Total scattering, surface ionization, and photoionization of a beam of H_3 metastable molecules^{a)}

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In a previous paper we reported a technique for generating an intense hyperthermal beam of hydrogen atoms and metastable H_3 molecules. From the flight time of the H_3 species between the source and detector we estimated that its lifetime exceeds $40\ \mu\text{s}$ and that it must therefore be in the $2p\ ^2A'_2$ excited Rydberg state. In this paper we report experiments utilizing this novel source of H_3 molecules. Beam-gas attenuation measurements indicate that the H_3 -Ar cross section is roughly ten times larger than the H-Ar cross section for translational energies in the 1 to 10 eV range. This observation is consistent with the assignment of the H_3 to that excited state, which has a much larger effective radius than a ground state hydrogen atom. The temperature dependence of the surface ionization of H_3 by heated tungsten and platinum filaments is used to obtain effective ionizational potentials of this species. These potentials suggest that upon interaction with a metal surface, the metastable state decays to the repulsive $2p\ ^2E'$ state which then surface ionizes to produce H_3^+ . The production H_3^+ and H^+ when the H_3 beam is irradiated with UV light from a high pressure mercury lamp was also observed and is attributed to the relatively low ionization potential ($\sim 3.7\ \text{eV}$) of the $2p\ ^2A'_2$ metastable state of H_3 .

I. INTRODUCTION

For the past 40 years the simplest neutral triatomic system, the triatomic hydrogen one, has been the subject of extensive investigations. The ground state potential energy surface of this species, relevant to the symmetric hydrogen exchange reaction, has been calculated by many workers through a variety of techniques dating from the first Eyring and Polanyi calculations¹ to the present.²⁻⁴ A thorough account of the history of these calculations is given by Truhlar and Wyatt.⁵ That surface has no minima and H_3 , in its electronic ground state, is unstable.

In apparent conflict with this theoretical result, several workers have reported the detection of a stable form of H_3 . The first report of the existence of such a species came from Devienne and co-workers.⁶⁻¹⁰ In their experiment a 1 to 12 keV beam of H_3^+ is neutralized in a first charge exchange chamber containing He and the neutral beam formed, cleansed of ions by appropriate electrostatic deflection plates, is reionized in a second charge exchange chamber and detected in a mass spectrometer as ions with a mass to charge ratio of 3. This was interpreted as evidence that some neutral H_3 molecules are formed in the first charge exchange cell and survived the traversal between that cell and the second charge-exchange chamber. Devienne observed that an appreciable fraction of these H_3 molecules lived for as long as a fraction of a microsecond.

A short time later Gray and Tomlinson¹¹ attempted to

reproduce this result with either D_2H^+ or D_3^+ and observed no signal, suggesting that no neutral species had been generated. They concluded that Devienne's result was not due to neutral H_3 but rather to the presence of an HD isotopic impurity in his experiment. It was not until 1972 that Barnett and Ray¹² also reported the observation of H_3 claiming to have identified this species in an experiment identical to Devienne's where the second charge-exchange process was now replaced by electric field ionization. That same year Nagasaki and co-workers,¹³ also in contrast to Gray and Tomlinson's results, reported the generation of a beam of neutral D_3 using the same technique. In their paper they noted the apparent conflict between their estimated lifetime which was 10^6 times larger than the theoretically estimated life time of the ground state of D_3 of about $10^{-12}\ \text{s}$. They attempted to reconcile this disagreement by suggesting that the neutral species they had observed could indeed be in an excited electronic state of H_3 , possessing a different lifetime from the ground state. In 1970, two years prior to the Nagasaki *et al.* results, the first theoretical study of the potential energy surfaces of excited electronic states of H_3 was carried out by Frenkel.¹⁴ He performed restricted Hartree-Fock calculations in order to interpret collision experiments of H_2 with metastable $2s\ H$ atoms¹⁵ and his results showed deep minima in the excited energy surfaces for H_3 (having D_{3h} symmetry) which could therefore support bound states.

The technique of neutralization and reionization of H_3^+ in order to study H_3 was not employed again until 1981 when Castro de Faria *et al.*¹⁶ also reported the observation of that neutral species. From measurements of dissociation cross sections they suggested that the H_3^+ ions resulting from ionization of H_3 are not vibrationally excited. This indicates that the H_3 was in an excited Rydberg state since the capture or removal of an electron into or from a Rydberg state should

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leave the H_3^+ core unperturbed. This technique has been used again recently by Gaillard and co-workers.¹⁷ By placing an electric field between the neutralization and reionization gas cells they were able to show that for fields of 1.5 to 50 kV/cm a fraction of the neutral triatomic molecules are destroyed. This indicates that the H_3 is in a weakly bound state with $n < 10$ (where n is the principal quantum number).

A different approach has entailed beam studies in which the dissociation products of the neutralized H_3^+ are detected directly. Vogler^{18,19} used a time-of-flight difference method and observed the spontaneous products of H_3 which are formed by the nonresonant neutralization of H_3^+ with H_2 . The H- H_2 fragment pairs are observed using two separate detectors operating in a coincidence mode such that the velocity vectors of the fragments may then be determined from the flight-time difference of the two fragments. This technique was also used by Cisneros and co-workers²⁰ to observe the angular distribution of the dissociation products D_2 and D following electron transfer from Cs to D_3^+ . Curtis *et al.*^{21,22} have also attempted this kind of experiment, producing H_3 by electron transfer from Mg to H_3^+ . However, in none of the above experiments¹⁸⁻²² was there any evidence observed for a metastable state of H_3 .

