Highly Excited States of Hydrogen Molecules. I. H_2, HD, and D_2[†]

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(Received 1 November 1971)

Highly excited states of hydrogen molecules have been formed by electron-capture collisions of 50—450-keV diatomic ions in hydrogen gas. Populations of the excited states ($n \geq 10$) have been determined by passing the molecules through an intense electric field which strips the excited electron from the molecule. The fraction of molecules in states $n \geq 10$ was approximately 10^{-3} with D_2^* being approximately a factor of 2 greater than H_2^*. The fractional yield of H_2^* varied as the stripping electric field to the $\frac{3}{4}$ power. Results are presented for molecular autoionization, excited-state population dependence on ion-source-electron energy, and state-mixing measurements.

I. INTRODUCTION

During the past several years many laboratories have been studying the population of the upper principal quantum states (n) of the hydrogen atom by electron capture. Excellent reviews have been published by Riviere[1] and Fedorenko et al.[2] In those studies a proton beam was passed through a gas cell where electron capture resulted in fast H atoms in all states of electronic excitation. These atoms were then passed through an electrostatic field ionizer, which stripped or removed the orbital electron from the hydrogen atom by virtue of the intense Stark effect. A functional relationship exists between the applied-field strength and the lowest (most tightly bound) quantum state of the excited electron which can be stripped by that field strength; on the basis of quantum calculations, the applied field which produces ionization is inversely proportional to n to the fourth power. The radiative lifetimes of these quantum states in an electric field[3] are greater than 10^{-7} sec for states $n \geq 10$; these long lifetimes exceed the particle transit time (10^{-7} sec) between the place of formation and ionization. Thus, measurement can be made of these highly excited atoms or molecules without appreciable loss due to radiative decay.

In our laboratory we have used the same techniques to explore the physics of the highly excited electronic states of the hydrogen molecule H_2.[4] The states have been characterized as Rydberg states in which the stable molecular ion forms an ionic core with a single electron sufficiently far removed from the core that it essentially moves in a Coulomb field of unit charge. These states have been found not only for H_2 but also for H_3; the latter, however, will be discussed in the following paper. A comparison of the experimentally mea-

sured populations of the excited states of H and H_2 revealed that the population of H_2 states are approximately $\frac{1}{2}$ that of the corresponding states in H. This population difference is due either to differences in the capture mechanism between a proton and an H_2^+ ion or to the process of molecular autoionization,[6-10] which will be discussed in Sec. III. Solov'ev et al.[5] have also measured the population of H_2^* from the electron capture of H_2^+ in hydrogen. Due to differences in the technique of data analysis and the state population being ion-source dependent (Sec. VIII), no comparison will be made with their data in the present paper.

The present paper is devoted mainly to a description of the measurements of the populations of H_2 Rydberg states and the effect of autoionization on the level population. Discrepancies between level populations of D_2 and H_2 are discussed in Sec. VII. In Sec. VIII measurements are described concerning the initial vibrational H_2^+ configuration (before electron-capture collision) dependence on the electronic population of H_2. In Sec. IX results are presented suggesting electronic-state mixing between long- and short-lived states.

II. APPARATUS

A schematic diagram of the apparatus used in these measurements is shown in Fig. 1. Ions were formed in an oscillating-electron- (PIG-) type source and were accelerated to energies of 50—500 keV by a conventional dc accelerator. After acceleration the ions were momentum analyzed and the H_2^+ beam was focused on the gas collision cell, where electron-capture collisions with H_2 gas produced fast H_2 in all states of excitation. On emerging from the hydrogen-gas cell the charged particles were removed by a set of electrostatic parallel condenser plates. The condenser plates
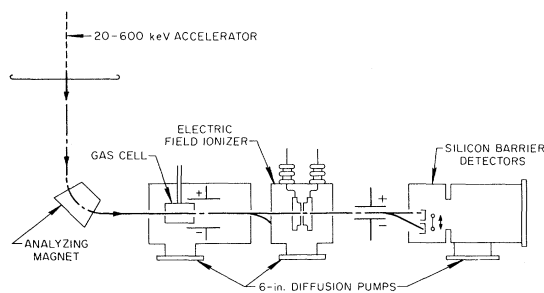
FIG. 1. Schematic diagram of apparatus.

were so arranged as to provide an electric field with a semisharp boundary so that state-mixing experiments could be carried out (see Sec. IX). In addition, the gas cell and condenser plates were mounted to move parallel to the beam axis to provide a variable path length (transit time) for measurement of H_2^* lifetimes due to autoionization or radiative decay. Two electrodes with $\frac{3}{4}$-mm spacing and with parallel surfaces formed the electric field ionizer. The beam was collimated by a $\frac{1}{8}$-mm aperture before passing through the $\frac{1}{4}$-mm aperture in the ionizer electrodes. In determining the electric field the applied voltage was divided by the electrode geometric distance without any correction due to field distribution in the electrode gap. Riviere and Sweetman[11] impressed a small ac voltage on top of the dc electrode voltage, giving rise to an ac signal proportional to the population of an individual n state. Due to the overlap of the population of the many angular momentum states only partial resolution between the n states was achieved. In the present measurements only integral populations (i.e., the sum of the population of states $n \geq 10$) were measured.

After emerging from the electrostatic-stripping cell the ions were deflected by a second condenser plate, which also analyzed the energy of the ions. The measurements consisted of determining the yield of ions (ratio of ions to neutrals) as a function of the field applied to the stripping electrodes. Ions produced by collisions with residual-gas molecules and edges of collimating apertures were subtracted as background signal. With measurements of H_2^* the detector must be more sophisticated than that which suffices for the simple case of determining the excited-state population of H^*. In the case of H^* the collector can be quite simple, the only requirement being that it must be sensitive to neutral H particles. In the case of H_2^*, in addition to the electron-capture collisions occurring in the first gas cell, there exist dissociative-type collisions producing both H^+ and H at one-half the energy of the incident H_2^+. Thus, arriving at the detector is a beam of neutral particles consisting of H_2 at full energy and H at half-energy. The

absolute intensity of each component was determined using an energy-sensitive high-resolution silicon-barrier detector.[12] Ions were detected in a similar manner, with H^+ and H_2^+ being separated in space by the second set of condenser plates. The 200-mm^2 silicon detector was sufficiently large to accept the angular divergence of the charged-particle beam due to the defocusing by the electric fields. The output of the silicon detector was amplified by a low-noise preamplifier and linear amplifier, with the separation of the H and H_2 spectrum being sufficient to use a simple pulse-height discriminator to block off the H counts from the counter.

