Velocity Distribution of Metastable H Atoms Produced by Dissociative Excitation of H_2†

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The velocity spectrum of metastable H(2S) atoms produced by electron bombardment of H_2 has been measured by a time-of-flight technique. Two distinct groups of metastables have been detected. The slower atoms are interpreted as arising from transitions to attractive states just above the H(1S)+H(2S) dissociation limit. The faster atoms are thought to arise from transitions to doubly excited repulsive states which have not previously been detected.

I. INTRODUCTION

RECENT remeasurements of the Lamb-shift separation ($2\,^2S_{1/2}$-$2\,^2P_{1/2}$) in atomic hydrogen have indicated the existence of a small but definite discrepancy with earlier measurements.[1,2] Attempts to improve upon these results have led to a search for more abundant sources of metastable hydrogen atoms than the conventional tungsten oven.[3] In particular, the production of large quantities of metastables by electron bombardment of molecular hydrogen has proven feasible.[4] However, the utilization of such a source has been greatly hampered by the lack of knowledge of the velocity spectrum of the resultant atoms. We report here a measurement of the velocity distribution of metastable H(2S) atoms produced by electron bombardment of H_2.

Because of the experimental difficulty in identifying the dissociation products, few measurements have been made involving dissociative processes leading to neutral atoms.[5,6] On the other hand, because of its relative simplicity, the H_2 molecule has received considerable theoretical attention in the calculation of electron-impact excitation cross sections,[7] details of dissociative mechanisms,[8] and in the more general problem of molecular potential curves.[9,10] A critical comparison of experiment and theory concerning dissociative excitation processes in H_2 would allow the testing of such basic concepts as the Franck-Condon principle[11] and the Winans-Stueckelberg approximation,[12] which are fundamental to an understanding of molecular transitions.

Although correlation of theory with optical data provides substantial information concerning the lowest-lying excited attractive states of H_2,[13] particularly near the minima of the potential curves, almost nothing is known about transitions to excited repulsive states. In any case, very little is known about the energy distribution of *neutral* atom dissociation products. Such information would provide a better understanding of the asymptotic behavior of the H_2 excited-state potential curves, namely, dissociation limits and relative position of classical turning points. It should be noted, however, that the energy distribution of *charged* products in the dissociative ionization of H_2 has been investigated, most recently by Dunn and Kieffer.[14] The present measurements provide some new quantitative information about the dissociative excitation of the hydrogen molecule.

II. METHOD

The metastable velocity spectrum has been determined by a time-of-flight technique which is illustrated schematically in Fig. 1. Recently a related technique has been employed to perform similar measurements on heavier molecules.[15] The bombardment region is a simple triode. A magnetically collimated electron beam is regularly pulsed on for 0.2 μsec in an H_2 atmosphere of about 10^{-4} Torr. A fraction of the metastable atoms produced in dissociative collisions between electrons and H_2 molecules (on the average considerably fewer than one metastable atom per pulse is detected) drift out of the source to a quench region located 10 cm away. Here a strong, well-localized electric field mixes the 2S and 2P states causing a decay to the ground state. The Lyman-α decay radiation then initiates a pulse in an EMR model 542G-08-18 photomultiplier which is

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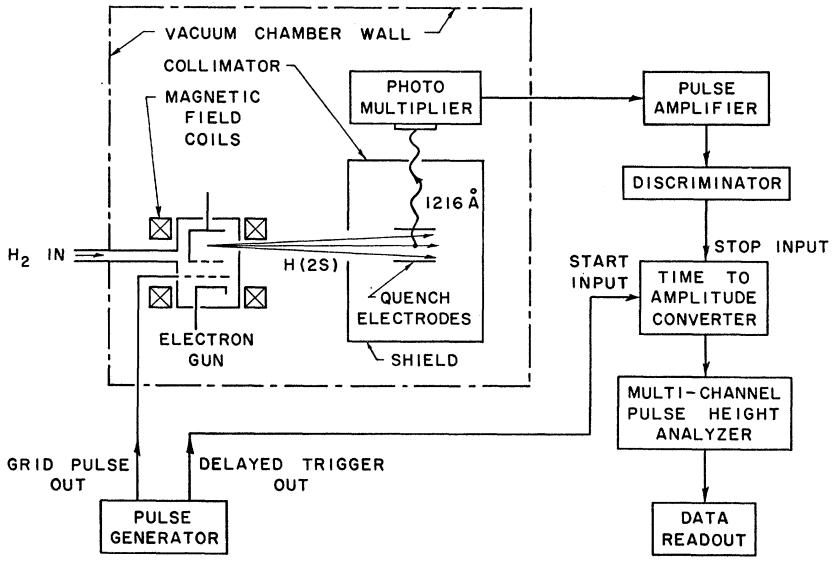

FIG. 1. Schematic diagram of experimental apparatus and circuitry.