At roughly the same time new experimental evidence for H_3 came from a novel experiment by Herzberg. While running H_2 at 1 Torr in a hollow cathode discharge different emission spectra were obtained from the cathode and anode regions. Subtraction of the two spectra resulted in a series of broad visible light bands that could be assigned to Rydberg to Rydberg transitions of H_3 .²³⁻²⁷

The findings of Herzberg stimulated theoretical calculations²⁸⁻³⁴ which have successfully described the rotation band spectra he observed. Recently, Mayne and co-workers³⁵ have calculated the absorption spectra of transition state configurations of H_3 and other theorists have already begun to extend electronic state calculations to larger systems, such as H_4 ^{36,37} and H_5 .³⁸ Because of this theoretical effort some interpretations of previous experiments have been changed. Watson,³⁹ reevaluating Vogler's past results,^{18,19} suggested that the energy distribution of the dissociation products observed is due to a predissociation from a Rydberg state of H_3 . The King and Morokuma calculation²⁸ shows that the predissociation process of the lowest excited state is exoergic by approximately 5.57 eV. On the basis of this theoretical result Watson proposed that Vogler's product energy distribution was due to that predissociation, thereby making Vogler's work the first experimental determination of the energy of a known electronic state of H_3 relative to the dissociation products of H_2 and H.

In light of Herzberg's results and in view of a private communication of our own results, Porter recently repeated his own charge-exchange experiments in an attempt to observe a long-lived species of H_3 . By increasing the angular resolution of his apparatus⁴⁰ as well as using K instead of Mg as the charge-exchange target, he was able to observe a metastable state of H_3 .^{41,42}

Recently, a great deal of interest has been generated in the spectroscopy of H_3 . Freeman and co-workers⁴³ attempted to reproduce Herzberg's result by colliding H_2 gas with

high energy (0.5 MeV) electrons, but failed to detect any H_3 emission. However, Figger and co-workers^{44,45} have recently begun to employ laser spectroscopy to study the hollow cathode discharge of H_3 . By placing the discharge tube in the tuning arm of a color-center laser they observed the discharge emission at a selected line of D_3 , as a function of laser frequency. This has proved extremely helpful in the observing and assigning of new spectral features of D_3 . Figger *et al.*⁴⁶ have also begun to perform emission spectroscopy on beams of D_3 created by charge-transfer D_3^+ with alkali metals. The D_3 molecules are produced in electronically excited states, such that after leaving the alkali metal cell they emit light in a collision free region, which is then measured spectroscopically. To date only transitions between the Rydberg states $n = 3$ and $n = 2$ have been observed but all the lifetimes measured by this technique are in good agreement with the *ab initio* calculation by King and Morokuma.²⁸ Additional spectroscopic experiments have recently been performed on beams of H_3 created by charge transfer of H_3^+ by Cs by Helm.⁴⁷ The H_3 metastable is further excited by a tunable laser beam, field ionized, and detected by a mass spectrometer. Transitions to high Rydberg levels were detected. In summary, with the exception of Herzberg's result,²³⁻²⁷ all of the H_3 experiments discussed so far have used H_3^+ ions (or their isotopes) having energies in the keV to MeV range which are then neutralized by charge exchange.

In a previous letter we have reported the first direct observation of a hyperthermal beam of metastable H_3 molecules, intense enough for scattering as well as spectroscopy experiments,⁴⁸ which is generated directly as a neutral species from a high temperature arc-discharge source.⁴⁹⁻⁵² In this paper we report scattering, photoionization and surface ionization experiments utilizing this new source of H_3 metastables. These experimental results confirm the nature of H_3 as due to a Rydberg metastable species.

II. EXPERIMENTAL

A. H_3 beam

Through characterization and development of an arc-discharge source for the production of hyperthermal hydrogen atoms, it was observed that this plasma source was capable of generating other novel molecular species. The beam apparatus is depicted schematically in Fig. 1. The discharge source is similar to that described previously.⁴⁸⁻⁵² It is placed in a vacuum chamber (VC1), pumped by a 20" Westinghouse oil diffusion pump, and is connected by a flexible bellows to a test stand consisting of a bell jar (VC2) pumped by a system comprising a 6" mercury diffusion pump, a freon-cooled chevron baffle, and a liquid nitrogen trap. Differential pumping between these two chambers is provided by a skimmer (S) with an orifice diameter of about 1 mm with a knife-sharp edge. Chamber VC2 contains a beam flag (F), a 10 Hz beam chopper (C1) which modulates and allows ac detection of the beam, a pair of electrostatic deflector plates (D) which eliminate ions from the beam, and an EAI 300 quadrupole mass spectrometer with an electron bombardment ion source (QMS).

The arc discharge in the H-atom source can be run con-

FIG. 1. A schematic view of the top of the machine: VC1, arc source vacuum chamber; AS, anode assembly; A, anode; C, cathode; M, magnet; S water-cooled copper skimmer; TA, translation assembly; T, translator; P1, 2 viewports; L, optical lens; C2, 150 Hz chopper; PM, photomultiplier; CP, current preamplifier; LI 1,2, lock-in amplifiers; SCR 1,2, strip charge recorders; VC2, bell jar vacuum chamber; C1, 10 Hz chopper; D, electric field deflectors plates; F, mechanical flag; QMS, quadrupole mass spectrometer; PA, EAI preamplifier (ESA-75); MSE, mass spectrometer electronics.

tinuously for many hours with a H_2 stagnation pressure of 50 to 100 Torr such that the pressure in chamber VC1 is of the order of 10^{-2} Torr and in chamber VC2 of the order of 10^{-5} Torr. The source (AS) can be moved with respect to the skimmer with the help of a translation assembly (TA) permitting the apparatus to be operated in two modes. The first mode, in which the nozzle is far away (about 17 cm) from the skimmer allows spectroscopic observation of the intense red emission of the plasma plume in front of the nozzle (as depicted in Fig. 1). The second mode involves moving the nozzle to within about 4 cm of the skimmer to maximize the intensity of the H-atom beam as detected by the mass spectrometer. This source produces a reliable, intense beam of hyperthermal hydrogen atoms.