III. RESULTS OF CAPTURE INTO EXCITED STATES

Before quantitatively determining the integral fraction of H_2^*, it was necessary to ensure that only single collisions occurred in the electron-capture gas cell. Otherwise, ionization or de-excitation collisions would deplete the excited-state fraction. Shown in Fig. 2 is the integral fraction of excited H_2 in states $n \geq 11$ as a function of the gas-cell pressure. Pressures were measured by an ion gauge which was calibrated by use of a capacitance manometer. In all the measurements the cell pressure was less than 10^{-3} Torr, thereby ensuring single collisions in the cell.

Il'in et al.[13] have presented a convenient method to show the relationship between the beam fraction in high-quantum-number states as a function of the field applied to the ionizer for H atoms formed by electron-capture collisions. Their result is reproduced here so that it may be conveniently compared to the more general result derived in the following discussion.

The yield or fraction $F(\mathscr{E})$ in excited states is given by

$$F(\mathscr{E}) = I^+(\mathscr{E})/I_0 , \tag{1}$$

where $I^+(\mathscr{E})$ is the positive-ion current produced by electric field $\mathscr{E}$ and I_0 is the total neutral current. The total neutral beam is given by summing over all principal quantum states n as

$$F_0 = \sum_{n=1}^{\infty} F_n . \tag{2}$$
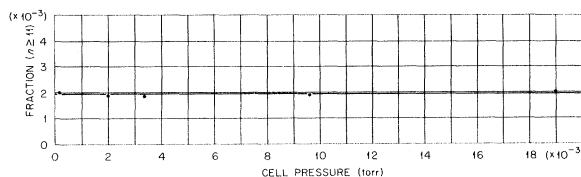
Jackson and Schiff[14] have calculated the electron-

FIG. 2. The fraction of H_2 in states $n \geq 11$ as a function of H_2-gas cell pressure.

capture cross section using the Born-Oppenheimer approximation.[15] Assuming that the electron-capture cross section can be represented for all gases in the same manner, we have

$$F_n/F_0 = a/n^3 , \tag{3}$$

where the parameter a depends on the particle energy and the target gas in the collision cell. Intense-Stark-effect[16] theory predicts that the electric field $\mathcal{E}_n$ required to ionize state n is given by

$$\mathcal{E}_n \gtrsim b/n^4, \tag{4}$$

where b is a constant that can be derived from experiment and theory. Combining (1) and (2), we obtain

$$F(\mathcal{E}) = \sum_{n=n_\mathcal{E}}^{\infty} \frac{F_n}{F_0} \simeq \int_{n_\mathcal{E}}^{\infty} \frac{a}{n^3} \, dn, \tag{5}$$

where $n_\mathcal{E}$ is the smallest principal quantum number ionized by field $\mathcal{E}$. For intense electric fields (10^4 V/cm) strong Stark splitting of the n levels exists and n can be regarded as continuous. Then, substituting (3) and (4) into (5), there results

$$F(\mathcal{E}) = 6.4 \times 10^{-4} \, a\mathcal{E}^{1/2} , \tag{6}$$

where $\mathcal{E}$ is in kV/cm.

The experimental results are shown in Fig. 3 where the integral fraction in states $n \gtrsim 10$ is plotted as a function of the square root of the applied field. The top figure is for protons from the capture collision $H^+ + H_2 \rightarrow H^* + H_2^+$ and the bottom figure is for the collision $H_2^+ + H_2 \rightarrow H_2^* + H_2^+$. For the H atoms the behavior is correctly predicted
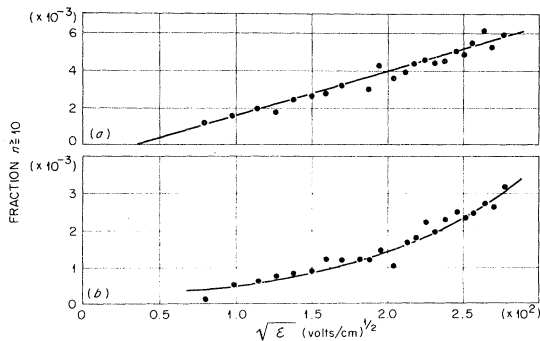

FIG. 3. (a) Fraction of hydrogen atoms in principal quantum states $n \gtrsim 10$ as a function of the square root of the applied electric field. Results are shown for 100-keV H^+ undergoing electron capture collisions in hydrogen. The capture probability is proportional to n^{-3}. (b) Fraction of H_2 in principal quantum states $n \gtrsim 10$ as a function of the square root of the applied electric field. Results are shown for 200-keV H_2^+ undergoing electron-capture collisions in hydrogen. Capture probability proportional to n^{-3}.
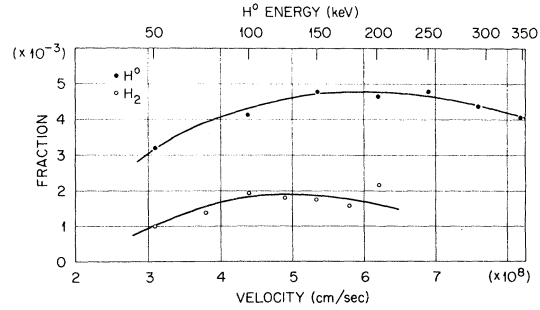

FIG. 4. Fraction of H and H_2 in excited states $n \gtrsim 11$ as a function of particle velocity. Electron-capture and dissociative collisions in H_2.

by Eq. (6). Obviously, H_2^* behaves differently than H^*. Other experimental observations are seen in Fig. 4, where the fraction in states $n \gtrsim 10$ is plotted as a function of the initial ion velocity or energy over the energy interval 50–350 keV. The fraction of H_2^* is less by a factor of 3 than that of H. It had been expected that if H_2 forms Rydberg states analogous to the H atom, then the population of H_2^* would be equal to H^*. Clearly all differences between the two are due to the properties of the H_2^+ core.