fed through several stages of fast (2-nsec rise time) amplification provided by EGG model AN101 amplifiers. The signal pulse then passes through an EGG model T100A discriminator and is converted to a logic pulse which activates the stop input of an EGG model TH200 time-to-amplitude converter (TAC). A trigger output pulse from the HP model 214A pulse generator, delayed 0.5 μsec from the trailing edge of the electron-gun pulse, activates the start input. Hence the TAC produces a logic pulse whose amplitude is proportional to the elapsed time between electron bombardment pulse and Lyman-α pulse. Finally the TAC output is registered in a TMC model 402C multichannel analyzer operating in the pulse-height mode, so that the data readout consists of the time-of-flight spectrum of the metastables. The background is eliminated from this spectrum by running the system for equal times with the quenching field on and off and then performing a subtraction. Calibration of the time scale is achieved by activating the TAC inputs with pulses from a Textronix model 180A time-mark generator whose reference crystal has been calibrated against WWV.

III. RESULTS

A. "Slow" and "Fast" Metastables

As can be seen from Fig. 2, two distinct groups of metastable atoms have been detected and are designated "slow" and "fast." The observed spectrum shows two maxima, at 10.5±0.6 μsec for the slow atoms, and at 3.2±0.3 μsec for the fast atoms. The time-of-flight axis of Fig. 2 does not scale linearly with velocity or energy. Hence to conserve probability, the transformation from a time-of-flight distribution $P(t)$ to a velocity distribution $P(V)$ and an energy distribution $P(E)$ must be made using the relations

$$P(V)=P(t)dt/dV, \quad P(E)=P(t)dt/dE \qquad (1)$$

and

$$V=L/t, \quad E=mV^2/2, \qquad (2)$$

where L is the path length (10 cm), m is the mass of the hydrogen atom and t is the time-of-flight. When plotted against velocity, the distribution shows maxima at 8.3±0.5 and (31±3)×10^5 cm/sec for the slow and fast atoms, respectively (see Fig. 3). The distribution in energy shows two less well-defined maxima, at values of 0.32±0.05 and 4.7±0.7 eV. The uncertainty in the results quoted above arises mainly from two sources, statistical fluctuations in the data, and uncertainty in the exact path length L because of the finite extent of the source and quench regions. Conclusive proof that metastables are being detected was provided by replacing the dc quenching field with an rf field of the correct frequency to drive the transition $2^2S_{1/2} \rightarrow 2^2P_{1/2}$. This produced a time-of-flight spectrum identical to that of Fig. 2 which could be made to vanish by tuning the radio frequency off resonance.

Velocity spectra have been taken systematically as a function of bombardment voltage up to 60 V as read on a laboratory voltmeter. The slow peak becomes observable in the time-of-flight spectra at a voltage of about 18±2 V with the fast peak appearing about 10.5±2 V higher. For several volts above their respective threshold, the statistical fluctuations in the data were such as to prevent an accurate determination of the peak centers. However, the statistics improved as the bombardment voltage was further increased and the peaks could then be accurately located. Within experimental error, the location of the two peaks did not change with increasing voltage from approximately 5 V above threshold to 60 V and was always consistent with the results quoted above. On the other hand, the relative intensity of the two peaks did vary markedly with voltage, as shown in Fig. 2. Space-charge effects were a serious problem in locating the thresholds.

