Experimental study of the triatomic hydrogen molecule through the collisional sequence $H_3^+ \rightarrow H_3 \rightarrow H_3^+$ undergone by fast beams in argon

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The neutralization-ionization method using two gas targets was employed to study the sequence $H_3^+ \rightarrow H_3 \rightarrow H_3^+$. The existence of long-lived states of the neutral molecule H_3 ($\tau \gtrsim 3 \times 10^{-7}$ s) is demonstrated, any ambiguity due to the presence of HD molecules being definitively removed. Dissociation cross sections of the molecular ion in argon have been measured and the dissociation cross section of the neutral molecule, the electron-capture, and the electron-loss cross sections have been estimated. The capture cross section for H_3^+ is extremely small (~ 1 b at 1 MeV) and decreases very rapidly with the velocity of the incident ion beam. It is suggested that these measured cross sections concern the formation of H_3 Rydberg states in a narrow band of n and l values.

I. INTRODUCTION

When a beam of stable H_3^+ molecular ions is sent through a gas target the electron-capture process gives rise to the production of a neutral beam of triatomic hydrogen molecules[1-3] which was observed to survive with appreciable intensity to times of flight as long as a fraction of a microsecond. The ground state of H_3 being supposed to be unstable,[4] it is admitted that the neutralizing electron is captured in long-lived Rydberg excited states.[2,3] Other stable ionic cores like He_2^+, ArH^+, and HeH^+ are known to capture electrons making up bound Rydberg states of molecules that would be unstable in their ground states. The purpose of this work was to study the formation of neutral H_3 molecules from a beam of H_3^+ and the ionization of the resulting neutral beam to regenerate an ionic H_3^+ beam.

The existence of a long-lived H_3 molecule was first reported by Devienne[1] in an experiment where a double charge exchange was reponsible for the sequence $H_3^+ \rightarrow H_3 \rightarrow H_3^+$. Three years later, Barnett and Ray[2] claimed to have identified that molecule in an experiment where the second charge exchange process was replaced by electric field ionization. However, it is not excluded that in both experiments an unavoidable contamination of deuterium in the hydrogen of the accelerator source produced much more HD^+ ions that H_3^+ ions in the last stage of the neutralization-ionization sequence. Separation of the two species cannot be accomplished by electromagnetic means. In order to circumvent this difficulty, Nagasaki *et al.*[5] looked for the D_3 molecules, but H_3 and D_3 are not exactly equivalent since significant differences between the rovibrational states of the respective cores can affect in different ways the stability of the Rydberg states formed by electron capture. By using the same successive charge exchange technique they were able to identify the neutral molecule D_3 with an estimated half-life longer than 10^{-7} s. More recently, de Castro Faria *et al.*[3] reported the observation in our laboratory of H_3 molecules by essentially the same method, their results presenting no ambiguity since H_3^+ and HD^+ were clearly distinguished from each other by their energy loss just before being detected.

Meanwhile, Herzberg[6] discovered, in a hollow cathode discharge tube through H_2 or D_2, new spectral lines in the visible region that were definitely assigned to the H_3 or D_3 molecules. In a series of posterior publications Herzberg *et al.*[7] reported and analyzed several emission bands of these triatomic molecules. These findings stimulated theoretical developments[8] that successfully described the observed rotational band spectra. It is now firmly established that the emisson band spectra due to Rydberg-Rydberg transitions in those molecules involve states derived from the $3l$ and $2l$ electron orbitals. It is not obvious that these states with relatively small principal quantum numbers are the same that are predominantly fed in the charge exchange collisions responsible for the $H_3^+ \rightarrow H_3$ neutralization process.

In the present work an attempt was done to clarify the nature of the excited molecular states present in the neutral beam emerging from a gas cell impinged on by swift H_3^+ ions. The population of the most excited states leaving the neutralization cell is probably spontaneously depleted by autoionization processes and the complete disappearance of the most weakly bound states was ensured by the presence of an ionizing electric field. The resulting long-lived H_3 neutral beam is still relatively intense even when both the incident energy and the ionizing field reach their maximum values. Nevertheless, the physical evidence is that they still correspond to high principal quantum number Rydberg states. As will be discussed in Sec. IV, they are also probably high orbital angular momentum states.

In the course of this paper analog results concerning the same charge transfer collisional sequence for the diatomic hydrogen molecule are also given. The analysis of the results will be largely founded on the comparison between

the H_2 and the H_3 cases.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

A. General arrangement

Figure 1 shows the schematic diagram of the experimental arrangement used in this study. Ionic (X^+) beams were extracted from a conventional rf source and were accelerated to energies of 133—1000 keV/amu by the 2.5-MV Van de Graaff accelerator of the Institut de Physique Nucléaire de Lyon (IPNL). After deflection through an angle of 45° with an analyzing magnet, the X^+ beam entered into the first gas chamber C_1 where electron-capture collisions with argon atoms produced fast neutral molecules (X^0) in all states of excitation. The resulting neutral species of all kinds were permitted to continue undeflected while the charged components of the beam were deflected by a magnetic field. At the exact position of the deflecting permanent magnet B it was possible to install electrostatic plates playing the same deflecting role. The emerging neutral beam was then reionized in a second gas chamber and the final charged beam was mass analyzed by a 90° magnetic spectrometer. All ions having the same energy and the same mass arrived at the solid-state detector located at the focal plane of the spectrometer. If there were more than one type of ions with the same energy and the same mass as, for instance, H_2^+ and D^+ or H_3^+ and HD^+, the different species were distinguished from each other by their energy loss in a thin (2300—5600 Å according to the incident energy) gold foil placed in front of the solid-state detector. Figure 2 shows an energy spectrum where the H_3^+ and HD^+ peaks are clearly resolved.