Another anomaly arises when the excited-state fractions of the isotopic mixtures of the hydrogen isotopes are compared as in Fig. 5. Plotted is the fraction in states $n \gtrsim 11$ as a function of the particle velocity for electron-capture collisions producing H_2, HD, D_2, and H_2 resulting from dissociative collisions of H_3^+ with H_2. The fraction of D_2^* was 50–100% greater than that of H_2^*, the population of H_2^* was equal to that for HD^*, while the population of H_2^* from the dissociative collision was less than that of H_2^*. The absolute yield of H_2^* from dissociation of H_3^+ was uncertain since
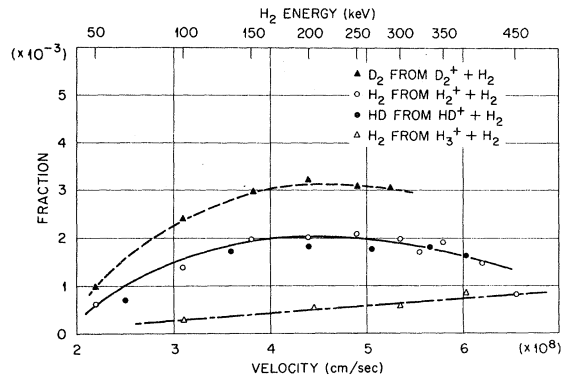

FIG. 5. Fraction of H_2, D_2, and HD molecules in states $n \gtrsim 11$ as a function of particle velocity. Excited states formed by electron-capture and dissociative collisions in H_2.
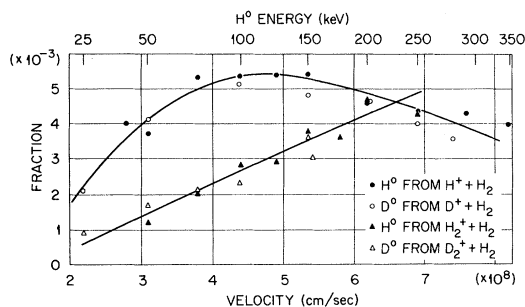
FIG. 6. Fraction of H and D in states $n \gtrsim 11$ as a function of particle velocity. Excited states formed by electron-capture and dissociative collisions in H_2.

the value depended on the angular distribution of the $H_2{}^*$. The difference between $H_2{}^*$ produced by capture and dissociative collisions suggests that the fraction in excited states was dependent on the initial vibrational-rotational state of the incident molecular ion.

To indicate that these differences arise from molecular structure, the fractions of H and D in states $n \gtrsim 11$ are plotted as a function of energy in Fig. 6. Shown are results obtained from formation of excited states by electron capture and from dissociative collisions. Within the errors of the experiment, the excited fraction of H and D are equal for the same collisional process.

Now to return to the anomalous behavior of H_2 when compared to H, the problem of the nonlinear behavior of H_2 when the fraction stripped is plotted as a function of the square root of stripping field will first be considered. Toward this end, it is necessary first to generalize the capture cross section to depend on principal quantum number n as n^{-m}. The fraction captured in quantum state n is then given by

$$F = F_n/F_0 = A/n^m. \qquad (7)$$

To determine the current at the electric field analyzer as a function of applied field, it is necessary to remember that there is both a minimum and a maximum value of n for which the molecule is stripped at the stripper. These values are denoted by n_0 and n_1, respectively. The minimum is determined by the stripper field $\mathscr{E}_s$ and is the same as that required for H:

$$\mathscr{E}_s = b/n_0^4 , \qquad (8)$$

because field stripping takes place at large values of r where the Rydberg states of H_2 and H are, for all practical purposes, identical. On the other hand, the maximum value of n is determined by the weak deflector field $\mathscr{E}_d$:

$$\mathscr{E}_d = b/n_1^4 . \qquad (9)$$

The functional purpose of the deflector voltage is to deflect incident-beam ions away from the stripper. It also has the unavoidable side effect of acting as a stripper for very weakly bound electrons. Thus, the current I after the stripper is given by

$$I = \sum_{n=n_0}^{n_1} \frac{A}{n_m} \int_{n_0}^{n_1} \frac{A}{n^m}\, dn = \frac{A}{m-1}\left(\frac{1}{n_0^{m-1}} - \frac{1}{n_1^{m-1}}\right). \qquad (10)$$

Wtih the help of (8) and (9), Eq. (10) becomes

$$I = \frac{A}{(m-1)\, b^{(m-1)/4}}\left(\mathscr{E}_s{}^{(m-1)/4} - \mathscr{E}_d{}^{(m-1)/4}\right). \qquad (11)$$

Figure 7 shows the functional relationship between the fraction with $n \gtrsim 10$ and the applied deflector field. The upper curve plots this fraction as a function of $\mathscr{E}^{3/4}$ and would be a straight line were it the case that $m = 4$. The lower curve plots this fraction as a function of $\mathscr{E}$ and would be a straight line were $m = 5$. In both plots straight lines have been drawn, using a least-squares fit to the data points. Both plots appear to fit the data and are distinct improvements over the case $m = 3$ shown in the lower curve of Fig. 3. Because of the deflector field, however, there is an additional condition that I should vanish at a field strength $\mathscr{E}_s = \mathscr{E}_d = 2 \times 10^3$ V/cm. Thus, the data indicate that electron capture into excited states of H_2 is proportional to n^{-4}, resulting in an electron-field relationship of $\mathscr{E}^{3/4}$.