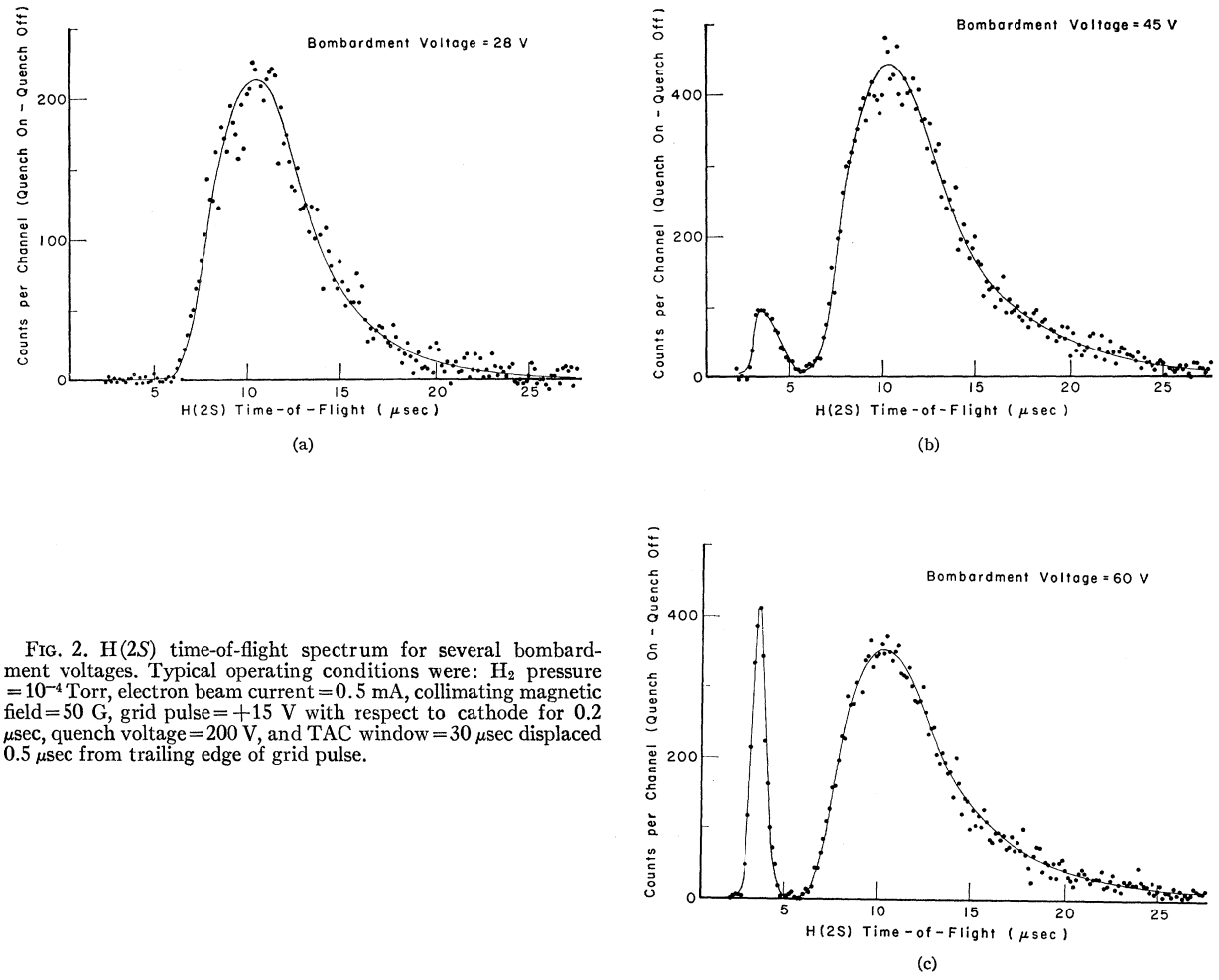

FIG. 2. H(2*S*) time-of-flight spectrum for several bombardment voltages. Typical operating conditions were: H_2 pressure $=10^{-4}$ Torr, electron beam current $=0.5$ mA, collimating magnetic field $=50$ G, grid pulse $=+15$ V with respect to cathode for 0.2 μsec, quench voltage $=200$ V, and TAC window $=30$ μsec displaced 0.5 μsec from trailing edge of grid pulse.

Displacement of the appearance potentials by several volts could be produced by varying the bombardment current.

The discussion of the following section indicates that the shape of the slow peak disagrees with theory, which predicts a broader velocity spectrum, containing fewer atoms in the peak, but more atoms in the wings. Numerous instrumental effects which might distort the velocity spectrum have been investigated with negative results. A brief discussion of these effects follows. Distortions of the spectrum due to less obvious mechanisms such as charged insulating layers in the electron-gun or plasma oscillations in the electron beam are thought to be unimportant and are not discussed.

1. *Instrumental Rounding*

A small amount of rounding or smoothing of the velocity distribution is introduced instrumentally, due to the finite time resolution of the multichannel analyzer, the finite duration of the electron-gun pulse, and the spatial extension of the quenching electric field. The extent of this smoothing is altogether too small, however, to account for the discrepancy observed in the slow metastable distribution referred to above.

2. *Pressure Quenching*

A metastable atom produced in the source must traverse a 10-cm-long drift space (from source to quench

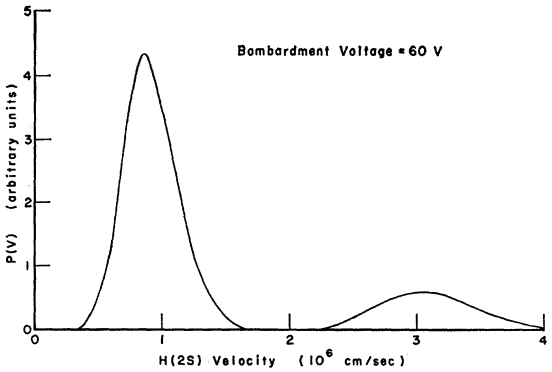

FIG. 3. H(2*S*) velocity distribution at bombardment voltage of 60 V.

region) containing H_2 at a pressure of about 10^{-4} Torr before it can be detected. Fite[16] has shown that a metastable may be quenched in a collision with an H_2 molecule. If the cross section for this process is velocity dependent, a distortion of the velocity spectrum would result. Using Fite's value of 0.7×10^{-14} cm^2 for the collision quenching cross section, a value of 40 cm is obtained for the mean free path between collisions, indicating that no serious problem should be presented by this effect. This conclusion was substantiated by measuring velocity spectra as a function of H_2 pressure. Variation of the H_2 pressure in the drift space from 0.1×10^{-4} to 4.0×10^{-4} Torr produced no significant change in the observed spectrum.