The incident beam was collimated by a pair of collimators, D_0 and D_1, 180 cm apart with apertures of 0.40 and 0.25 mm, respectively, before passing through the 0.8-mm entrance aperture of the first gas chamber. Before reaching C_1 the beam was intercepted by an electrically isolated fast rotating chopper which measured the incident beam current which was employed to normalize all the measurements. The second gas chamber C_2 with a 0.8-mm entrance aperture was mounted 170 cm downstream from the exit aperture of C_1. Both gas chambers were filled with argon and the gas pressure could be varied from 0.4 to 40 mTorr. Pressure and/or current could be monitored by the Rutherford scattering yield of protons by the argon atoms of the gas targets. Pumping speed coupled with the dimensions of the apertures was such that a pressure ratio of approximately 1000 was obtained across the apertures. Even when the pressure in the gas cells reached their maximum values the vacuum in the extension was kept less than 10^{-5} Torr. In normal working conditions it was at least one order of magnitude better.

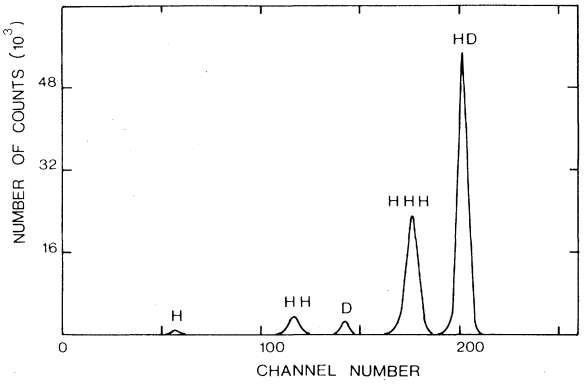

FIG. 2. Energy spectrum of particles with a 750-keV H_3^+ incident beam as seen by the solid-state detector through a 2300-Å gold foil. Three small peaks show that some fragments of the dissociation of the H_3^+ and HD^+ ions in the foil (H^+, $2H^+$, and D^+) are scattered in the foil and do not reach the detector.

The counting rates at the solid-state detector with the mass-3 beam were 2000 counts/s at 250 keV/amu and they decreased so fast that for energies higher than 500 keV/amu they were too low to permit statistically significant measurements. In some experiments counting rates as high as 10^4 counts/s were reached and fast electronics were employed. Sufficient data were accumulated in each case to reduce counting statistics to less than 5% in the most unfavorable case.

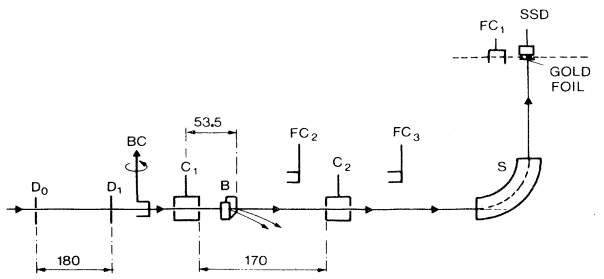

FIG. 1. Schematic diagram of the experimental setup. D_0, D_1: circular collimators. C_1, C_2: gas cells. B: deflecting magnet. S: magnetic spectrometer. SSD: movable solid-state detector. FC1: movable Faraday cup. FC2, FC3: retractable Faraday cups. BC: beam chopper. Dimensions are given in cm.

B. Role of the deflecting field

Electron capture and loss affecting swift atomic or molecular projectiles introduce only negligible changes in their longitudinal momentum so that the system composed by the analyzing magnet associated with the solid-state detector could not distinguish the beam resulting from successive charge exchanges from the unperturbed main beam of the same mass. To overcome this difficulty a deflecting field might be applied after the first gas target. However, this field had the unavoidable side effect of acting as an ionizer for very weakly bound electrons.[2] Therefore the deflecting field removed the charged species from the beam but at the same time could reduce the neutral component by field ionization. Higher the applied field, more efficient it was in its main purpose but more severe could be the destroying effect on the neutral beam.

A compromise was then searched which heavily depends on the angular divergence of the incident beam. In our investigation of the mass-2 and mass-3 molecules a permanent magnet is used to produce the deflecting field. The maximum value of B was 8.15×10^{-2} T. When a charged beam moves with velocity $\vec{v}$ in a magnetic field $\vec{B}$ it experiences a motional electric field $\vec{E}=\vec{v}\times\vec{B}$. In our case, this velocity-dependent electric field was of the order of a few kV/cm but such an electric field could account for the Stark ionization of an appreciable fraction of the neutral beam that emerged from C_1. The choice of the deflecting field and the corrections due to the presence of an energy-dependent destruction factor in the middle of the neutralization-ionization sequence of collisions deserve some specific comments.