Although a theoretical discussion is deferred to a later section, it is necessary at this point to anticipate part of that discussion, in order to avoid confusion. It will be noticed, in the foregoing, that in some aspects, Rydberg states of H_2 were
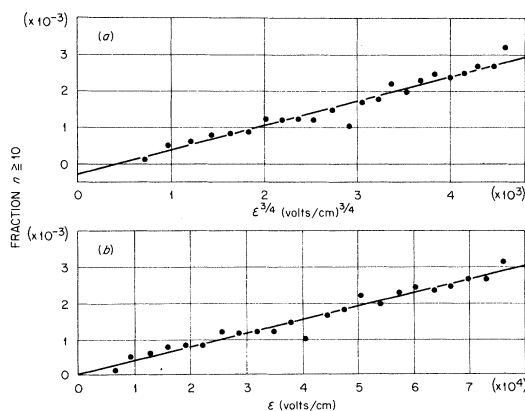

FIG. 7. (a) Fraction of H_2 in principal quantum states $n \gtrsim 10$ as a function of applied electric field to the $\frac{3}{4}$ power. 200-keV $H_2{}^+$ in H_2. Capture probability proportional to n^{-4}. (b) Fraction of H_2 in principal quantum states $n \gtrsim 10$ as a function of the applied electric field. 200-keV $H_2{}^+$ in H_2. Capture probability proportional to n^{-5}.

considered to be practically identical to Rydberg states of H, while the two were considered to differ in other aspects. In particular, H_2 and H were assumed to behave identically in the field-stripping process, but not in the electron-capture process. To understand the differences and similarities between high-n Rydberg states of H_2 and H, it is necessary to notice that the electric field produced by the H_2^+ core in the Rydberg states of H_2 approaches the Coulomb field produced by a proton for large values of r, but deviates strongly from a Coulomb field for small values of r. Thus, those phenomena, such as field stripping, which depend only on the core field at large values of r are expected to be similar for H_2 and H. On the other hand, the charge-exchange pickup process will be shown to depend most strongly on the incident-ion field at small values of r, thereby implying substantial differences between the electron-capture cross sections for H_2^+ and H^+.

However, before concluding that the capture cross sections for H_2^+ and H^+ are appreciably different, it is necessary first to consider alternative explanations as to why the fraction of H_2 excited neutrals might be less than that for H. One possible explanation is the process of predissociation in which the electron is captured by the H_2^+ ion into a level whose potential curve crosses a repulsive level, thereby leading to two H atoms. These capture events are, however, soft collisions which should perturb the vibrational structure of the H_2^+ core only slightly. Thus, predissociation should be a minor contributor to the loss of H_2. Apparent loss of H_2 could be manifested in the process of electric field stripping of the H_2 molecule, and then while the H_2^+ ion was still in the region of the intense field of the stripping cell it could undergo electric field dissociation of the uppermost $v = 17$ and 18 vibrational levels. This effect is approximately an order of magnitude less than the loss observed in the present experiment.

More pertinent to the loss of excited H_2 is the process of autoionization. Autoionization in molecules was first observed by Beutler and Jünger[6] in 1936. During the past few years photoionization cross-section measurements of Cook et al., Dibeler et al., and Chupka et al.[7] clearly demonstrated the existence of the autoionizing states in the hydrogen molecule. In essence the autoionization process can be understood as follows: The ion core of the Rydberg state can exist in any one of the vibrational-rotational states characteristic of the hydrogen molecular ion. When energetically allowed the ion core can give up some of its energy to the outer electron and revert to a lower vibrational-rotational state. The outer electron would be ejected with a characteristic energy equal to the energy change in the core minus the binding

energy of the electron in state n. Until recently, characteristic autoionization lifetimes were thought to be $\sim 10^{-14}$ sec. Thus, one would expect that molecular states would decay by autoionization in a time short compared to the transit time between the point of formation and field ionizer. This transit time is of the order of 10^{-7} sec. What is surprising is the fact that the measured Rydberg molecular population is so great in view of the generally short-lived behavior of autoionizing states. Thus, we are forced into the position of explaining the existence of the Rydberg states (with excited cores) in the present experiment. Suffice it to say at this point, that the fact that Rydberg states of H_2 can autoionize could be a possible explanation for the reduced number of Rydberg H_2 states observed in Fig. 4. However, the effect of autoionization on the n dependence is shown in Fig. 7 and is in the wrong direction, as will be seen later.

IV. AUTOIONIZATION

Several workers[8-10] have theoretically studied the autoionization from Rydberg states of molecular systems due to a coupling of vibrational energy in the ionic core to the outer Rydberg electron. In particular, Russek et al.[8] have calculated the autoionization lifetime by taking advantage of the analogy of the ionic core of a molecule in a high Rydberg state with an atomic nucleus and of the analogy of the autoionization process with the internal conversion process in nuclear physics. The energy difference between the ground and first excited electronic states of the ionic core is large compared with the energy difference between the Rydberg levels for high n. Therefore the effect of the outer electron was neglected in determining the core electronic structure. However, the deviation from pure Coulombic form of the interaction potential between the core and outer electron can both mediate autoionization transitions and perturb the energy levels of nonautoionizing outer-electron states from a $1/n^2$ sequence. This shift is similar to the shift in energy levels produced by an ordinary nucleus which has a magnetic and a quadrupole moment.

The autoionization process was formulated in terms of techniques used to determine internal-conversion coefficients in nuclear physics. As is well known for this process, the excited nucleus interacts directly with one of the atomic electrons, gives up its excitation energy to that electron, and reverts to a lower state. The Hamiltonian for the molecule in a Rydberg state can be written as

$$H(\vec{r}, \vec{R}) = H_c(\vec{R}) + H_e(\vec{r}) + V(\vec{R}, \vec{r}), \qquad (12)$$

where $\vec{r}$ is the radius vector from the center of ion-

core mass to the outer electron, $\vec{R}$ is the internuclear separation of the core, H_c is the Hamiltonian of the ion core, H_e is the Hamiltonian of the outer electron with unit nuclear charge, and $V(\vec{R}, \vec{r})$ is the perturbing potential, i.e., the difference between a Coulomb potential and that due to the H_2^+ core. This term is expanded in a multipole series. The term $V(\vec{R}, \vec{r})$ in general includes a nonstatic dipole contribution varying as r^{-2} and a quadrupole contribution varying as r^{-3}. The monopole term was included as part of H_e. A polarization term describing polarization of the core by the outer electron varies as r^{-4} and was neglected. Exact wave functions describing the electronic, rotational, and vibrational states were used to determine the eigenvalues or energy levels of the unperturbed states. The transition rate per unit time was found to be given by

$$W = 2.5 \times 10^{17} \times |M_{e1}|^2 \times |M_c|^2$$

$$\times |\text{Clebsch-Gordan coefficients}|^2,$$

where M_{e1} is the electronic matrix element for a particular transition and M_c is the core matrix element for a particular transition. These transition rates have been calculated for H_2 and HD up to $n = 14$. H_2 with its inversion symmetry has only a quadrupole moment; however, HD has a nonstatic or instantaneous dipole moment as well as a quadrupole moment; thus the lifetimes should be shorter for HD.