3. *Space-Charge Quenching*

If no positive-ion neutralization takes place, an electric field exists in the source region due to the net electronic space charge. Slow metastables, which must drift about 1 cm through such a field, are preferentially quenched, since they experience the field for a longer time. A theory of the space-charge fields associated with the present cylindrical geometry has been given by several authors.[17,18] If the relevant geometrical parameters are substituted and a typical beam current of 0.5 mA is assumed, an average space-charge field of about 6 V/cm is obtained over the source region. Application of the Bethe-Lamb theory[2] of the lifetime of the $2S$ state in an external electric field indicates a cutoff velocity V_c of approximately 1×10^5 cm/sec; i.e., atoms with speeds less than 1×10^5 cm/sec would be quenched in the source. This speed is somewhat smaller than the observed cutoff of 4×10^5 cm/sec (see Fig. 3). Convincing experimental evidence that space-charge effects were not distorting the velocity distribution was obtained by varying the bombardment current over the range 0.06 to 0.50 mA. No change in the spectrum was detected.

4. *Positive-Ion Quenching*

Electron bombardment of H_2 at energies above 15.4 V results in the production of molecular ions. A metastable encountering such an ion can be quenched by its local field. Similarly, an encounter with a free electron could quench a metastable but the much greater electron velocity permits neglecting this effect. Purcell[19] has given a theory of the positive-ion quenching of metastables. If the extreme case of complete positive-ion neutralization of a 0.5-mA primary electron beam is assumed, the present geometry yields a V_c of about 1×10^4 cm/sec, well below the observed cutoff. In addition, ion quenching should be a sensitive function of bombardment current and pressure. As previously noted, variation of these parameters did not affect the velocity spectrum.

5. *Prequenching*

In the normal mode of operation, the photomultiplier is collimated so as to view the metastables only while they are in the quench region. The quench region, identical to that used by one of the authors in a previous experiment,[1] produces a highly localized ($\sim$1 cm) electric field. Nevertheless, a small fringing field does exist which may preferentially quench slow metastables before they get into view of the photomultiplier.

An electrolytic tank method has been previously employed to determine the fringing field along the beam axis. Application of the Bethe-Lamb theory shows that only metastables with speeds less than 5×10^4 cm/sec would be appreciably prequenched. To test the conclusion that prequenching was not important, the collimator was removed and the photomultiplier allowed to view most of the drift space. Again no change in the velocity spectrum was observed.

B. Anisotropy of Velocity Distribution

The data presented above were obtained with the source oriented so as to detect metastables at an angle of 90° with respect to the electron-beam axis. Although the apparatus was not specifically designed for the purpose, an attempt was made to investigate the angular dependence of the velocity spectrum by tilting the axis of the electron beam to an angle of 77° with respect to the metastable drift path. This resulted in no visible effect on the slow metastable peak but a marked change in the fast peak. Figure 4 presents the time-of-flight spectrum of the fast metastables obtained for both orientations of the electron beam, other conditions being approximately the same. A resolution of the fast peak into two distinct peaks has occurred for the 77° case, one centered at a velocity of $(2.9\pm0.3)\times10^6$ cm/sec and the other at $(2.1\pm0.2)\times10^6$ cm/sec. These correspond to energies of 4.4 ± 0.9 and 2.3 ± 0.5 eV. This compares with the single-peak maximum at 4.7 ± 0.7 eV for the 90° geometry.

C. Velocity Spectrum of Deuterium Metastables

The velocity spectrum of metastable deuterium atoms formed by the dissociative excitation of D_2 was obtained by the technique described above, using an untilted geometry. A spectrum similar to that for hydrogen was observed but with the fast and slow peaks shifted to lower velocities as shown in Fig. 5. The slow peak is centered at a velocity of $(6.1\pm1.0)\times10^5$ cm/sec and the fast peak at $(2.2\pm0.2)\times10^6$ cm/sec. The maxima in the energy distributions fall at 0.3 ± 0.15 and 5.1 ± 0.5 eV, respectively. Within experimental error, these energies are the same as those for hydrogen metastables.