When a stable molecular ion captures an electron in a Rydberg orbital the resulting neutral molecule may display a fairly long radiative lifetime despite its high excitation. In this long-lived state the molecule may be described as an ionic core with a single electron sufficiently far way from the core to be described by the single-particle Hamiltonian $\mathscr{H}=-\frac{1}{2}\nabla^2+V(r)$. In the presence of a static electric field $\vec{E}$ which is taken to lie along the z axis, a zE term must be added to the above Hamiltonian (atomic units are used unless otherwise indicated). The potential energy $V(r)$ is not precisely known but far outside the ionic core $V(r)$ is essentially Coulombic with unit charge, $V(r)=-1/r$. Therefore, in the presence of an electric field there are no true stationary states and the electron will inevitably tunnel through the Coulomb barrier and be carried away by the field.[9] At low fields, however, tunnelling occurs very slowly and field ionization is appreciable only for electrons with binding energies smaller than the critical value $W_c\approx-24[E(\text{kV/cm})]^{1/2}$ meV. If the simple hydrogenic model is supposed to hold in the case of a neutral molecule it may be said that all the Rydberg states with a principal quantum number greater than $n_c\simeq24[E(\text{kV/cm})]^{-1/4}$ are field ionized. This hydrogenic model is well suited to alkali-metal atoms[10] but it is expected to give only qualitative results for molecules. The reasons are at least twofold. First, it is possible that the non-Coulombic aspects of $V(r)$ are important far away from the ionic core and that a r^{-1} potential is not a good approximation even for high-n Rydberg states. Second, the ionic core is not a frozen core and energy transfer from core excitations to the Rydberg electrons is very probable.[2] Molecular ions emerging from a rf source are normally vibrationally excited. The time of flight between the accelerator source and the neutralization cell is sufficiently short ($\sim10^{-6}$ s) so that it can be expected that a large fraction of the neutral molecules are core excited. For instance, Dabrowski and Herzberg[7] observed that the interprotonic average distance measured by Gaillard *et al.*[11] using foil induced dissociation of an H_3^+ beam is somewhat larger than both the theoretical and their experimental value and they explained this discrepancy by the vibrational excitation of the beam produced by a rf source. Then the core excitation energies are expected to be comparable to the binding energy of Rydberg states even with relatively small values of n.

In order to investigate the secondary role played by the deflecting magnetic field, it was replaced by a pair of electrostatic deflecting plates that are 10.2 cm long and 0.52 cm apart. The angular divergence of the incident beam defined by the pair of collimators D_0 and D_1 was set equal to 0.35 mrad for practical reasons, mainly for beam stability and intensity considerations. Multiple scattering and molecular dissociation are responsible for a distinct increase of the divergence of the charged component of the beam transmitted through the first gas target. As a consequence, transverse electric fields of more than 1 kV/cm were required to keep the charged beam completely away from the entrance aperture of the second gas cell.

Figure 3 shows the number of H_3^+ ions counted by the solid-state detector as a function of the applied electric field. The vertical scale results from the normalization of the measurements at different energies to a common value at $E=20$ kV/cm. The steep rise of the curves at small values of the transverse field reveals the presence of an extended tail of the primary H_3^+ beam. As expected, for a higher energy a stronger field was required to reduce the effect of the tail in the same way. All curves merge into a unique one for high values of the deflecting field. This universal curve describes the attenuation of the neutral beam by field ionization. The motional electric fields corresponding to the deflecting magnetic field were calculated for each incident energy and curves like those of Fig. 3 were employed to obtain the correction factor that accounts for the velocity-dependent destruction of the neutral beam between the two gas cells. All results presented in this paper for the H_3 molecule refer to a neutral beam that would be submitted to an electric field of 20 kV/cm.

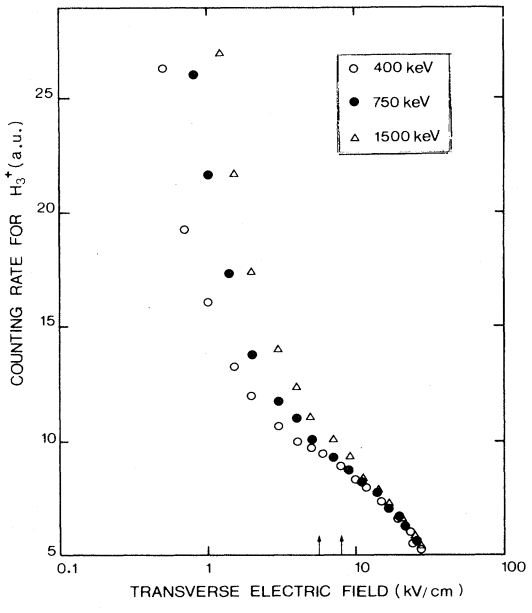

FIG. 3. Number of detected H_3^+ ions vs the transverse electric field for different energies. Curves were normalized in order to coincide at $E=20$ kV/cm. Arrows indicate the two extreme electric motional fields associated to the permanent magnet.

In doing so the correction factors for the lower and higher energies differ from each other by less than 10%. In the frame of a strict hydrogenic model such a field would imply that all Rydberg levels bound by less than 107 meV (or with $n > 11$) are field ionized.

As a necessary test to ensure that the rise of the curves of Fig. 3 for small fields was mainly due to geometrical effects and not to the contribution of short-lived H_3 molecules the deflecting field was displaced 39 cm upstream. A smaller field was then required to suppress the effects of the tail of the charged primary beam (see Fig. 4). In fact, if an important short-lived population were still present at about 10 or 20 cm from the exit aperture of the first gas cell then a larger number of final H_3^+ ions would be observed for the same deflecting field. It is worth mentioning that the HD^+ counting rate was observed to be constant in the field interval where the H_3^+ data are presented in Fig. 3.

From the measurements performed with the slowest molecules it was determined that the excited states emerging from the deflecting field have a lifetime longer than $\sim 3\times 10^{-7}$ s.