As shown in Fig. 2, during the operation of the discharge we observed a $m/e = 3$ 10 Hz ac ion signal in the mass spectrometer when the beam was run with H_2 and chopped at that frequency, and a $m/e = 6$ ion signal when the beam was run with D_2 . Figure 3 shows that by varying the stagnation pressure in our arc-heated source we are able to vary the ratio of the $m/e = 3$ to $m/e = 1$ signal from 0 to about 1. As seen in that figure the signals for H and H_3 increase and their ratio decreases as the stagnation pressure is reduced. As a result, we may use the stagnation pressure to control the relative amount of H_2 with respect to H.

We have determined that the $m/e = 3$ signal cannot be attributed to ions present in the beam before it enters the mass spectrometer. Indeed that beam passes through an electric field produced by a pair of deflector plates [(D), Fig. 1] which has sufficient strength (1 kV/cm) to

deflect any charge particles out of the initial beam direction. Furthermore, as can be seen in Fig. 2, the signal virtually vanishes when the electron beam is turned off.

The additional possibility that the origin of the observed $m/e = 3$ signal is H_3^+ formed in the ionizer by some ion molecule reaction involving ions formed by electron bombardment is precluded by observing that under our experimental conditions the expected signal from such a process would be less than 10^{-3} of the observed $m/e = 3$ signal. This subject is treated in greater detail in Appendix A.

A crude energy analysis of this metastable H_3 species utilizing ion-retarding elements in the optics of the mass spectrometer indicates a translational energy distribution function having, for a source stagnation pressure of 70 Torr, a peak at about 8 eV, and a width of about 7 eV. From these measurements we can estimate flight times and obtain a lower bound for the lifetime of the observed H_3 species of the order of 40 to 100 μ s. A calibration of the detector indicates an absolute H_3 flux per unit solid angle of the order of 10^{21} molecules/(s sr). Under identical experimental conditions the same peak position is obtained for the H atoms but the width is decreased to about 3 eV. This indicates that both the H and H_3 are heated to about the same extent in the plasma. Upon decreasing the arc source stagnation pressure to 55 Torr, the peak of the energy distribution function for both H and H_3 shifts upwards to about 13 eV. This observation indicates that decreasing the stagnation pressure increases the effective temperature of the plasma.

As additional confirmation of the presence of H_3 in our beam we observed emission spectra of the plasma plume

FIG. 2. ac ion current as a function of m/e . In each panel the lower curve is the ac background obtained with the electron beam turned off, and the upper curve is the ac mass spectrometer ion current signal (with the beam chopped at 10 Hz) shifted upwards by 0.2×10^{-10} A for convenience of display. Electron impact current: $100 \mu\text{A}$. Electron accelerating voltage: 60 V. Ion source pressure: 2.1×10^{-5} Torr measured by an uncalibrated ion gauge. (a) H_2 in the molecular beam source; (b) D_2 in that source; (c) and equimolar mixture of H_2 and D_2 in that source. For all the panels the stagnation pressure in the molecular beam source was 60 Torr. (Nozzle conditions changed slightly.)

which compares well with Herzberg's spectra.²⁶ This plasma plume appears directly in front of the nozzle of the beam source. Our spectra were obtained through a quartz port using a 0.5 m Jarrell–Ash monochromator pointed at the plasma plume from a direction perpendicular to it as shown in Fig. 1. Figure 4 shows an energy level diagram for H_3 and its dissociation products. The spacing of the H_3 energy levels correspond to the equilateral triangle configuration and is the one calculated by King and Morokuma.²⁸ They were referred to the energy of those products using the calculated values of Kulander and Guest.⁵³ The two transitions which we observed previously⁴⁸ are also indicated.

The most likely candidate state for the H_3 metastable molecule produced in our beam⁴⁸ is $2p\ ^2A_2''$, the second excited state of this species. The first excited state, $2s\ ^2A_1'$, can

FIG. 3. dc ion current as a function of pressure for $m/e = 1, 2$, and 3 . Mass spectrometer electron impact current is $100 \mu\text{A}$ and electron accelerating voltage is 60 V. Error bars represent 90% confidence limit.

predissociate to the $2p\ ^2E'$ repulsive ground state by coupling with a vibrational mode of symmetry e' . However, for the $2p\ ^2A_2''$ state there can be no vibronic predissociation²⁴ and only a rovibronic mechanism would permit predissociation to occur. We can also rule out any higher metastable Rydberg states for reasons outlined in Appendix B of this paper.

B. Scattering cell

Interesting information may be obtained by the study of the scattering of a beam of molecules by a gas target. From

FIG. 4. Energy level diagram for H_3 . The vertical arrows indicate the two electronic transitions we observed previously (Ref. 48).

FIG. 5. Top cross sectional view of photoionization/scattering cell with mounting flanges. Hatched area of drawing indicates the pipe walls.

the measurement of the attenuation of the beam it is possible to derive a total collision cross section. Since the metastable H_3 would be expected to have a large radius, due to the Rydberg nature of the state it is in, we felt it would be informative to measure its total scattering cross section with a reference gas such as argon. For the experiment we utilized as a scattering chamber an aluminum cell whose surfaces were black anodized. A sketch of this cell, together with its mounting flanges, is given in Fig. 5. The path length through the cell is 4.0 in. when the 1/4 in. diam. apertures indicated in that figure are in place, and 2 in. otherwise. A pair of deflection plates, between which a 1 kV/cm electric field is

produced, are mounted before the entrance to the cell to deflect any ions out of the beam and permit only neutral species to enter the cell. Figure 6 shows the scattering cell in place in the bell jar. (VC2). Approximately one and a half orders of magnitude pressure differential could be maintained between the cell and the bell jar such that pressure in the latter never rises above about 1×10^{-4} Torr (while the arc-discharge beam is on). The pressure in the scattering cell was measured using an uncalibrated Schulz-Phelps gauge and a Granville-Phillips high-pressure ionization gauge controller (series 224). The intensity of the beam was measured as usual by electron impact mass spectroscopy as described in Sec. II A.