[16] W. L. Fite, R. T. Brackmann, D. G. Hummer, and R. F. Stebbings, Phys. Rev. **116**, 363 (1959).
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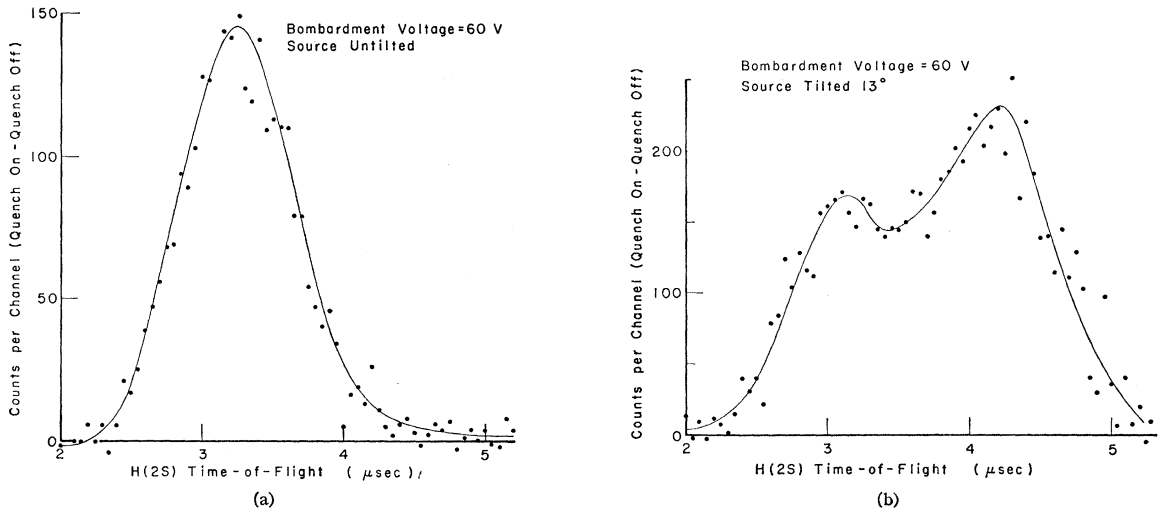

FIG. 4. H(2S) "fast" metastable time-of-flight spectrum for two orientations of the source with respect to the metastable drift path. The TAC window has been adjusted to 10 μsec.

IV. DISCUSSION

A. Slow Metastables

The slow metastables arise from processes like

$$H_2(X\,^1\Sigma_g^+) \rightarrow H_2(^1\Sigma_u^+) \rightarrow H(2S)+H(1S), \quad (3)$$

where the excitation, by electron bombardment, is to singly-excited bound states of the molecule. Lamb and Retherford[2] originally suggested that slow metastables could be obtained from Franck-Condon "forbidden" transitions to bound states above their dissociation limit. Such a transition is illustrated in Fig. 6 where a single bound state is drawn to represent all states which can yield a slow metastable upon dissociation.[20] While these transitions are forbidden in a classical sense, the quantum-mechanical statement of the Franck-Condon principle[11] predicts a small but finite transition probability. The threshold for metastable atom production by such processes should be at about 15 V, which is somewhat lower than the observed value of 18±2 V. Attractive molecular states which can contribute in varying degrees to the yield of slow metastables by a direct process such as Eq. (3) are

$$B\,^1\Sigma_u^+, \quad B'\,^1\Sigma_u^+, \quad e\,^3\Sigma_u^+, \quad E\,^1\Sigma_g^+, \quad \text{and} \quad a\,^3\Sigma_g^+.$$

Relative cross sections for direct excitation above the dissociation limit are not known. It is probable that indirect processes are also involved in the production of

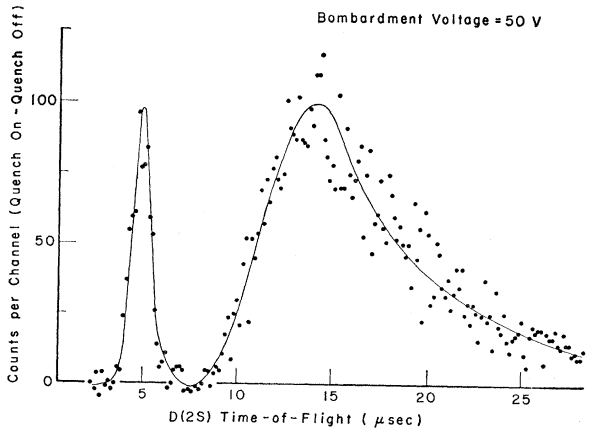

FIG. 5. D(2S) time-of-flight spectrum.

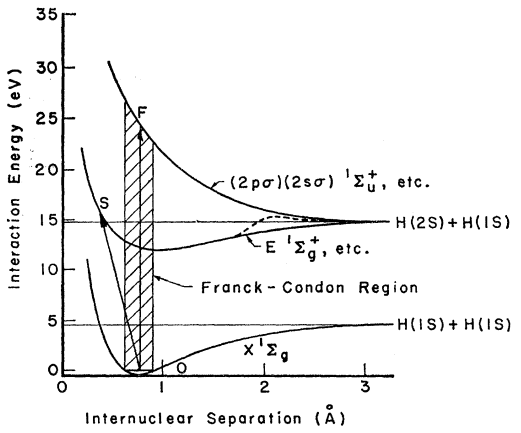

FIG. 6. Potential-energy curves for H_2, showing the ground state and representative excited states which can dissociate to a metastable atom. OS is a Franck-Condon "forbidden" transition to an attractive state above its dissociation limit. OF is an "allowed" transition to a repulsive state. Such transitions produce slow and fast metastables, respectively. The dashed curve represents the hypothesized potential maximum at large internuclear separation.

