[7]V. H. Dibeler, R. M. Reese, and M. Krauss, J. Chem. Phys. 42, 2045 (1965); G. R. Cook and P. H. Metzer, J. Opt. Soc. Am. 54, 968 (1964); W. A. Chupka and J. Berkowitz, J. Chem. Phys. 48, 5726 (1968).
[8]A. Russek, M. R. Patterson, and R. L. Becker, Phys. Rev. 167, 17 (1968).
[9]J. N. Bardsley, Chem. Phys. Letters 1, 229 (1967).
[10]R. S. Berry, J. Chem. Phys. 45, 1228 (1966).
[11]A. C. Riviere and D. R. Sweetman, in *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases, Paris*, 1963, edited by P. Hubert (S. E. R. M. A., Paris, 1964), p. 105.
[12]J. A. Ray and C. F. Barnett, IEEE Trans. Nucl. Sci. 16, 82 (1969).
[13]R. N. Il'in, V. A. Oparin, E. S. Solov'ev, and N. V. Fedorenko, Zh. Tekhn. Fiz. 36, 1241 (1966) [Sov. Phys. Tech. Phys. 11, 921 (1967)].
[14]J. D. Jackson and H. Schiff, Phys. Rev. 89, 359 (1953).
[15]J. R. Oppenheimer, Phys. Rev. 31, 66 (1928).
[16]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Springer, Berlin, 1957).
[17]J. R. Oppenheimer, Phys. Rev. 31, 349 (1928).
[18]R. S. Berry and S. E. Nielsen, Phys. Rev. A 1, 395 (1970).
[19]F. H. M. Faisal, Phys. Rev. A 4, 1396 (1971).
[20]G. H. Dunn, J. Chem. Phys. 44, 2592 (1966).

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Highly Excited States of Hydrogen Molecules. II. H_3 †

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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

oscillating-electron- (PIG-) type discharge and accelerated to an energy of 300 keV by a conventional accelerator. The energetic ions were passed through a momentum analyzer and the desired species H_3^+ was incident on a differentially pumped H_2-gas collision cell maintained at a pressure of the order of 10^{-4} Torr which ensured only single collisions in the gas cell. Upon emerging from the collision chamber the beam was passed through a set of electrostatic deflection plates to remove the charged particles. Detection of H_3 was by means of an electric-field-stripping cell which removes the highly excited electron from the H_3^+ nucleus. After the H_3^+ particles emerged from the stripping cell they were passed through another set of electrostatic deflection plates and detected by a high-resolution silicon-barrier detector. The fraction of excited H_3 was determined as a function of electric field applied in the electrostatic-stripping cell.

Passing a H_3^+ beam through a gaseous collision chamber results in the following collisional processes:

$$H_3^+ + H_2 \rightarrow H_3^* + H_2^+ \quad (1)$$

$$\rightarrow H_2 + H + H_2^+ \quad (2)$$

$$\rightarrow 3H + H_2^+, \quad (3)$$

$$H_3^+ + H_2 \rightarrow H_2^+ + H + H_2, \quad (4)$$

$$H_3^+ + H_2 \rightarrow H_2 + H^+ + H_2, \quad (5)$$

$$H_3^+ + H_2 \rightarrow 2H + H^+ + H_2 \quad (6)$$

$$\rightarrow 2H^+ + H + H_2 + e \quad (7)$$

$$\rightarrow 3H^+ + H_2 + 2e. \quad (8)$$

Not listed are the ionization collisions of the H_2 target molecule and vibrational and rotational excitation of the projectile and target. Reaction (1) is a direct electron-capture collision forming H_3 whose lifetime is greater than the transit time ($\sim 10^{-7}$ sec) of the particles between the collision cell and stripping ionizer. The capture of H_3^+ in H_3 into repulsive states (reactions 2 and 3) produces neutral particles that are undistinguishable from the dissociative-collision products of reactions 4–7. The initial energy E_0 of the H_3^+ ion is equipartitioned such that the collision products, both ions and neutrals, have energy $\frac{1}{3}E_0$ and $\frac{2}{3}E_0$. The silicon-barrier detector used was capable of discriminating the neutral H_3, H_2, and H formed; however, at the energy used in this measurement the cross section for neutral production via reactions 2–7 is much greater than the cross section for production of quasistable H_3. Thus, the number of H atoms at $\frac{1}{3}E_0$ and H_2 molecules at $\frac{2}{3}E_0$ far exceed the countable H_3 which gives rise to a probability that H_2 and H will arrive at the detector in coincidence. Another difficulty of determining the total flux of H_3 involves the dynamics of the collisional processes. Ideally, the total flux of H_3 formed in electron-capture collisions could be determined easily since any capture into repulsive levels would produce $H_2 + H$ or 3H which would arrive at the detector position in coincidence and give rise to a pulse height corresponding to a particle of energy E_0. However, in the spontaneous dissociation of H_3^*, internal molecular potential energy is converted into kinetic energy with spatial symmetry in the center of mass or moving frame of reference. Only those particles (H and H_2) scattered in the near forward or backward direction will pass through the collimating apertures of the ionizer which has an angular acceptance of 0.09 mrad. Thus, the stored potential energy converted into transverse energy in the laboratory system of coordinates prevents the detection of the total H_3 molecules formed by the capture process. Since we were unable to determine the flux of H_3 neutral particles formed, we measured the H_3^+ particle flux as a function of the field on the stripping cell and then normalized to results obtained for the fraction obtained when H_2 at the same velocity was the incident particle.