C. Surface ionization

Since our metastable H_3 species has some similarities to an alkali atom in that they both have low ionization potentials (about 3.7 eV for $2p^2A' H_3^{28}$) and an outer shell having one electron only, it is expected to surface ionize when colliding with a heated filament having a high work function. Rubidium atoms have an I.P. (4.18 eV) close to that of metastable H_3 and exhibit an ionization efficiency of 90% on platinum at 1200 K and 100% on tungsten at 1400 K.⁵⁴ If metastable H_3 does indeed ionize upon interaction with a hot filament, this process could prove to be a highly selective detector for this species in the presence of high ionization potential atoms or molecules.

To perform this experiment it was necessary to modify the ionization region of the mass spectrometer. Two ceramic blocks were set on opposite sides of the mass spectrometer ionization chamber such that from these blocks either a platinum or tungsten filament could be suspended through the middle of the ionization region. This filament is electrically insulated from the rest of the electronics and does not affect the normal operation of the mass spectrometer ion source. This was verified by testing the mass spectrometer with just background gas and observing no change in the

FIG. 6. A schematic view of the top of the machine with scattering cell installed. Labels are the same as in Fig. 1 with the following additions: L, quartz lens; ML, 200 W high pressure mercury lamp; PS, power supply for mercury lamp; QW, quartz window; IG, ion gauge; CAT, time-averaging computer; X-Y, x-y recorder; SM, spherical mirror.

original mass spectrum with either a hot or cold surface ionization filament. When surface ionization measurements are to be made, the electron impact ionizer is turned off and the filament wire may be heated by passing a dc current (0–2.0 A) through it with the help of an HP 6236A power supply. Any ions formed and detected under such conditions can be due only to surface ionization processes occurring on the filament.

By varying the current to the filament it is possible to control its temperature. The latter was measured using a micro-optical pyrometer (Pyrometer Instrument Co., Bergenfield, N.J., model 95) having a reported accuracy⁵⁴ between $\pm 4^\circ$ at 1000 K and $\pm 10^\circ$ at 2800 K).

This arrangement permits us to measure the efficiency for producing any ion as a function of the temperature of the filament since the absolute intensity of the incident beam can be measured with the help of the electron bombardment ionizer (Sec. II A) and is known as a function of stagnation pressure.⁴⁸ The 0.005" in. diameter wire subtends about 5% of the cross-sectional area of the beam in the ionizer region, which permits us to estimate the flux incident on the wire. By taking the ratio of the ion flux of a particular mass emanating from the hot filament to the incident neutral flux of H_3 the ionization efficiency for the production of that particular ion is obtained (assuming that the H atoms and the H_2 molecules present in the beam cannot surface ionize under these experimental conditions).

D. Photoionization cell

Due to the relatively low I.P. of its $2p^2A_2''$ state, it should be possible in principle to photoionize H_3 with visible or ultraviolet light of an appropriate wavelength ($\lambda < 3300 \text{ \AA}$). To perform this experiment we used the same cell as for the total scattering experiments, as shown in Figs. 5 and 6. The inside of the cell may then be illuminated by focusing the light from an appropriate source through a quartz window into the cell. The light that is not absorbed by the beam is reflected by a spherical mirror at the end of the cell, producing a double pass illumination. That light may excite or ionize some of the H_3 passing through the cell. Since the momentum carried away by the ejected electron is very small, the ions formed will not be significantly deflected and will traverse the cell to be ultimately detected by the mass spectrometer located at the end of the bell jar and in line with the neutral beam. The cell is made of aluminum and is black anodized to help prevent light being reflected into VC2. In addition, the entrance and exit apertures help decrease the amount of the mercury lamp scattered light from entering the mass spectrometer and producing a background signal on the electron multiplier.

For these photoionization experiments we decided to use a broad, intense source of excitation that would extend well into the UV. A Bausch & Lomb (cat. no. 33-86-36-01) 200 W, short-arc, super-pressure mercury lamp which is enclosed in a quartz envelope was selected. It has a high luminance and an exceptionally high spectral radiance in the ultraviolet. This light source is known to give a continuous, fairly uniform intensity spectrum covering the UV, visible, and infrared region of the electromagnetic spectrum except

for the very high-intensity discrete lines which are characteristic of the mercury arc spectrum. For the 440 nm mercury line (the most intense line in the output spectrum of the lamp) we calculate an intensity for it of $3.6 \times 10^{14} \text{ photons cm}^{-2} \text{ s}^{-1}$.⁵⁵

Through the use of two quartz lenses [one inside the mercury lamp unit (ML) and one outside (L) Fig. 6] the output of the lamp is focused directly into the cell through which the neutral beam must pass before reaching the mass spectrometer. Figure 6 shows the lamp position on the exterior of the vacuum chamber. Testing the mass spectrometer with the lamp no produced no change in the background signal, indicating that any stray light which may be escaping from the cell does not interfere with the normal operation of the mass spectrometer.

III. RESULTS AND DISCUSSION

A. Total scattering

Figure 7 shows the logarithm of the transmittance I/I_0 (ratio of the beam intensity measured by the electron bombardment mass spectrometer with target molecules in the cell to the beam intensity without scattering gas in the cell) for H, H_2 , and H_3 as a function of the pressure of argon, measured by an uncalibrated Schultz–Phelps gauge. These points lie on a straight line as expected from theory.