[20] Evidence for Franck-Condon "forbidden" transitions in H_2^+ is discussed by D. P. Stevenson [J. Amer. Chem. Soc. 82, 5961 (1960)].

slow metastables.[21] For example, (i) molecules may dissociate into higher atomic states which can cascade to the metastable state,[6] (ii) the $C\,^1\pi_u^+$ and $c\,^3\pi_u^+$ states, normally thought to yield an $H(2P)$ atom upon dissociation, may yield a metastable via some mechanism like rotational coupling to one of the Σ^+ states near a crossing. Lack of detailed information about the various dissociative excitation processes discourages any quantitative calculation of the slow metastable velocity spectrum. However, a qualitative prediction can be obtained from the theory of Harriman.[8] Application of the Franck-Condon principle to the theory of molecular transitions leads to the following expression for the probability, $P(E)$, that a dissociative excitation takes place:

$$P(E)=\left[\int_0^\infty U(r)V_E(r)dr\right]^2. \tag{4}$$

Here U is the ground-state vibrational wave function, V_E is the vibrational wave function for the bound molecular state with energy E above the dissociation limit, and r is the internuclear distance. [A derivation of Eq. (4) is also given on p. 199 of Ref. 13.] Harriman has evaluated the integral of Eq. (4) in three levels of approximation: (1) using a harmonic-oscillator wave function for $U(r)$ and a WKB approximation wave function for $V_E(r)$ derived from a modified Morse potential, (2) replacing the modified Morse potential by a linear potential, and finally (3) employing a Gaussian error function for $U(r)$ and a delta function at the classical turning point for $V_E(r)$ (Winans-Stueckelberg approximation[12]). Similar results were obtained in all cases. The latter method yielded a simple analytical expression for $P(E)$,

$$P(E)\propto e^{-E/E_0} \tag{5a}$$

or

$$P(t)\propto 1/t^3 e^{-(t_0/t)^2}. \tag{5b}$$

In Eq. (5b) the energy variable has been converted to time-of-flight t via $E\propto 1/t^2$. Figure 7 shows a plot of the form given by Eq. (5b) superposed on the observed time-of-flight spectrum. The Harriman distribution has been fitted to the experimental points by the method of least squares. It is seen that the fit is poor, the Harriman distribution being less sharply peaked than the observed distribution. In seeking an explanation for this discrepancy, the Harriman distribution was modified to allow for the velocity distribution of the molecular hydrogen. Over the range of values of t studied in this experiment, this modification produced negligible change in the values of $P(t)$.

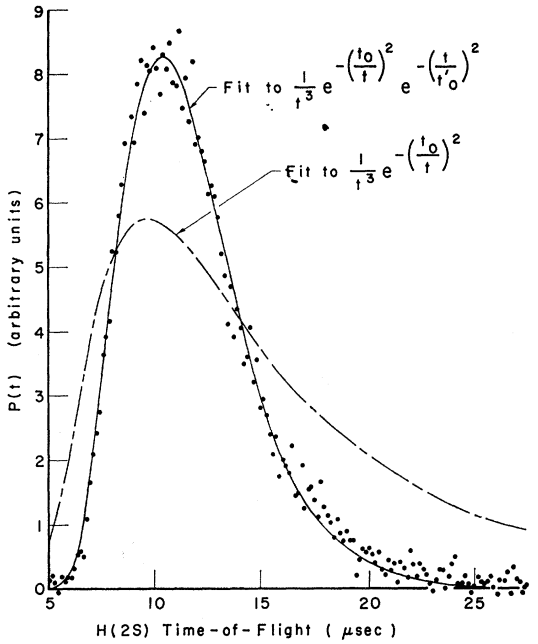

FIG. 7. Least-squares fits of two functions to the slow metastable time-of-flight spectrum. The functions and parameters are discussed in the text.

Alternatively, the Harriman distribution of the form of Eq. (5a) can be adjusted to fit the experimental points over the upper energy range 0.6 to 1.3 eV. An example of this fit is shown in Fig. 8. The parameter E_0 was determined to be 0.21 ± 0.02 eV. The departure between experiment and the Harriman theory at low energies may be described by introducing the function $R(E)$, which represents the "probability of escape" of metastables with energy E. $R(E)$ is constructed by taking the ratio of the experimental to the theoretical values of $P(E)$ in the energy range 0 to 0.6 eV. Figure 9 shows a curve of $R(E)$ versus E obtained by averaging the results of a number of experimental runs. It is seen that the probability of escape $R(E)$ has fallen to 0.5 for an energy of 0.3 eV.