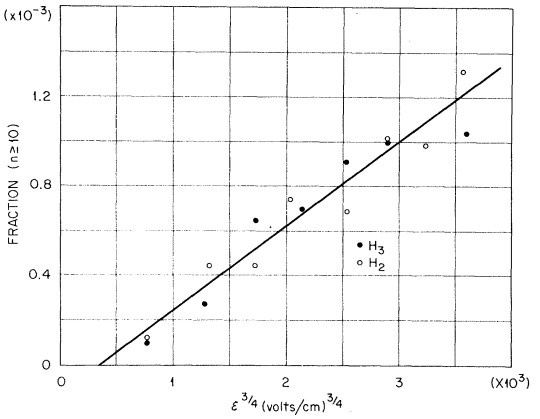

FIG. 1. Fraction of $H_2(n \geq 10)$ and $H_3(n \geq 10)$ formed by electron capture of molecular ions in hydrogen. The fraction is plotted as a function of the $\frac{3}{4}$ power of the applied electric field. Energy of H_3^+ is 200 keV; energy of H_2^+ is 133 keV.

RESULTS AND DISCUSSION

Results obtained from the measurements are shown in Fig. 1 where the fractions of H_2 and H_3 ($n \geq 11$) are plotted as a function of $\mathcal{E}^{3/4}$. The electric field dependence of $\frac{3}{4}$ power results from considerations of the probability of electron capture into state n and is discussed in detail in I. Both H_2 and H_3 exhibit a linear relationship with $\mathcal{E}^{3/4}$. Since the H_3^+ current as a function of $\mathcal{E}$ was of the same order of magnitude as that of the H_2^+ current

formed, the results are normalized such that the fraction of H_3 in high-n states is of the order of 10^{-3}. If the H_3^+ counting rate at electric field $\mathcal{E}_n$ was compared to the counting rate of H_3 as detected by the neutral-particle counter then the fraction $H_3(n \geq 11)/H_3(\text{total})$ was approximately 1. Obviously, most of the H_3^+ capture collisions were into repulsive states of H_3, such that the neutral particles did not arrive at the energy-sensitive detector.

The probability that a HD^+ could be contaminating the H_3^+ prevents one from concluding absolutely that excited states of H_3 exists. Both HD and H_3 exctied states would behave similarily in the electrostatic-stripping field. Several precautions were taken to minimize any contamination of the H_3^+ beam by HD^+. An ion source was used that had not been used previously with deuterium gas such that the only source of HD came from the natural abundance of D_2 in H_2. Also, the ion-source pressure was maintained at a high value to enhance the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$. Pulse-height analysis of the neutral beam by the silicon-barrier detector indicated only a small flux of particles (HD and H_3) with full acceleration energy. The pressure in the hydrogen collision cell was increased to several microns such that the pulse-height peak at E_0 disappeared first, and then at higher values the pulse-height peak at $\frac{2}{3} E_0$ disappeared indicating that all the diatomic and triatomic particles were dissociated in the gas cell. The same disappearance of particles was observed when the charged-particle detector was set to receive only particles at $\frac{2}{3} E_0$. If a measurable quantity of D or HD was contributing to the signal then the pulse height at $\frac{2}{3} E_0$ would not have disappeared with increased H_2 pressure. These precautions and the results obtained demonstrate with a high degree of confidence that the H_3^+ signal obtained as a function of $\mathcal{E}$ was not HD^+.

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[1]C. F. Barnett, J. A. Ray, and A. Russek, preceding paper, Phys. Rev. A 5, 2110 (1972).

[2]J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. 4, 121 (1936); J. O. Hirschfelder, *ibid.* 6, 795 (1938).

[3]I. Shavitt, R. M. Stevens, F. L. Menn, and M. Korphes, J. Chem. Phys. 48, 2700 (1968).

[4]F. M. Devienne, Entropie 24, 35 (1968); Compt. Rend. 267, 1279 (1968); 264, 1400 (1967); *Sixth International Conference on the Physics of Electronic and Atomic Collisions* (MIT Press, Cambridge, 1969), p. 789.

[5]J. Gray and R. H. Tomlinson, Chem. Phys. Letters 4, 251 (1969).

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e-H Scattering by the Faddeev Approach

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1*s*-1*s* elastic and 1*s*-2*s* inelastic total cross sections for *e*-H collision have been calculated with and without exchange effects using the Faddeev formalism as developed by Sloan and Moore. We have considered the effect of coupling to 1*s* and 2*s* intermediate states. Our theoretical results have been compared with the existing experimental findings and other theoretical calculations. In the intermediate-energy region, our results for the inelastic process are found to be in close agreement with the experimental observations. Our results for both systems indicate that coupling to states other than the initial and final ones causes a reduction in the cross sections, and even up to 500 eV the effect of exchange is not negligible.

INTRODUCTION

In the theoretical study of electron-atom collision problems, the *e*-H scattering process has enjoyed the widest investigation for its simplicity. But it is still not possible to find any approximation that gives uniformly good results for all energies. The close-coupling (cc) method,[1,2] is based on an expansion of the wave function for the system into the infinite set of eigenstates of the target atom, though only a few eigenstates are considered in a practical calculation and as such the effects of higher bound and continuum states are neglected. Recently Burke *et al.*[3] have suggested a modification of the cc formalism in which the effect of the higher bound and the continuum states are included by a pseudostate expansion. Holt and Moiseiwitsch[4] have introduced a simplified second Born approximation where the coupling effects due to the higher states have been approximated by a