C. Neutralization-ionization sequence

Let us consider in detail the $X^+ \rightarrow X^0 \rightarrow X^+$ sequence where the neutralization process occurs in the first gas cell and the ionization process in the second one. The argon thickness in each gas cell is represented by x_i (in atoms/cm^2) with $i=1,2$. The cross sections are as follows:

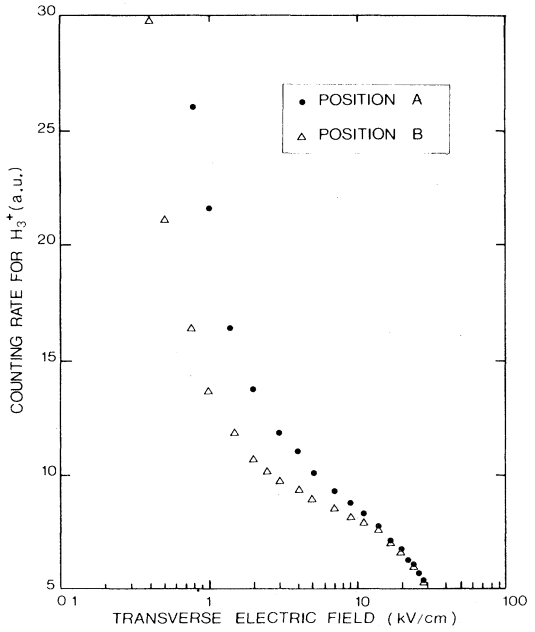

FIG. 4. Number of detected H_3^+ ions as a function of the transverse electric field. For the curve A, the center of the deflecting plates was at 53.5 cm downstream from the exit aperture of C_1. For the curve B this distance was reduced to 14.5 cm. Curves were normalized in order to coincide at $E=20$ kV/cm.

σ_c, electron capture by X^+; σ_l, electron loss by X^0; σ_d^+, dissociation of X^+; and σ_d^0, dissociation of X^0.

The probability that an incident molecular ion be neutralized after passing through C_1 is given by

$$P_{10}=\frac{\sigma_c}{\sigma_d^0+\sigma_l-(\sigma_d^+ +\sigma_c)} \times\{\exp[-(\sigma_d^+ +\sigma_c)x_1]-\exp[-(\sigma_d^0+\sigma_l)x_1]\} . \quad (1)$$

On the other hand, the probability for a molecule X^0 to emerge from the C_2 target in the ionized state X^+ is given by

$$P_{01}=\frac{\sigma_l}{\sigma_d^0+\sigma_l-(\sigma_d^+ +\sigma_c)} \times\{\exp[-(\sigma_d^+ +\sigma_c)x_2]-\exp[-(\sigma_d^0+\sigma_l)x_2]\} . \quad (2)$$

The probabilities P_{10} and P_{01} depend on both the target thickness and the projectile velocity v. The above expressions were obtained in the approximation where it was admitted that they are both numerically much less than unity. A neutral molecule produced in C_1 does not necessarily reach C_2. It can be destroyed by the magnetic deflecting field or by collision with the residual gas in the beam line. Moreover, the molecule can leave C_1 in a predissociated excited state with a short lifetime as compared with the time of flight between the two cells. All the three above-mentioned effects are velocity dependent. The field ionization by the motional field was discussed in Sec. II B and can easily be accounted for. It corresponds to the complete elimination of the neutral molecules with a Rydberg electron bound by less than a value that depends on the molecule velocity. The collisional and decay effects correspond to an attenuation of the neutral beam along its path. If we use T to represent the probability that a neutral molecule emerging from C_1 reach C_2, then the yield of the neutralization-ionization sequence may be written as

$$Y(x_1,x_2,v)=P_{10}(x_1,v)T(v)P_{01}(x_2,v) . \quad (3)$$

The vacuum between the two chambers was considered good enough and the half-lifes long enough to justify neglecting the collisional and decay effects or, at least, their v dependence in the projectile velocity interval considered. Then the velocity dependence of the transmission probability is that of the ionization by the motional field.

Of course, the cross sections are defined for a given pair of molecule and molecular ion states. If many states are involved appropriate integrals must be evaluated. In the following, the cross sections must be seen as average values over all the pairs of states involved.

Both probabilities P_{01} and P_{10} present their maximum value for the gas thickness

$$x_m(v)=[\sigma_d^0+\sigma_l-(\sigma_d^++\sigma_c)]^{-1} \times\ln[(\sigma_d^0+\sigma_l)(\sigma_d^++\sigma_c)^{-1}] \quad (4)$$

and the maximum value of the yield will be given by

$$Y(x_m,x_m,v)\equiv Y_m(v)=(\sigma_c/\sigma_l)P_{01}^2(x_m,v)T(v)\ . \quad (5)$$

For a proton beam impinging upon a thick gas target $P_{10}\rightarrow\sigma_c/\sigma_l$, where the capture and loss cross sections refer now to the processes $H^+\rightarrow H$ and $H\rightarrow H^+$, respectively. This quantity is the equilibrium neutral fraction $\Phi_0(v)$ in the atomic case. The analysis of the data will be based on the variations of the ratio $Y_m(v)/\Phi_0(v)$, where $Y_m(v)$ was given by this experiment and $\Phi_0(v)$ was found in the literature.[12]

D. Determination of σ_d^+ for H_2^+ and H_3^+

Molecular ion transmission through the first gas chamber was employed to measure σ_d^+ for H_2^+ and H_3^+ in argon. Since $\sigma_c \ll\sigma_d^+$, the transmission factor $P_{11}(x)$ is simply proportional to $\exp(-\sigma_d^+x)$ for a given velocity. Figure 5 shows the attenuation of 400-keV/amu H_2^+ and H_3^+ beams with the gas pressure. A semilog plot of each set of points could be fitted by a straight line, the slope of which was determined by a least-squares fit. The results are given in Table I. By imposing a $v^{-\alpha}$ dependence for σ_d^+ a v^{-1} law can be firmly established from the measured values since we obtained $\alpha=1.01\pm0.06$ for H_2^+ and $\alpha=0.95\pm0.06$ for H_3^+.