The theoretical studies of Russek *et al.* can be summarized as follows: (i) Transition rates in which there are no changes in electronic angular momentum are much faster than those with change in angular momentum. (ii) All states with $l > 0$ decay in a time short compared with the transit time of the particle from point of formation to the electric-stripping region. Thus, only states with $l = 0$ or s states are measurable. (See, however, Sec. VI, in which more recent theoretical results are reviewed negating this last contention.) (iii) Fast transition rates require a small change in the vibrational quantum number. Excited-state lifetimes governed even by $\Delta v = 1$ transitions have lifetimes such that they may be observed experimentally. (iv) Lifetimes of autoionizing states vary as n^3. (v) Transition rates are insensitive to the rotational quantum state of the core. (vi) HD transition rates are two orders of magnitude faster than those for H_2. Some autoionization lifetimes are comparable to experimental transit times, which suggests that by varying the transit time these lifetimes may be observed.

The generalization of Eq. (10) required if autoionization can occur between the times of electron capture and detection is

$$I = \int_{n_0}^{n_1} \frac{A}{n^m} e^{-\lambda n t} \, dn = \int_{n_0}^{n_1} \frac{A}{n^m} e^{-ct/n^3} \, dn, \qquad (13)$$

if it is accepted that autoionization lifetimes vary as n^3. In general, this integral cannot be evaluated for an arbitrary value of m, but it can be approximated by a Taylor expansion

$$I \simeq \frac{A}{m-1}\left(\frac{1}{n_0^{m-1}} - \frac{1}{n_1^{m-1}}\right) - \frac{Act}{m+2}\left(\frac{1}{n_0^{m+2}} - \frac{1}{n_1^{m+2}}\right)$$

$$= \frac{A}{(m-1)b^{(m-1)/4}}\left(\mathscr{E}_s^{(m-1)/4} - \mathscr{E}_d^{(m-1)/4}\right)$$

$$- \frac{Act}{(m+2)b^{(m+2)/4}}\left(\mathscr{E}_s^{(m+2)/4} - \mathscr{E}_d^{(m+2)/4}\right). \qquad (14)$$

The second term in Eq. (14) subtracts from the first. Thus, given that electron capture varies as n^{-m}, then downstream from the capture process the curve of I vs $\mathscr{E}_s^{(m-1)/4}$ increases less rapidly than a straight line. Therefore, as pointed out earlier, were the capture process for H_2^+ described by $m = 3$ as is the case for H^+, then autoionization alone could not possibly account for a linear relationship between I and $\mathscr{E}^{3/4}$. The variation of I with $\mathscr{E}$ would rise slower than $\mathscr{E}^{1/2}$, not faster.

V. ELECTRON CAPTURE

The above discussion would tend to point to the electron-capture process as being responsible for the difference between H_2 and H in excited-state fractions.

From the earliest papers in electron capture by protons,[17] it was realized that the n^{-3} dependence of electron capture depends on the fact that at high energies, capture is almost entirely to $l = 0$ states. Thus, rapid autoionization of $l > 0$ states would not be expected to appreciably affect the excited-state fractions in H_2, unless the capture process for H_2^+ differs significantly from that for H^+. That this is the case is indicated by several aspects of the capture process: (a) A major point made by Jackson and Schiff[14] in discussing electron capture by protons is that the nucleus-nucleus repulsive term makes a major contribution to the electron-capture cross section. Far away from the proton which does the capturing, the sum of the potential-energy terms of both constituents of the target hydrogen atom with the incoming proton vanishes as r^{-2}. This has the effect of making the preponderant contribution to the Born matrix element come from regions near the capturing proton. (b) Even without the contribution of Jackson and Schiff, Oppenheimer[17] found that capture is almost entirely to s states, which alone of all angular momentum states have appreciable density at the nucleus. (c) The capture cross section varies as n^{-3}, precisely the factor which determines s-state density

at the nucleus.

Thus capture predominantly takes place in the region in which H_2^+ and H^+ differ significantly. Considering that capture does take place near the nucleus, it follows that in H_2^+ the capture would occur near one or the other proton in the H_2^+ core. It would capture to an s state relative to that proton which is not a pure s state relative to the center of mass of the H_2^+ core. It will, with varying probabilities, be in higher-angular-momentum components (which autoionize rapidly) as well as in s states. After the higher-angular-momentum components autoionize, only the s-state fraction is left. As a consequence, the excited-state fraction of H_2 should be lower than that for H in any experiment that measures this fraction in times long compared to 10^{-11} sec after formation.

VI. AUTOIONIZATION LIFETIMES

The theoretical calculations of Russek $et\ al.$[8] indicated that the autoionization lifetimes for molecular states were comparable to transit times and suggested that by changing the transit time these lifetimes may be observed. Also, theory predicted lifetimes of HD and H_2 to be vastly different. The obvious way to change the transit time is to increase or decrease the particle velocity; however, since the electron capture into a particular excited state is velocity dependent, it was necessary to maintain a fixed or constant velocity. Arrangements were made to manually move the gas collision cell along the beam axis so that the particle transit time was changed from (4.2 to 10.5) $\times 10^{-8}$ sec for 200-keV H_2^+ particles. Using dc detection techniques it was necessary to subtract two integral fractions at fields $\mathscr{E}_1$ and $\mathscr{E}_2$ to determine the population of state n_i. The subtraction of two large numbers resulted in large errors and erratic behavior for the state population. By taking the slopes of the fraction vs $\mathscr{E}^{3/4}$ better statistics were obtained. The slopes a for H_2 and HD as a function of transit time are shown in Fig. 8. The measured lifetimes are an average lifetime for all states $n \geq 10$ and are essentially equal for HD and H_2, whereas the theoretical prediction of Russek $et\ al.$ was for the lifetime of HD to be two orders of magnitude less for HD than H_2. To compare the H_2 measured average lifetime to that predicted from autoionization and radiative decay, the population of each state was weighted with the capture probability, and the time for the aggregate curve to decrease to its $1/e$ point was taken as the decay time expected for a mixture of states. This procedure resulted in an average lifetime for states $n \geq 10$ of 4 μsec for radiative decay in a field-free region[3]; 1.2 μsec for autoionization of H_2 was predicted by Russek $et\ al.$[8] The average measured lifetime was 3.3 $\times 10^{-7}$ sec approximately a factor

of 4 less than predicted. In addition, the measured lifetimes changed from day to day by a factor of 2–3.