With no gas in the scattering cell ($p = 0$), by definition

FIG. 7. Fractional attenuation of mass spectrometer signal as a function of argon pressure within the stagnant gas cell for $m/e = 1, 2$ and 3. I_0 is the intensity of the species with no gas in the cell and I is the corresponding intensity with gas in the cell. The pressure was measured with an uncalibrated Schultz–Phelps gauge. Lines are least-square fits to the points. The path length in the gas cell is 4 in. The beam stagnation pressure is 57 Torr.

$I/I_0 = 1$, but this reference point is not included in Fig. 7. The lowest pressure at which we could make reproducible measurements was about 0.5×10^{-3} Torr. The line for H in that figure does have a linear intercept of 1.0, as expected, but those for H₂ and H₃ do not, displaying a steeper slope between $p = 0$ and $p = 0.5 \times 10^{-3}$ Torr than the rest of the corresponding line. This suggests the presence in the H₂ and H₃ beams components of larger cross section than those implied by the $p > 0.5 \times 10^{-3}$ Torr measurements. For H₃, this may indicate higher Rydberg states than the $2p^2A_2''$ one which, for reasons not presently understood, were not completely quenched by the deflection field, or did not decay radiatively by the time they reach the scattering cell (see Appendix B). We limit our discussion to the reproducible $p > 0.5 \times 10^{-3}$ Torr results.

From these results one can obtain the effective total cross section Q , and from it the corresponding interaction radii. The method we used to calculate Q is based on that of Rosin and Rabi⁵⁷ and is partially described by Levine and Bernstein.^{58(a)} The probability that a beam molecule of laboratory velocity v_b will pass through a scattering chamber of length l without being deflected is given by

$$P(v_b) = \exp(-l/\lambda), \quad (1)$$

where λ is the mean free path. This means that the beam flux is an exponentially decreasing function of the length of the scattering path, a result similar to the Beer-Lambert law for the attenuation of a beam of light by absorption.

From the slope S of plots of $\ln(I/I_0)$ vs the target gas pressure in the scattering cell, Q may be approximately calculated using the Rosin-Rabi equation.⁵⁷ This equation is

$$Q = 2(\pi)^{1/2} J(z) \left(\frac{\ln(I/I_0)}{nl} \right), \quad (2)$$

where

$$J(z) = z^2 \int_0^\infty \left[\frac{x^5}{\Psi(x)} \right] \exp(-zx^2) dx, \quad (3)$$

$$\Psi(x) = x \exp(-x^2) + (2x^2 + 1) \int_0^x e^{-y^2} dy, \quad (4)$$

$$z = \frac{m_b T_t}{m_t T_b}, \quad (5)$$

$$x = v_b / \left(\frac{2kT_t}{m_t} \right)^{1/2}. \quad (6)$$

In these expressions n is the scattering target gas number density, k the Boltzmann constant, l the scattering path length, and m , v , and T stand for mass, velocity, and temperature, respectively, while the subscript b refers to the beam molecule and the subscript t refers to the target molecule. Rothe has shown that for I/I_0 in the range of 0.1–1.0 the deviation between this approximate expression of Eq. (2) and the exact equation is 5% at most.⁵⁹ The quantity $J(z)$ defined by Eq. (3) is obtained from Rosenberg's table.⁶⁰ The angle subtended by the entrance aperture to the mass spectrometer at the midpoint of the scattering center is about 1° . This leads to an underestimation of the integral cross sections, and in the absence of other errors would be a lower limit to the correct cross section.

We may now employ Eq. (2) to obtain the total cross section for scattering by argon (Fig. 7). For our present measurements, substituting in the appropriate experimental values for our apparatus with a 4 in. path length, Eq. (2) yields

$$Q = [3.05 \times 10^{-18}(S)] \text{ \AA}^2, \quad (7)$$

where S is the slope in Torr⁻¹. By using a least-square fit of the data points of Fig. 7 we can get values for S and therefore Q for collisions of H, H₂, and H₃ with Ar. These cross sections are listed in Table I for a source stagnation pressure of 57 Torr. The uncertainties in Table I represent 95% confidence level. Since however the pressures were measured with an uncalibrated Schultz-Phelps gauge, those uncertainties only represent reproducibility errors but not the accuracy of the measurements.

There have been many experimental^{58,61} and theoretical⁶⁰ studies on the absolute total cross sections for scattering of atomic hydrogen by argon. However, these studies were done at energies up to only 1 eV and cannot be directly compared with our result since this is the first scattering experiment using H atoms in the 5–15 eV energy range. It has been shown⁶² that at high energies the major contribution to the elastic cross section comes from scattering by the repulsive core, resulting in a linear dependence of the logarithm of the cross section on the logarithm of the velocity. If we use this functional form to extrapolate the results of Das and co-workers⁶³ to our energy (~ 13 eV), we obtain a cross section of $4.4 \text{ \AA}^2$. This differs from our total cross section of $1.7 \text{ \AA}^2$ by a factor of 2.5. This difference can be attributed to our angular resolution, our broad hydrogen atom energy distribution, the lack of calibration of our Schulz-Phelps ionization gauge and the fact that an extrapolation of over more than an order of magnitude in energy was involved.

Let us also discuss our results in terms of the relative cross section Q^* which is defined as

$$Q_{X-\text{Ar}}^* = \frac{Q_{X-\text{Ar}}}{Q_{\text{H}-\text{Ar}}}, \quad (8)$$

where $Q_{X-\text{Ar}}$ is the cross section of the beam species X with Ar, and $Q_{\text{H}-\text{Ar}}$ is the cross section of the H with Ar. This ratio eliminates the errors due to the lack of calibration of the Schulz-Phelps gauge. Our experimental results for Q^* are also given in Table I. Rothe and Bernstein⁶⁴ report that in

TABLE I. Total attenuation cross section by argon target, at a source stagnation pressure of 57 Torr.