E. A test of the method: the H_2 case

If we suppose that in the neutralization process of H_2^+ the capture occurs essentially in the stable molecular ground state of H_2, then both σ_c and σ_l must exhibit a velocity dependence similar to that observed in the atomic case. Consequently, the v dependence of the quantity

$$Y_m(v)/\Phi_0(v)$$

is that of $P_{01}^2(x_m,v)$. If we tentatively accept that σ_d^+ and σ_d^0 vary with v in the same way and since, for atomic hydrogen, σ_l is proportional to v^{-1}, it results that P_{01} must be independent of v. In addition, x_m must be a linear function of v and consequently the ratio

$$Y_m(v)/\Phi_0(v)$$

for H_2 is expected to be constant. This is well the case as can be seen in Table II, where the measured x_m and Y_m values are also presented. All the different assumptions about the velocity dependence of the cross sections seem to hold.

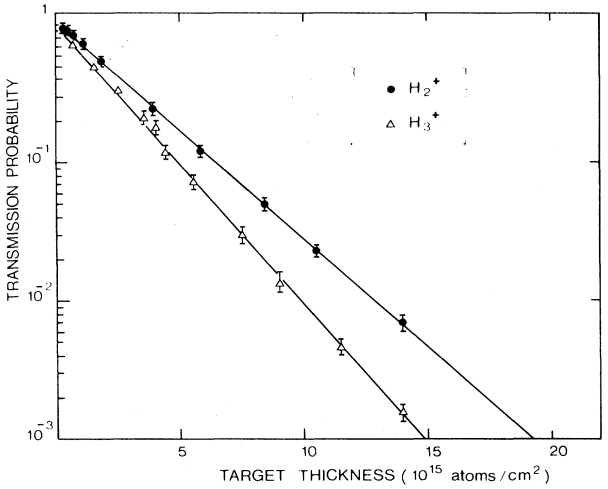

FIG. 5. Exponential attenuation of the direct beams of 400-keV/amu H_2^+ and H_3^+ projectiles vs the gas target thickness.

The experimental method consisted in measuring the number of H_2^+ ions arriving at the solid-state detector: x_2 was first fixed at a given value and the number of H_2^+ ions was measured as a function of x_1, then x_1 was fixed and the same quantity was measured as a function of x_2. Both curves present a flat maximum for the same value of the gas thickness (or the gas pressure), namely, for x_m. With $x_1=x_2=x_m$ the numerical value of Y_m was obtained for each energy. From Eq. (4) and the measured values of x_m and σ_d^+ we deduced $\sigma_d^0+\sigma_l$ assuming that σ_c is negligible as compared with σ_d^+. The values so obtained are shown in the last column of Table II. A fit to a $v^{-\alpha}$ law gives $\alpha=1.03\pm0.09$, which further justifies some previous assertions concerning the velocity dependence of the cross sections. A constant value for the ratio Y_m/Φ_0 is clear experimental evidence that the dependence on v of the σ_c/σ_l ratio is the same for the diatomic and the monatomic species.

In the frame of a very simple model, Bohr[12] has found that $\sigma_l\propto v^{-1}$ for not too heavy target atoms and incident velocities much larger than the electronic orbital velocities. On the other hand, he has also found that for s states $\sigma_c\propto v^{-6}$ when the incident velocity is of the same order as the orbital velocity of the captured electron. If the conditions established by Bohr to obtain these simple power laws were simultaneously fulfilled for σ_l and σ_c then

TABLE I. Dissociation cross section σ_d^+ for H_2^+ and H_3^+ in argon.

H_2^+		H_3^+	
E/A (keV/amu)	σ_d^+ (10^{-16} cm^2)	E/A (keV/amu)	σ_d^+ (10^{-16} cm^2)
300	3.61±0.22	250	5.21±0.30
400	3.16±0.10	300	4.68±0.19
600	2.67±0.19	400	4.10±0.25
800	2.17±0.16	500	3.80±0.22
1000	1.98±0.20		

TABLE II. Experimental values of x_m, Y_m, Y_m/Φ_0, and $(\sigma_d^0+\sigma_l)$ for H_2 in argon.

E/A (keV/amu)	x_m (10^{15} at/cm^2)	Y_m	Y_m/Φ_0	$\sigma_d^0+\sigma_l$ (10^{-16} cm^2)
300	2.1±0.2	$(3.5\pm0.3)\times10^{-5}$	$(6.5\pm0.6)\times10^{-3}$	6.7±0.8
400	2.6±0.3	$(9.6\pm0.4)\times10^{-6}$	$(4.4\pm0.2)\times10^{-3}$	4.9±0.4
600	3.0±0.3	$(4.1\pm0.3)\times10^{-6}$	$(4.2\pm0.3)\times10^{-3}$	4.3±0.4
800	3.7±0.3	$(2.3\pm0.2)\times10^{-6}$	$(3.8\pm0.3)\times10^{-3}$	3.5±0.6
1000	4.1±0.4	$(2.0\pm0.2)\times10^{-6}$	$(4.5\pm0.5)\times10^{-3}$	3.0±0.6

$\Phi_0 \propto v^{-5}$. This is never the case and the experimental data[13,14] do not follow an exact $v^{-\alpha}$ law; however, in small velocity intervals such a law is a satisfactory approximation. For protons on argon in the 0.3—1.0-MeV range the values given by Allison[13] can be fitted by a $v^{-\alpha}$ law with $\alpha=4.8$. If the same kind of v dependence is imposed to our $Y_m(v)$ values obtained for diatomic hydrogen molecules the best power is found to be 4.7 ± 0.5. Then the evidence is that for fast moving H_2^+ projectiles in argon the capture of the neutralizing electron proceeds mainly through the ground state as in the atomic case.