In a more recent paper Berry and Nielsen[18] have recalculated the autoionization rate using perturbed-stationary-state theory. They have found that (a) the monopole potential is the dominant contribution to the electronic-vibrational coupling; (b) lifetimes are proportional to n^3; (c) transition rates are greatest for $\Delta v = 1$ transitions; (d) $v = 5 \to 4$ transition rates of $np\sigma$ states of H_2, HD, and D_2 with $n = 10$ are (8, 6.5, and 4.9) $\times 10^{11}$ sec^{-1}, respectively; (e) for high-n states, $n > 8$, autoionization dominates predissociation. With these more recent calculations we are still unable to explain the lifetimes (Fig. 8) and the relative populations of H, H_2, HD, and D_2 (Figs. 4 and 5). Since Berry and Nielsen make the same physical assumptions as do Russek $et\ al.$, but treat the monopole contribution to the autoionization interaction more exactly, their results must supersede the results of Russek $et\ al.$ insofar as the lifetimes of s states are concerned. More recently, Faisal[19] has shown that the internal-conversion model of Russek $et\ al.$ yields the same results for the lifetimes as those obtained by Berry and Nielsen, if the monopole term is treated exactly. As it now stands, the common model used in both papers predicts (i) lifetimes for s states of H_2 to be short compared to transit times and (ii) lifetimes of H_2 and HD to be comparable. The latter prediction is, indeed, borne out by experimental observation. The former prediction is most certainly not. If that prediction were correct, it would mean that virtually no Rydberg states of H_2 should be seen at all. The fact that experiment contradicts the predictions of the model strongly indicates that the model must in some way be amended to take care of something so far
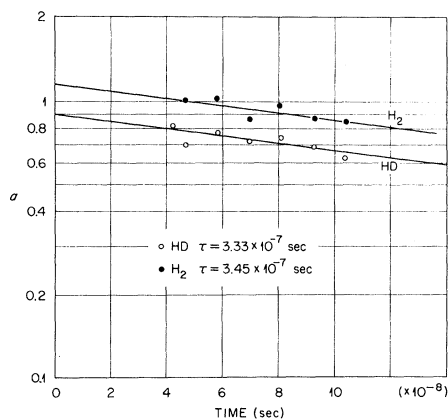

FIG. 8. Slope a of the curve F vs $\mathscr{E}^{3/4}$ as a function of H_2 and HD transit time. a is proportional to excited-state fraction.
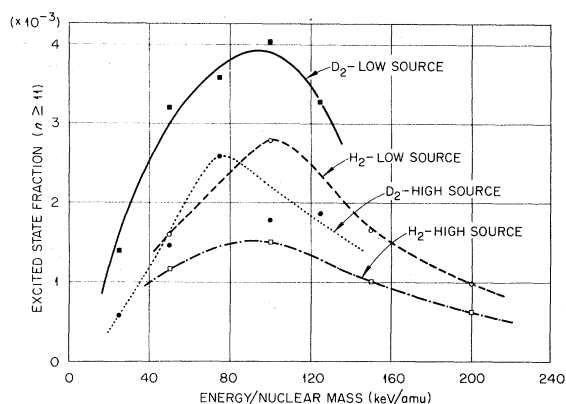
FIG. 9. Fraction of H_2 and D_2 in principal quantum states $n \geqq 11$ as a function of particle energy. Shown are the state populations for "low-source" and "high-source" conditions.

missing.

VII. POPULATION OF H_2 AND D_2

Throughout our measurements of the excited states of hydrogen molecules we have found that the population of the highly excited n states of D_2 has been considerably greater than that for H_2. This apparent anomaly can be partially explainable on the basis of available energy to promote the autoionization process. If the $n = 11$ state is taken as an example it is known that the orbital-electron binding energy is 0.113 eV so that when the H_2-ion core undergoes a spontaneous transition from one vibrational level to the adjacent lower level ($\Delta v = 1$), then at least 0.113 eV of energy must be available to autoionize the $n = 11$ level. Examining the vibration structure of H_2 reveals that any vibrational transition up to and including the $v = 11 \rightarrow 10$ transition supplies sufficient energy to autoionize the $n = 11$ state. Higher vibrational quantum states are much slower to autoionize as insufficient energy is available from a single vibrational jump. However, it is known that the number of vibrational states of H_2 is 19, while for D_2 the number of states is 27. Since the potential-well depth is the same for H_2 and D_2, the energy-level spacing is less for D_2 than for H_2. By taking the Franck-Condon overlap integrals of the wave functions, the expected population can be calculated for the various vibrational states.[20] This is valid only if the assumption is made that the vibrational-level distribution remains the same as that of the H_2^+ formed in the ion source and does not change in the electron-capture collision. Summing the relative populations of the vibrational states above $v = 11$ for H_2 and $v = 12$ for D_2 we find the relative state population that is stable against autoionization is 0.0193 for H_2 and 0.05951 for D_2. Thus the

number of states stable against the $n = 11$ autoionizing transition is a factor of 3 greater for D_2 than for H_2. From Fig. 5 it is seen that the population of excited D_2 is approximately 1.5 times greater than that of H_2.

VIII. ION-SOURCE EFFECTS ON LEVEL POPULATION

With the use of the PIG-type ion source the absolute fraction of particles in highly excited states changed erratically from day to day. In Fig. 9 results are shown for the excited fraction plotted as a function of the energy per unit nuclear mass for both H_2 and D_2. The source parameter has been figuratively described as "low source" and "high source." The low-source mode can be described as minimum gas flow, anode to cathode potential less than 500 V, and low discharge current. Under these conditions single collisions prevailed in the ion-source region. The high-source mode consisted of high operating pressure, large discharge currents, and multiple collisions in the source. Operation in the low-source mode should produce H_2^+ in vibrational states as predicted by the Franck-Condon principle. In the high-source mode the same distribution, but with a higher average vibrational level, should be produced initially, but due to deactivation collisions the average vibrational-state population would be less. Thus, the fraction of particles using the low-source mode of ionization should be greater than that found for the high-source mode. Experimentally, this was confirmed, as shown in Fig. 9. The fraction of either H_2 or D_2 is nearly a factor of 2 greater for the single-collision operating conditions.