		X		
		H	H ₂	H ₃
Experiment	$Q/\text{\AA}^2$	1.7 ± 0.7^a	3.3 ± 0.9^a	17.3 ± 0.8^a
	$Q_{X-\text{Ar}}/Q_{\text{H}-\text{Ar}}$	1.0	1.9	10
Theoretical model	$Q/\text{\AA}^2$	...	3.8	17
	$Q_{X-\text{Ar}}/Q_{\text{H}-\text{Ar}}$	...	2.2	10

^a Since the pressures were measured with an uncalibrated Schulz-Phelps gauge, these uncertainties represent reproducibility errors rather than the absolute accuracy of the measurements.

atom-molecule total cross section measurements, while the absolute cross sections may vary over a range of $\pm 10\%$, the ratio of the cross section of two gases were reproducible to within $\pm 3\%$. In the case of our data for H_2 we obtain a $Q_{\text{H}_2-\text{Ar}}^*$ of 1.9.

This value can be rationalized on the basis of a very simple energy-dependent hard sphere radius model for argon. Taking the radius of H to be $0.53 \text{ \AA}$, the effective Ar radius (for high energy collisions) which will produce a value of $Q_{\text{H}-\text{Ar}}$ of $1.7 \text{ \AA}^2$ is $0.21 \text{ \AA}$. Using an effective radius for H_2 as $0.90 \text{ \AA}$ ($1/2$ of the H_2 internuclear distance plus the H radius), this yields a H_2 -Ar hard sphere collision cross section of $3.8 \text{ \AA}^2$ and a $Q_{\text{H}_2-\text{Ar}}^*$ of 2.2. This is in reasonable agreement with the measured values of $3.3 \text{ \AA}^2$ and 1.9, respectively. Independently, the H_2 -Ar collision cross section has been measured as a function of relative energy up to 100 meV .⁶⁵ Extrapolation to $\sim 13 \text{ eV}$ furnishes a value of $12.4 \text{ \AA}^2$ and a $Q_{\text{H}_2-\text{Ar}}^*$ with respect to the Das *et al.* results⁶² of 2.8, compared to our measured result of 1.9, which is not unreasonable, in view of the gross nature of the model and extrapolations used.

For H_3 we measure a $Q_{\text{H}_3-\text{Ar}}^*$ of 10. This large value may at first appear excessive but this is not the case considering that the H_3 molecule is in an excited Rydberg state. With a bond distance some $0.02 \text{ \AA}$ smaller than H_3^+ (as determined by Herzberg *et al.*²⁶), the metastable molecule may be pictured as a stable H_3^+ core having an equilateral triangle equilibrium geometry, with the Rydberg electron (which makes it neutral) in a $2p$ orbital perpendicular to the plane of the triangle. As a result, the triangle contracts slightly to accommodate the additional electron. Figure 8 shows a representa-

tion of this molecule with a hydrogenic $2p_z$ orbital (perpendicular to the plane of the nuclei) representing the $2p$ Rydberg orbital of H_3 . The Bohr radius for a hydrogenic orbital in the $n = 2$ state is $2.12 \text{ \AA}$. Taking this as the radius of H_3 in the $2p^2A_2''$ state and the effective argon radius of $0.21 \text{ \AA}$ obtained from the H scattering experiment, this furnishes a $Q_{\text{H}_3-\text{Ar}}$ of $17 \text{ \AA}^2$ and a $Q_{\text{H}_3-\text{Ar}}^* = 10$, in surprisingly good agreement with the measured values of $17 \text{ \AA}^2$ and 10, respectively. From this simple analysis we see that it is quite reasonable for H_3 to have a collision cross section with Ar an order of magnitude greater than that with a hydrogen atom.

We also performed similar experiments with a higher stagnation pressure in the arc source. As previously observed in Sec. II A, increasing the stagnation pressure lowers the translational energy of all species in the beam and thereby should increase its scattering cross section. Figures 9 and 10 show data for the scattering of H and of H_3 generated at a 65 Torr stagnation pressure by argon and propane as target gases. The corresponding cross sections are shown in Table II and III. The precision uncertainties listed represent a 95% confidence level. For the scattering of hydrogen atoms with argon we see that the cross section has increased by a factor of 1.7 as the stagnation pressure was increased from 57 to 65 Torr.

Using the same analysis as before we calculate an effective Ar radius of $0.43 \text{ \AA}$. Extrapolating again Das and co-workers⁶³ results to our peak energy of about 10 eV (pertaining to a 65 Torr stagnation pressure) we get a cross section of $5.2 \text{ \AA}^2$. This is greater than our measured value of $2.9 \text{ \AA}^2$ by a factor of 1.8, but is closer to the 65 Torr result than the 57 Torr ones. As expected, as the stagnation pressure increases, with a concomitant lowering in translational energy, our cross sections move towards the Das *et al.* results.

FIG. 8. Pictorial representation of the $2p_z$ Rydberg orbital of H_3 molecules in the $2p^2A_2''$ state. The solid points represent the nuclei. The Rydberg orbital perpendicular to the plane of the nuclei and is represented by a 90% boundary surface of a hydrogenic $2p_z$ orbital (Ref. 101).

FIG. 9. Fractional attenuation of mass spectrometer signal as a function of target gas pressure measured with an uncalibrated Shulz-Phelps gauge for $m/e = 1$. I_0 is the intensity of that species with no gas in the cell and I is the corresponding intensity with gas in the cell. Lines are least squares fit to points. The path length of the gas cell is 2 in. The beam stagnation pressure is 65 Torr. Solid symbols: Ar target. Open symbols: propane target.

FIG. 10. Fractional attenuation of mass spectrometer signal as a function of target gas pressure measured with an uncalibrated Schulz-Phelps gauge for $m/e = 3$. I_0 is the intensity of this species with no gas in the cell and I is the corresponding intensity with gas in the cell. Lines are least squares fit to the points. The path length in the gas cell is 2 in. The beam stagnation pressure is 65 Torr. Solid symbols: Ar target. Open symbols: propane target.