III. EXPERIMENTAL RESULTS FOR TRIATOMIC HYDROGEN

A. Cross sections determination

The experimental procedure was the same as described in Sec. II. Figure 6 shows some typical curves of the H_3^+ yield as a function of the gas thickness in one chamber when the pressure in the other chamber is kept constant. For all projectile energies a flat maximum is observed just like in the diatomic case. For the accompanying HD^+ ion similar curves were obtained with their maximum shifted relative to those of H_3^+ of the same velocity. In fact, these curves differ from those obtained for H_2^+ only by a scaling factor. The presence of a maximum is an unequivocal assignment of the existence of a neutral molecule between the two gas targets. In all the cases the $Y(x_1,x_2)$ curves decrease very slowly on the low-pressure side, a combined effect of the difficulty to empty the gas cells and of the different nature of the residual gas in the beam line and of the gas which normally fills the cells. This inconvenience, however, barely influences the positions of the maxima and does not affect the value of the maximum Y_m. All the relevant results are presented in Table III. As explained in Sec. II B the electron stripping effects of the deflecting field are always referred to an electric field of 20 kV/cm.

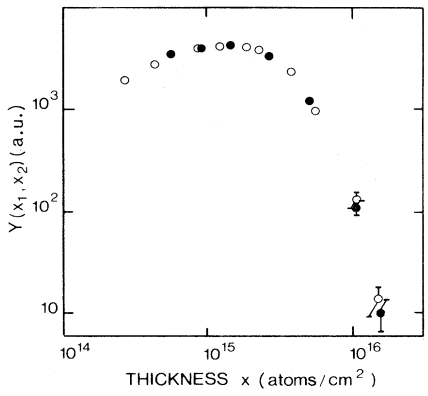

FIG. 6. Yield of the neutralization-ionization sequence for 750-keV H_3^+ as a function of the argon thickness. ●, $x_1=1.30\times10^{15}$ at/cm^2, $x=x_2$. ○, $x_2=1.25\times10^{15}$ at/cm^2, $x=x_1$.

The linear dependence of x_m on the velocity is not as clear cut as in the case of H_2^+ projectiles but it can be taken for granted. An outstanding result is that Y_m/Φ_0 is no more a constant but decreases rapidly with the projectile velocity, indicating that σ_c/σ_l does not vary with v in the same way as in the diatomic case. It is important to analyze separately the behavior of the loss and of the capture cross sections. It is reasonable to suppose that σ_d^0 and σ_d^+ are nearly equal for the triatomic species. This is equivalent to say that the dissociation of H_3 occurs when the ionic core itself is dissociated or, alternatively, that the outer electron plays a negligible role in the dissociation process. Then Eq. (4) can be rewritten in the approximate form

$$x_m\sigma_l \simeq \ln[(\sigma_d^+ +\sigma_l)/\sigma_d^+] , \tag{6}$$

where σ_c is again neglected when compared to σ_l and σ_d^+.

The value of σ_l can now be extracted from the measured values of x_m and σ_d^+. This procedure, however, introduces large uncertainties in the values of σ_l. A $v^{-\alpha}$ fit to the four experimental points gives $\alpha=1.1\pm0.3$. Thus, it is evident that there is not a strong dependence of σ_l on v. On the same grounds we get from Eq. (5)

$$\sigma_c \simeq \sigma_l Y_m \{\exp(-\sigma_d^+ x_m)-\exp[-(\sigma_d^+ +\sigma_l)x_m]\}^{-2} , \tag{7}$$

where Y_m is the experimental value corrected for the ionization by the motional electric field. The values of σ_c so obtained are given in the last column of Table III. The uncertainties are of at least 30%. In Fig. 7 both Y_m and σ_c are plotted as a function of the velocity and are fitted by a $v^{-\alpha}$ law with $\alpha=9.6\pm0.6$ and $\alpha=10.4\pm1.5$, respectively. The capture cross sections of H_3^+ are many orders of magnitude less than those measured for H^+ in the same gas.

The electron-capture cross sections are strongly dependent on the principal quantum number of the final states. For large values of n an n^{-3} law results from the Born-

TABLE III. Experimental values of x_m, Y_m, Y_m/Φ_0, σ_l, and σ_c for H_3 in argon. Values of Y_m and those derived from them correspond to an electric field of 20 kV/cm. Uncertainties in the values of σ_l and σ_c are estimated to range from 30% to 60%.