The deficiency in slow metastables could be explained as a real molecular effect if those states contributing a predominance of the slow metastables possessed potential maxima at large internuclear separation. Such a maximum is indicated by the dashed curve in Fig. 6. Clearly the slowest metastables seen in a dissociation from this modified potential curve would classically possess an energy equal to the height of the maximum above the dissociation limit. In the absence of detailed potential curves for large internuclear separation, the existence of potential maxima has been the subject of some discussion. Herzberg and Monfils[22] have indicated

[21] Second-order processes like

$$H_2+e\rightarrow H_2^++2e,$$
$$H_2^++e\rightarrow H(2S)+H^++e,$$

can be ruled out by numerical considerations. If it is assumed that all H_2^+ ions produced during a typical gun pulse are trapped by electron space charge, a density of about 10^6 ions/cc will exist at the end of the pulse. This must be compared with an H_2 density of about 10^{12} molecules/cc.

[22] G. Herzberg and A. Monfils, J. Mol. Spectry. 5, 482 (1960).

that the experimental determination of the dissociation energy of H_2 could be in error because of such maxima. King and Van Vleck[23] have estimated the effect of van der Waals interaction on some of the relevant potential curves. They calculated a potential maximum of about 0.10 eV in the $C\,{}^1\pi_u{}^+$ state arising from $1S$-$2P$ dipole-dipole resonance between the separated atoms. A more recent calculation by Browne[10] indicates a barrier height of only 0.02 eV in this state. It is not clear whether this particular mechanism or related mechanisms are active in all states.[23a] However, it is possible that the selection rules governing the excitation process may favor the population of a single excited state. Thus the observation of a low-energy cutoff in the slow metastable spectrum could indicate the existence of a potential barrier in only one of the molecular states listed above. It should be stressed that this is not necessarily the correct interpretation of the low-energy cutoff. It is entirely possible that a different explanation can be advanced to account for this feature of the energy distribution.

The analysis of the data leading to the function $R(E)$ constitutes only one way of presenting the experimental observations. The results may also be described, for example, in terms of the function[24]

$$P(t) \propto \frac{1}{t^3} \exp\left[-\left(\frac{t_0}{t}\right)^2\right] \times \exp\left[-\left(\frac{t}{t_0'}\right)^2\right]. \qquad (6)$$

A least-squares fit of this function to typical data is shown in Fig. 7. Best values of $t_0 = (1.6 \pm 0.3) \times 10^{-5}$ sec and $t_0' = (8.5 \pm 1.5) \times 10^{-6}$ sec were determined.

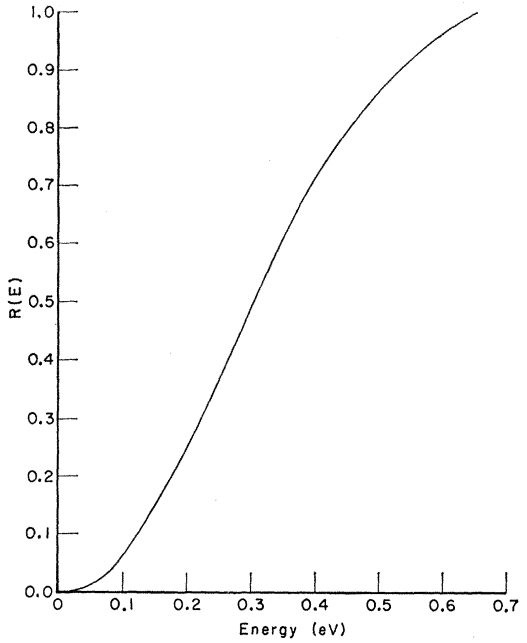

FIG. 9. The ratio $R(E)$ of experimental to theoretical slow metastable energy distributions, for low energies.

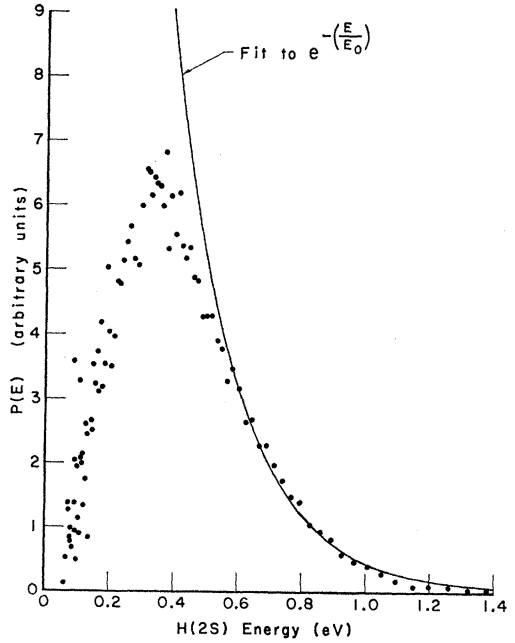

FIG. 8. Least-squares fit of the Harriman distribution function $P(E)$ to the measured slow metastable energy spectrum. The fit is restricted to the energy range 0.6–1.3 eV. The points represent experimental results which have been converted to a distribution versus energy.