For H_3 we see that the cross section for scattering by Ar has increased by a factor of 1.7 as well, in going from 57 to 65 Torr stagnation pressure. The fact that both the H_3 and H cross sections increased by the same factor is not unreasonable. Both H_3 and H have roughly the same translational energy at the same stagnation pressure, presumably because they are heated to the same extent in the plasma discharge. Under these conditions, their cross sections should be affected in a similar manner, as observed. Using the effective Ar radius obtained at the 57 Torr source stagnation pressure experiments and the H_3 radius of 2.12 Å we calculate a hard sphere scattering cross section for H_3 plus Ar to be 20 Å² and a $Q_{H_3-Ar}^*$ of 7. This is in reasonable agreement with our measured values of $Q_{H_3-Ar} = 30$ Å² and $Q_{H_3-Ar}^* = 10$, respectively.

TABLE II. Total attenuation cross section by argon target, at a source stagnation pressure of 65 Torr.

		X	
		H	H_3
Experiment	$Q/\text{Å}^2$	2.9 ± 0.5^a	30 ± 7^a
	Q_{X-Ar}/Q_{H-Ar}	1.0	10
	$Q/\text{Å}^2$	...	20
Theoretical model			
	Q_{X-Ar}/Q_{H-Ar}	...	7

^a Since the pressures were measured with an uncalibrated Schulz-Phelps gauge, these uncertainties represent reproducibility errors rather than the absolute accuracy of the measurements.

TABLE III. Total attenuation cross section by propane target, at a source stagnation pressure of 65 Torr.

		X	
		H	H_3
Experiment	$Q/\text{Å}^2$	20.9 ± 2.7^a	25.4 ± 1.6^a
	Q_{X-O_2}/Q_{X-Ar}	7	0.85
Theoretical model	$Q/\text{Å}^2$	...	29
	$Q_{X-C_2H_6}/Q_{H-Ar}$	...	1.4

^a Since the pressures were measured with an uncalibrated Schulz-Phelps gauge, these uncertainties represent reproducibility error rather than the absolute accuracy of the measurements.

Lastly, we wanted to see what effect a larger scattering target would have on the cross sections. For this reason we chose to use propane as another scattering gas. The results obtained using propane at the same stagnation pressure (65 Torr) of the previous experiment are also shown in Fig. 9 and 10 and listed in Table III. We see that the H-propane cross section has increased by a factor of 7 compared to the H-Ar one at the same energy. An increase in the cross section is expected since the H atom is small compared to the target and will be very sensitive to a change in the latter's size. In contrast, there is no significant change in the cross section for H_3 -propane [$(25.4 \pm 0.6) \text{Å}^2$] compared to H_3 -Ar [$(30 \pm 7) \text{Å}^2$]. This as well is not unexpected since the large size of the metastable H_3 molecule will make it relatively insensitive to a change in the target size.

Using the same analysis as for the argon experiment at 57 Torr we calculate an effective propane radius of 0.92 Å from the H plus propane scattering cross section at 65 Torr (with 0.53 Å as the radius for H). Taking 2.12 Å as the radius of the H_3 molecule (as justified in the H_3 + Ar scattering analysis) and the effective propane radius we just calculated, we obtain a scattering cross section of 29 Å² for H_3 against propane at 65 Torr stagnation pressure. Again, this compares well with the measured value of 25 Å². These values are listed in Table III.

The reason for the similar cross sections for H_3 -Ar and H_3 -propane becomes obvious by comparing the "true" sizes of the two scattering molecules. For solid Ar the average radius (half the distance between closest atomic centers) is 1.6 Å.⁶⁶ For propane, by adding together the appropriate bond distances⁶⁷ (taking into account the geometry of propane), we get a spherical radius of ~2.5 Å. The change in size in going from argon to propane is small compared to the radius of the H_3 but not of the H, suggesting that the scattering cross section of H_3 from those two molecules should be comparable in magnitude but the cross section of H should be significantly smaller, as observed.

B. Surface Ionization

Figure 11 shows plots of ionization efficiency against filament temperature for different stagnation pressures using a tungsten filament. From this figure we see that at 80

FIG. 11. Ionization efficiency (I_{eff}) as a function of tungsten filament temperature for the production H^+ and H_3^+ ions, (a) stagnation pressure = 80 Torr, (b) stagnation pressure = 75 Torr, (c) stagnation pressure = 70 Torr.

Torr stagnation pressure the onset of $m/e = 3$ ions occurs at approximately 1100 °C and has maximum value of approximately 10^{-6} at about 2000 °C. It is interesting to analyze why such low ionization efficiencies were observed, since in the case of Rb atoms of similar ionization potential, efficiencies of 100% are observed for ionization by a tungsten filament.⁶⁸ However, as the H_3 in our beam is an electronically excited species, one should expect that the most likely process would be for the H_3 to deexcite electronically to the repulsive ground state when colliding with the metal surface, resulting in the production of neutral H_2 and H . This is consistent with our observation that surface ionization to H_3^+ is a very weak channel in the interaction H_3 with a metal surface. Nevertheless, this production of H_3^+ ions is the first reported observation of the surface ionization of a metastable molecule, the $2p^2A_2'$ state of H_3 . As a result, surface ionization could prove to be in the future a unique and highly selective detector of molecules which are in excited metastable electronic states.