E/A (keV/amu)	x_m (10^{15} at/cm^2)	Y_m	Y_m/Φ_0	σ_l (10^{-16} cm^2)	σ_c (10^{-16} cm^2)
250	1.40±0.15	$(1.96\pm0.16)\times10^{-9}$	$(1.63\pm0.13)\times10^{-7}$	4.7	1.7×10^{-7}
300	1.35±0.20	$(6.20\pm0.70)\times10^{-10}$	$(1.14\pm0.12)\times10^{-7}$	6.1	4.2×10^{-8}
400	1.60±0.20	$(1.51\pm0.21)\times10^{-10}$	$(6.87\pm0.10)\times10^{-8}$	5.0	9.5×10^{-9}
500	1.90±0.25	$(6.90\pm1.00)\times10^{-11}$	$(4.93\pm0.86)\times10^{-8}$	3.4	4.4×10^{-9}

Oppenheimer approximation.[15] In the ionic core model of the H_3 molecule the above results imply that the capture proceeds through highly excited Rydberg states. However, since the most excited states are previously eliminated by the stripping field the observed neutral molecules cannot be in extremely high-n states. Another reason must be found to explain these abnormally small cross sections.

Berkner *et al.*[16] have measured some collision cross sections of H_3^+ ions in the 0.4—1.8-MeV range impinging upon H_2 or N_2 gases or Li vapor. Our measured total attenuation cross sections in argon gas compare well with their similar results for N_2. Electron-capture cross sections are also reported. They could not distinguish the nondissociative neutralization ($H_3^+ \rightarrow H_3$) from the dissociative neutralization ($H_3^+ \rightarrow 3H$ and $H_3^+ \rightarrow H + H_2$). The dissociative channels are by far the dominant ones. The total capture cross sections given by Berkner *et al.* are orders of magnitude larger than our specific values for the nondissociative channel. Moreover, their measured capture cross sections obey an approximate $v^{-\alpha}$ law with $\alpha \simeq 6.0$ for N_2. By comparing this power of v with those obtained for H and H_2 data we interpret these results as meaning that the capture leading to dissociative channels are those occuring in the repulsive H_3 ground state.

The power α in the $v^{-\alpha}$ dependence of σ_c seems to be a distinctive fingerprint of the nature of the electron final state in the capture process by H_3^+. Then it is evident that captures leading to the long-lived molecules we have observed do not occur in the same quantum states as captures leading to dissociative channels.

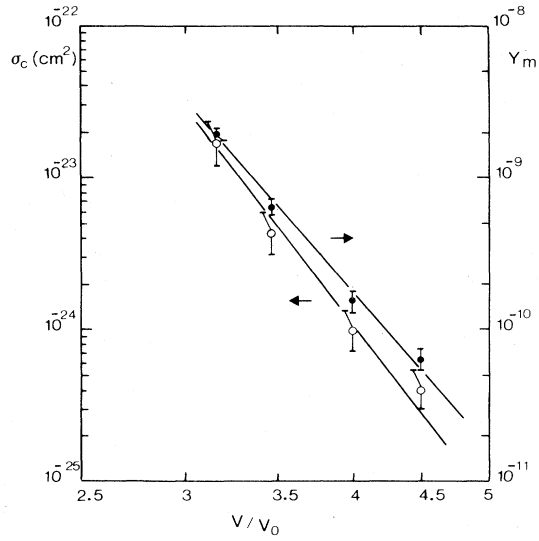

FIG. 7. Maximum yield Y_m and the estimated capture cross section σ_c vs the velocity of the incident H_3^+ ions. The two straight lines are the best fits mentioned in the text.

B. Field ionization measurements

Looking for a better understanding of the differences between diatomic and triatomic molecules we have extended our field ionization studies to higher values of the electric field. The deflecting magnetic field was replaced by electrostatic plates and a fixed transverse field of 1.5 kV/cm was applied. Halfway between the exit aperture of the first gas target and the deflecting plates the field ionizing cell was mounted as shown in Fig. 8. The variable longitudinal field could attain a maximum value of 50 kV/cm. We measured the fraction of the neutral beam destroyed by Stark ionization as a function of the field between the plates. For doing so the number of H_3^+ ions arriving at the solid-state detector was registered alternatively for zero longitudinal field and for the desired value E. The destroyed fraction is given by

$$F(E)=[\bar{N}(0)-N(E)]/\bar{N}(0)\ ,$$

where $N(E)$ is the measure of the number of H_3^+ ions for a longitudinal field E and $\bar{N}(0)$ is the average of the two measures of the number of H_3^+ ions performed just before and just after the measure made with the field E. Counting statistics were reduced to less than 3% in all the cases. For a longitudinal field less than or equal to the transverse field the fraction $F(E)$ is equal to zero in the limits of the experimental error (±4%). Figure 9 shows $F(E)$ for longitudinal fields from 1.5 to 50 kV/cm. There is a conspicuous difference between the diatomic hydrogenic species H_2 and HD and the triatomic molecule. A large fraction of the neutral triatomic molecules is destroyed by fields of a

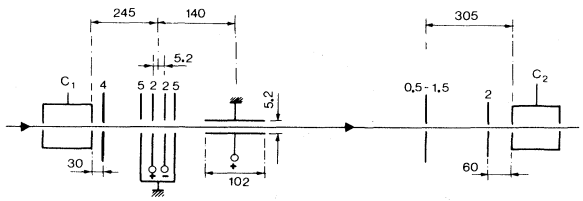

FIG. 8. Experimental arrangement for the field ionization measurements. All distances are given in mm. The number associated with each collimator is its cross-sectional diameter.

few thousands of V/cm whereas the flux of the diatomic molecules seems not to be modified.

We have also studied the behavior of a special diatomic molecule in the same ionization fields, namely, the HeH molecule. The HeH^+ ion is stable in its ground states but this is not the case for the neutral molecule. However, it was experimentally shown[17] that this molecule has long-lived Rydberg states. In Fig. 9 we can see that it behaves like H_3 and not like the two other diatomic molecules that are stable in their ground states. These results are additional evidence of the weakly bound character of the outer electron in the H_3 molecules produced by collisional neutralization of a fast H_3^+ beam.