To obtain quantitative data, the PIG-type source was replaced by a filament-type source with the ionizing electrons having an energy resolution (~ 0.5 eV) determined by the temperature of the filament. The procedure was to create H_2^+ ions in low vibrational levels using electrons near the ionization threshold and then raise the vibrational-level population to an equilibrium value by increasing the electron energy. The ions were converted to neutrals and excited states determined as described previously. The results of this study are shown in Fig. 10 where the fraction in states $n \geq 10$ is plotted as a function of the ion-source-electron energy. Three curves are shown: (a) 200-keV H_2, (b) equal-velocity 400-keV D_2, and, for comparison, (c) 200-keV H beam. The abscissa scale was calibrated by determining the onset of helium ionization at 24.7 eV. For both H_2 and D_2 the fraction decreases rapidly as the electron energy or average vibrational level increases from the threshold at 15.7 eV. Again the fraction in states $n \geqq 10$ for D_2 was greater than that of H by a factor of 1.3 for higher electron energies and 1.5 for
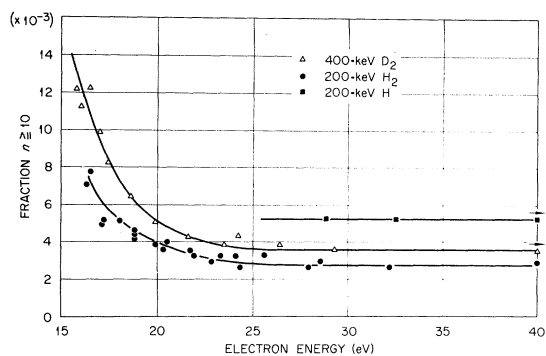
FIG. 10. Fraction of excited states $n \gtrsim 10$ for equivelocity D_2 and H_2 as a function of the electron energy in the ion source. Also shown for comparison are values obtained for 200-keV hydrogen atoms.

FIG. 11. Excited-state fraction $n \gtrsim 10$ of H_2 as a function of the electron bombarding energy for two ion-source pressures.

electron energies less than 25 eV.

To ensure that only single collisions were occurring in the ion source the pressure was increased from the normal 1.2×10^{-4} Torr to 3.6 $\times 10^{-4}$ Torr. The results are shown in Fig. 11, where the fraction in states $n \gtrsim 10$ is plotted as a function of electron energy. Results are indistinguishable for the two pressures.

The data in Figs. 10 and 11 are juxtaposed to the results one would expect if the lower vibrational levels were decaying by autoionization and the upper vibrational levels were stable by virtue of energy considerations. One supposition can be made in that the present theory and thinking of autoionization and concepts of molecular Rydberg states are inadequate to explain the present results. For example, the polarization potential in the electronic-vibrational coupling has been assumed to be negligible, since the polarization varies as $1/r^4$, which falls off much faster than the dipole term. However, the coefficient of this term can be large, giving rise to a large polarization potential. With polarization the binding energy of the orbital electron increases as the internuclear separation increases. Estimates have been made that corrections as great as a few tenths of a volt should be made to the Rydberg energies. Thus, for low vibrational states one would expect the binding energy for H_2 and H to be the same; therefore the fractions of H_2 and H stripped would be equal. At higher vibrational states (increased internuclear separation) the Rydberg electron in H_2 would be more strongly bound than the corresponding state in H, and the fraction of H_2 ionized by the electric field would therefore be less than that of H. In addition to the increased binding energy, the lifetimes of the Rydberg states would be longer, and more vibrational states would be stable against autoionization.
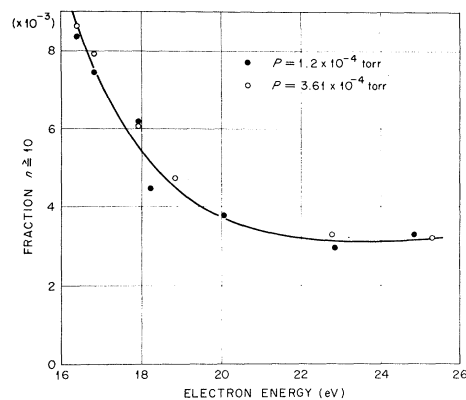
The data displayed in Fig. 10 indicate that the

variation in lifetime from day to day was probably the result of changes in the relative population of the H_2^+ coming from the source. Without great care it was impossible to restart the ion source under the same conditions that it operated in the previous day.

IX. STATE MIXING

Since the more exact calculations of Berry and Nielsen[18] on the adiabatic breakdown formulation and Faisal[19] on the internal-conversion formulation, it is now known that from either approach to the common model, the monopole contribution to the autoionization interaction is sufficiently strong that autoionizing s states will have lifetimes commensurate with those of p states. However, during the time that the experimental data were being taken, this was not yet known. As a consequence, a state-mixing experiment was undertaken which probably would not have been attempted if the present understanding of the theory were available. In order to motivate the experiment, it is necessary to consider it in the historical context.
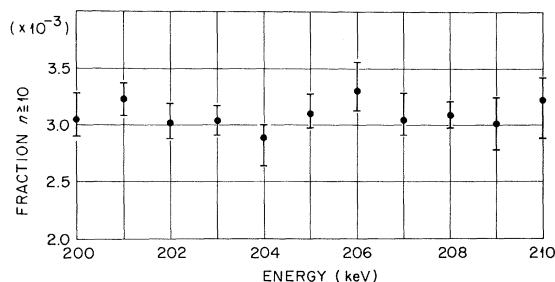

FIG. 12. Oscillations produced by ns, np state mixing in the deflector-region electric field. Plotted is the fraction of H_2 in states $n \gtrsim 10$ as the accelerator voltage is increased in discrete steps.
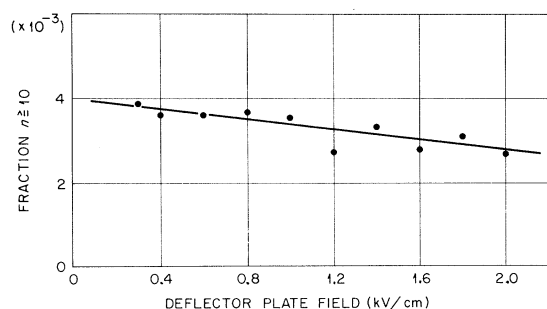
FIG. 13. Influence that the deflector-region electric field has on the excited-state fraction $n \gtrsim 10$ of 200-keV H_2.

