speeds of the molecules in our collimated beam, (ii) the time resolution of our TOF data taking system (iii) unresolved rotational structure, (iv) the size of our source region, (v) the acceptance solid angle of our detector, and (vi) recoil momentum imparted by the inelastically scattered electron. Of these effects (ii) dominates for energies above about 0.6 eV and (i), (iii), and (vi) dominate for energies below about 0.4 eV.

For each energy spectrum in the figures the number of counts vanishes as the energy approaches zero. This is a kinematic effect and may be simply explained as follows. In order for a metastable to be detected, the fragment velocity must be pointed toward the detector. In the laboratory reference frame, the fragment velocity is the vector sum of the initial laboratory velocity of the dissociating molecule (after collision with an electron) and the velocity of the metastable fragment relative to the center of mass of the molecule. Since the velocity of the molecules is predominantly transverse to the flight path even after a collision with an electron, dissociation fragments with nearly thermal c.m. speeds have a small probability of reaching the detector. This argument also shows that near-thermal fragment energies derived from flight times slightly underestimate the true c.m. fragment energy.

Predicted positions for peaks arising from excitation of the molecules from the $v=0$, $J=0$ level of the $^1\Sigma_g^+$ ground state to some of the vibrational levels (lowest J in each case) of the $D^1\Pi_u(3p\pi)$, $D'^1\Pi_u(4p\pi)$, and $B''^1\Sigma_u^+(4p\sigma)$ states of H_2 followed by predissociation via the $B'^1\Sigma_u^+(3p\sigma)$ repulsive state are indicated in Figs. 3–5. These predictions were made using the measurements of the dissociation energies for H_2, HD, and D_2 by Herzberg and Monfils[18] and vibrational-rotational energy-level data of Monfils,[19] obtained from photoabsorption experiments. In the cases of H_2 and D_2 it appears that the D state is the dominant predissociating state. For their TOF experiment on H_2 using 30-eV electron-bombarding energy, Czarnik and Fairchild[3] reported peaks at 0.68 and 0.86 eV, which they attributed to predissociating high-lying molecular Rydberg levels. These features are not evident in our H_2 data at 100-eV electron-bombarding energy. In the HD spectrum the discrete features are much more prominent than in H_2 or D_2, however they do not appear to be caused by a single predissociating state.

An attempt was made in the H_2 case to estimate the relative contributions of predissociation and direct dissociation to the energy spectrum. A nonlinear least-squares fit to the TOF data was performed using a model that allowed direct dissociation via the B' state and predissociation of vibrational levels $v=3$ through $v=14$ of the D state. The slow-peak data contains evidence for processes other than D-state predissociation in that metastable fragments are observed above the maximum energy allowed for this process (>0.94 eV in energy or <13.2 μsec in time).

Each predissociation peak was assigned an empirical line shape that was Gaussian in energy and centered at the appropriate expected peak energy (see Fig. 3). All the Gaussians had the same width (FWHM), and this width as well as the 12 amplitudes were parameters of the fit. The direct dissociation of the B' state was modeled according to the Winans-Stueckelberg approximation.[20] The relative probability of observing an H(2S) fragment from direct dissociation was a free parameter. The shape of the B' internuclear potential curve above the dissociation limit was taken to be a straight line constrained to pass through the known coordinates of the B' $v=8$ level,[21] which is the highest vibrational level for which coordinates are known. The slope of the straight line is the last of the 15 free parameters in the fit.

Only TOF data in the range 8.50–38.75 μsec was used in the fit. This range excluded the fast peak and the low-energy data that was judged distorted because of kinematic effects. The fit yields a value for the FWHM of the predissociation peaks of 0.09 eV. The relative contributions

(normalized to the $v=6$ amplitude) of the major predissociating vibrational levels are as follows: $v=4$ (0.59), 5 (0.85), 6 (1.0), 7 (0.57), 8 (0.27), and 9 (0.19). Using the results of this fitting procedure, we estimate that for H_2 at 100-eV electron-bombarding energy 58% of the slow-peak H(2S) fragments result from direct dissociation of the B' state, and 42% result from predissociation of the D state via the B' state. The results of the least-squares fit are presented as only estimates because the model for H(2S) production does not include all the possible predissociation and dissociation channels mentioned earlier.

ACKNOWLEDGMENTS

The authors would like to thank Gary Bivings and Charles Drutman for valuable help in the construction of the electron gun. This research was sponsored by The Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. 75-2864.

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