IV. CONCLUDING REMARKS

It was shown in this paper that H_3 molecules can exist in long-lived states ($\tau \gtrsim 3\times 10^{-7}$ s). The evidence that these states are weakly bound consists of the following: (i) they are formed from the molecular ion H_3^+ by electron capture with cross sections much smaller than those oberved with H_2^+ and H^+ ions of the same velocity; (ii) they are destroyed by electric fields that leave the H_2 and HD molecules unaltered.

The experimental data have shown that the dependence on the projectile velocity of the electron-capture cross section is the same for H_2^+ and H^+. Then it can be said that the molecule H_2, as observed in this experiment, is predominantly in its stable ground state. On the other hand, the electron-capture cross section for H_3^+, as can be deduced from the behavior of the observed neutralized molecules, exhibits a much stronger $v^{-\alpha}$ dependence. With some reasonable assumptions a value of 10.4 ± 1.5 was found for α. Such a strong dependence was theoretically established by Dettmann *et al.*[18] for the electron capture to the continuum (ECC). In a recent paper, Breinig *et al.*[19] presented a comprehensive discussion of experimental results concerning ECC and showed that small and strongly v-dependent capture cross sections are characteristic of this process. It is physically very reasonable to argue that there is a smooth transition from the region of high Rydberg states to the continuum. Hence, results concerning the cross sections of ECC cannot be very different from those related to Rydberg states just below the continuum. However, our measured values of the cross sections are still orders of magnitude smaller than the scarce measured values of capture cross sections in high-n Rydberg states of atoms.[19]

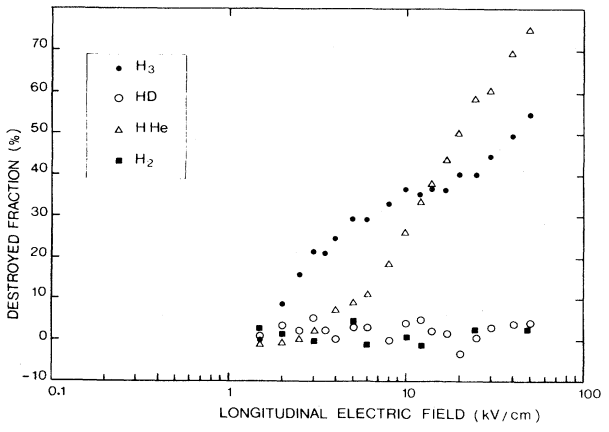

FIG. 9. Destroyed fraction of four different molecular beams by a longitudinal electric field. Distance between the exit aperture of the neutralization gas chamber and the center of the deflector plates was 24.5 cm. Results were obtained with an energy of 250 keV/amu and a transverse electric field of 1 kV/cm.

On the other hand, all the results reported here refer to H_3 molecules that survive passing across an electric field of 20 kV/cm. Thus, it is certain that we are not concerned with extremely high-n Rydberg states (as previously noted electronic states with $n > 11$ would be field ionized in a hydrogenic frozen core model).

A possible explanation for this apparent contradiction can be found in a paper by Band[20] where the experimental results of Barnett *et al.*[21] on the neutralization of H_2^+ ions in a hydrogen gas cell are discussed. The H_2^+ as well as the H_3^+ ions can leave the ion source of accelerators in vibrationally excited states. The vibrational energies of H_2^+ (H_3^+) are larger than the expected binding energies of molecular Rydberg electrons with $n \gtrsim 8$ (12) in the simple hydrogenic model. Autoionization occurs when the vibrational energy of the ionic core is transferred to the most weakly bound electron. The calculated lifetimes[20,22] associated to the autoionization process in H_2 when the vibrational state of the core changes by a single vibrational quantum number ($\Delta v = 1$) and a low angular momentum electron is ejected are at least three orders of magnitude smaller than the beam transit time from the neutralization chamber to the deflecting field. It is expected that a similar situation could also be found in the case of H_3. Then, all high-n—low-l Rydberg states would be fully depleted by autoionization long before reaching the deflecting field. Following Band,[20] states of high-n and high-l quantum numbers are able to survive the time elapsed by the beam from the cell to the region of the field. These relatively long lifetimes are due to the vanishingly small values of the Rydberg electron wave functions in the core region, an effect that increases with increasing l. Then, in our experimental arrangement, only a small fraction of the originally neutralized beam would reach the deflecting field. The small fraction that survived the Stark field would be composed of molecules in n Rydberg states spanning a few values of n and with high orbital angular momentum quantum numbers. This would explain both the small values and the v dependence of the capture cross section.

Recently, Morgan *et al.*,[23] following a suggestion of Berry and Nielsen,[22] invoked a rovibronic mixing mechanism that would strongly couple low-v—high-n states with high-v—low-n states in H_2 molecules. This could mean that for molecular Rydberg states n might not be a good quantum number. However, there is accumulating evidence[24] that highly excited Rydberg molecules which are stable against predissociation and autoionization and which present radiative lifetimes long enough to survive 1 μs or so are formed in states of high orbital angular momentum.

In conclusion our experimental results on the comparison of electron capture by H_2^+ and H_3^+ ions show that the electron-capture cross section of H_3^+ is strikingly different from what is observed in the formation of the stable molecule H_2. They also show that the H_3 molecules are easily destroyed by field ionization. This new information strongly suggests that the observed Rydberg states have principal quantum numbers that do not exceed ~ 10, but have rather large angular momenta.

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