B. Fast Metastables

Because of their relatively large energy and higher threshold potential, the fast metastables are believed to arise from processes like

$$H_2(X\,{}^1\Sigma_g{}^+) \rightarrow H_2({}^1\Sigma_u{}^+) \rightarrow H(2S)+H(1S), \qquad (7)$$

where the excitation, by an electron impact, is Franck-Condon "allowed" but to a doubly excited repulsive state of the molecule.[25] Such a transition is illustrated in Fig. 6 where a single repulsive state is drawn to represent all states which can yield a fast metastable upon

[23] G. W. King and J. H. Van Vleck, Phys. Rev. **55**, 1165 (1939).

[23a] *Note added in proof.* Calculations by E. R. Davidson [private communication and J. Chem. Phys. **43**, 834 (1965)] reveal the existence of potential maxima in other states.

[24] An expression of the form of Eq. (6) can be derived by modifying the Harriman distribution to take into account collisional quenching of metastables during their time of flight. A numerical estimate of the cross section for collisional quenching may be obtained from the value of t_0'. It is, however, many times larger than the value obtained by Fite (Ref. 16). In addition, the fact that t_0' is found to be substantially independent of pressure leads to a value for the cross section which varies with pressure. For these reasons, the interpretation in terms of collisional quenching is regarded as untenable, and Eq. (6) is offered here as an empirical equation, which represents the data very closely.

[25] All known singly-excited states which can yield a metastable upon dissociation are attractive and have been listed above.

dissociation. An internal check on the correctness of this picture is obtained by noting that both fragments of the dissociation indicated in Eq. (7) would be expected to come off with about the same kinetic energy. Hence, the fast metastable threshold should be displaced above the slow metastable threshold by about twice the observed fast metastable energy of 4.7±0.7 eV. This agrees roughly with the observed threshold difference of 10.5±2 eV.

The resolution of the fast peak into two distinct peaks on tilting the source indicates that at least two repulsive states with different symmetry properties are contributing fast metastables. Dunn[26] has discussed anisotropies in the angular distribution and energy of molecular dissociation products. From considerations of initial- and final-state symmetries, he finds that definite anisotropies can be expected. The present data are too crude to allow more than these qualitative remarks.

The doubly excited repulsive states of H_2 which yield the fast metastables by dissociative excitation under electron impact have not previously been discussed in the literature. Their existence, however, can be inferred from consideration of the hydrogen molecular ion. Indeed a close analogy can be drawn between the present work and the study of fast and slow protons from the dissociative ionization of H_2 carried out by Dunn and Kieffer.[14]

The $(2p\sigma)\,^2\Sigma_u^+$ state of the molecular ion is repulsive, indicating that the molecular states $(2p\sigma)(2s\sigma)\,^{1,3}\Sigma_u^+$ behave similarly. The energy of such states can be crudely estimated by adding the repulsive energy of a $2p\sigma$ electron (calculated from the repulsive ionic state[27] $^2\Sigma_u^+$) to the energy at dissociation of the $(1s\sigma)(2s\sigma)$ molecular states. If this is done at an internuclear separation of 0.74 Å (equilibrium position for the H_2 ground state $X\,^1\Sigma_g^+$), it places the $(2p\sigma)(2s\sigma)$ states about 16 eV above the H(1S)+H(2S) dissociation limit. In turn, this implies that the fast metastables appear at a bombardment voltage 15 V higher than the slow metastables.

The above estimate is expected to be too large since it neglects screening of the $2p\sigma$ electron by the $2s\sigma$ core. This may explain why the prediction of a 16-V threshold difference compares poorly with the observation of 10.5±2 V. Clearly it would be interesting to obtain a more precise theoretical number.

V. CONCLUSIONS

In the present experiment, new quantitative information has been obtained regarding the energy spectrum of metastable atoms produced in the dissociative excitation of molecular hydrogen by electron bombardment. The work is preliminary, in the sense that more accurate results can be obtained with a more refined apparatus. But several interesting features of the spectrum have been established. The spectrum can be resolved into two distinct groups, each with a well-defined appearance potential. The "slow" metastables, arising from transitions to singly excited states of H_2 just above the H(1S)+H(2S) dissociation limit, show a cutoff at low energy. This cutoff, which is apparently independent of instrumental effects, may indicate the existence of potential maxima in the relevant H_2 potential curves at large internuclear separation. The "fast" metastables, arising from transitions to previously undetected doubly excited repulsive states[28] of H_2, show a marked angular dependence for angles near 90° with respect to the incident electron beam. It is desirable to further investigate such anisotropies since they can aid in the identification of the doubly excited states.

Finally, the present measurement of the bombardment energy difference between the appearance of slow and fast metastables has for the first time located the H_2 doubly excited states with respect to the H(1S)+H(2S) dissociation limit. Simply from the standpoint of molecular spectroscopy, it is desirable both to make a more accurate measurement and to calculate the location of these states.

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[26] G. H. Dunn, Phys. Rev. Letters **8**, 62 (1962).

[27] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. (London) **A246**, 215 (1953).

[28] Such states in the molecule are analogous to the united-atom case of the doubly excited levels in He recently investigated by M. E. Rudd [Phys. Rev. Letters **15**, 580 (1965)].