According to Russek et al.,[8] the predicted lifetimes of the ns and np states were of the order of 10^{-7} and 10^{-11} sec, respectively, which suggested that only s states had lifetimes sufficiently long for experimental observations. Consequently, the beam that enters the electric field just outside the gas cell will be mainly composed of ns states. State mixing would then take place in the first electric field region; the probability of being in the ns state oscillates (ideally) between 1 and 0. However, each time the excited molecule was in the np state a probability exists that it would decay by autoionization. After the beam left the electric field region, it would still be a mixture of long-lived s states and short-lived p states, with the percentages of s and p states dependent on the transit time in the electric field. In principle this percentage could be changed by changing the energy of the incident particle, thereby changing the transit time. A beating between the s and p states should then be observable by looking for maxima and minima in the excited-state fraction as a function of the initial accelerating energy. The time between the peaks of the oscillating excited-state fraction would be given by

$$\Delta T = -\tfrac{1}{2} d (M/e V_1^3)(V_2 - V_1), \tag{15}$$

where d is the length of the deflection plates used to produce the electric field, V_1 and V_2 are the energies of successive maxima of the fraction, M is the H_2 mass, and e is the electronic charge.

This ΔT, or beating time, is also equal to

$$\Delta T = 2 \pi \hbar/(E_p - E_s), \tag{16}$$

where $E_p - E_s$ is the energy difference between the two states and varies linearly with the applied electric field.

The fraction of H_2 in states $n \gtrsim 10$ is plotted as a function of accelerator voltage in Fig. 12. The error bars represent the scatter and reproducibility of the data. Although the evidence is not conclusive, an oscillation appears to be present with maxima occurring at approximately 5 keV. The data are reproducible with time. With these maxima occurring at 5 keV the beating time is 2.2×10^{-10} sec, resulting in an energy separation between the s and p states of 4.9×10^{-5} eV. The energy separation for the s and p states ($n \gtrsim 10$) in the field-free region is less than 8×10^{-7} eV.

In addition to the beating observable with particle energy, the deflector-plate electric field should also change the s-p mixture leaving the field region. In Fig. 13 the fraction of H_2 $n \gtrsim 10$ is plotted as a function of the field applied to the deflector plates. The fraction decreases by 35% as the deflector field is increased by 0.3 to 2×10^3 V/cm. This field was sufficient to ionize only those states $n \gtrsim 24$. The fraction of states $n \gtrsim 10$ for hydrogen atoms was essentially independent of this deflecting field.

These two measurements indicate qualitatively that state mixing is taking place in the deflector field. Thus contrary to the current status of the theory, it appears that there are long- ($\sim 10^{-7}$ sec) and short-lifetime states ($\sim n^{-11}$ sec) and that these can be mixed by an external electric field. Obviously, more detailed quantitative measurements must be made to sort out the various competing processes.

†Operated by Union Carbide Corp. for the U. S. Atomic Energy Commission.

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Highly Excited States of Hydrogen Molecules. II. H_3 †

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(Received 1 November 1971)

Highly excited principal quantum states of H_3 molecules formed by electron-capture collisions of H_3^+ in H_2 gas have been observed. An intense electric field was used to strip the orbital electron from the excited H_3. Comparisons with data obtained with excited H_2 indicates that the fraction of H_3 ionized was proportional to the $\frac{3}{4}$ power of the electrostatic-stripping field.

INTRODUCTION

During the past several years in our laboratory we have been studying the properties and behavior of the highly excited principal quantum states of the diatomic hydrogen molecule H_2. We have characterized these states as Rydberg states analogous to the hydrogen atom in which the stable molecular ion H_2^+ forms an ionic core with the orbital electron sufficiently removed from the nucleus such that it moves in a field of unit charge. These studies are described in detail in the preceding paper[1] hereafter referred to as I. This concept of the highly excited states of H_2 has lead to the prediction that any molecule which has a stable ionic core should exist in high principal quantum states. The molecular configurations of H_3 and HeH are examples of molecules that form repulsive ground electronic states. Early calculations of potential-energy surfaces for the various H_3 nuclear configurations (linear and triangular) have been made by Hirschfelder *et al.*[2] and more recent calculations[3] indicate the absence of a potential minimum or well for the ground electronic state. However, it is known both experimentally and theoretically that the molecular ion H_3^+ exists, as it is formed in copious quantities in ion sources by the interchange reaction: $H_2^+ + H_2 \rightarrow H_3^+ + H$. In this paper we describe the measurements to test our hypothesis by

accelerating H_3^+ to high energies, forming H_3^* by electron capture in a hydrogen-gas cell, and detecting H_3 by the method described in I.

The existence of H_3 has been studied by Devienne[4] using two methods: (i) the merging of a H_3 beam, which was formed by electron capture in collisions of H_3^+ with H_2; (ii) the ionization of H_3 by collisions in a deuterium-gas cell. In both methods the resulting H_3^+ was momentum analyzed and detected. His results are suprising in that a large current of H_3^+ was detected in relation to peaks of H_2^+ and H^+ formed by either H_3^+ dissociative collisions or electron-capture collisions into repulsive levels in the initial collision cell. Gray and Tomlinson[5] in investigating the HeH system using a method similar to Devienne found HeH molecules with a lifetime of at least 10^{-8} sec. They also searched for the existence of D_3 and HD and were unable to detect a signal. Using these methods neither of these two investigations were capable of knowing whether or not the H_3 or D_3 existed in a bound excited state or in the ground state. The present experiment measures only the relative fraction of H_3 in principal quantum states $n \geq 10$ by stripping the orbital electron in an intense electric field.

APPARATUS AND METHOD

The apparatus and methods used are described in detail in I. Briefly, ions are formed in an