As described previously, varying the stagnation pressure should allow us to probe the effect of higher transla-

tional energies on the surface ionization. Indeed, upon decreasing that pressure from 80 to 75 Torr [Fig. 11(b)], the onset of the $m/e = 3$ species drops from 1100 to 500 °C and the position of the corresponding inflection point decreases from 1800 °C to 1200 °C. Further lowering the stagnation pressure to 70 Torr decreases the onset to 150 °C and the position of the inflection point to 800 °C. At all stagnation pressures the maximum ionization efficiency observed is always approximately 10^{-6} . There are at least two factors which are capable of influencing the ionization efficiency versus filament temperature curves. First, as the translational energy increases, the temperature needed to produce significant surface ionization decreases. Second, as the filament temperature decreases the amount of adsorbed material on it increases. This effect tends to shield the metal from the incident beam. Our onset and inflection point temperature results indicate a strong correlation with stagnation pressure and therefore with translational energy. However, the ionization efficiency at the inflection point temperature appears to be approximately independent of translational energy.

The ratio of the number of ions (n_+) to atoms (n_a) evaporating from a surface with which they are in equilibrium is given by the Saha–Langmuir equation^{69–71}

$$\frac{n_+}{n_a} = \left(\frac{1 - r_+}{1 - r_a} \right) \frac{\omega_+}{\omega_a} \exp \left[\frac{e(\Phi - I)}{kT} \right], \quad (9)$$

where r_a and r_+ are the reflection coefficients for atoms and ions, respectively; ω_+/ω_a is the ratio of the statistical weight of the ionic state and the atomic state involved; I is the ionization potential of the atoms; Φ is the thermionic work function of the surface; and e the electronic charge. A plot of the natural logarithm of the ionization efficiency vs the inverse of the temperature of the filament should result in a straight line whose slope is proportional to the difference between the work function of the filament and the ionization potential of the surface-ionized species. These types of plots have proved useful in determining work functions of surfaces by measuring the surface ionization of an atomic species having a known ionization potential.⁷²

Using this technique and the known tungsten work function (4.58 eV), one should be able to evaluate the ionization potential of H_3 . The data of Fig. 11 were replotted in this manner and are shown in Fig. 12, with the resulting effective ionization potentials obtained from Eq. (9) given in Table IV. We first observe that the ionization potential increases slightly with increasing stagnation pressure. At low stagnation pressures the high translational energy of the H_3 may lower the effective ionization potential since some of that translational energy may become available for surface ionization. If this is the case, the more accurate ionization potential would be the one obtained at a higher stagnation pressure, which is 5.4 eV.

An inspection of the energy level diagram for H_3 in Fig. 4 shows that this ionization potential is some 1.7 eV too large to be originating from the $2p^2A_2'$ state, whose ionization potential is about 3.67 eV.⁴⁷ However, it agrees reasonably well with the estimated ionization potential of 5.6 eV from the $2p^2E'$ repulsive ground state obtained by adding to the

FIG. 12. Natural logarithm of the ionization efficiency (I_{eff}) plotted as a function of the inverse of the tungsten filament temperature, for the production of H^+ and H_3^+ ions, (a) stagnation pressure = 80 Torr, (b) stagnation pressure = 75 Torr, (c) stagnation pressure = 60 Torr. Lines represent least-squares fits to the points.

3.67 eV figure the splitting of 1.90 eV between the $2A_2''$ and ground $2p^2E'$ levels estimated theoretically, assuming that the latter can still be described as a Rydberg state.²⁸ We have already stated that the most likely process to occur when H_3 interacts with a metal surface is for it to deexcite electronically, probably to the ground repulsive state, which would result in the production of neutral H_2 and H . However, since the time scale for electron transfer ($\sim 10^{-14}$ s) is faster than for dissociation, ($\sim 10^{-12}$ s) it is possible that some of the molecules in this repulsive $2p^2E'$ ground state could surface ionize to form H_3^+ before dissociation into neutral H_2 and H . Our measurements indicate that surface ionization to H_3^+ is indeed a weak channel, which is consistent with this interpretation. It would appear then that the majority of the $2p^2A_2''$ H_3 deexcites to the $2p^2E'$ repulsive state and a small fraction of those quickly surface ionize to form H_3^+ . If this is

TABLE IV. Effective surface ionization potential for a tungsten filament.

Pressure/Torr	Ionization potential/eV	
	H	H_3
70	5.1	4.9
75	5.3	5.1
80	5.2	5.4

indeed the case, this is the first measurement of the ionization potential of a repulsive state by surface ionization.

Due to the unexpected value of the ionization potential we repeated the measurements using a filament with a different work function in order to verify the consistency of the measurements. A platinum filament ($\Phi = 5.36$ eV) was used and the results are shown in Fig. 13. An immediate difference which is observed between the tungsten and platinum filament results is their behavior with respect to the stagnation pressure of the beam. For platinum, no surface ionization was observed at 80 Torr. At 75 Torr [Fig. 13(a)] a small amount of H_3^+ is observed. At 65 Torr [Fig. 13(b)] the H_3^+ ionization efficiency is about 10^{-6} at the inflection point temperature, which is also typical of the tungsten results. However, the ionization efficiency characteristic temperatures appear to be insensitive to stagnation pressure with an onset of about 300 °C and an inflection at about 1100 °C [Figs. 13(b) and 13(c)]. One explanation for this contrast in behavior between the platinum and tungsten filaments is that there is some species adsorbed on the latter which is not adsorbed on the platinum filament, resulting in a surface ionization efficiency process which is more sensitive to the translational energy of the H_3 in the tungsten case.

Figure 14 shows the Saha-Langmuir plots of the platinum surface ionization data. Table V displays the ionization

FIG. 13. Ionization efficiency (I_{eff}) as a function of platinum filament temperature for the production of H^+ and H_3^+ ions, (a) stagnation pressure = 75 Torr, (b) stagnation pressure = 65 Torr, (c) stagnation pressure = 60 Torr.

potentials obtained from this data. Disregarding the result for 75 Torr (because the signal was very weak and the errors large) the platinum results support the conclusion that the surface ionization to form H₃⁺ occurs from the repulsive ground state of H₃.

It should be mentioned that in this series of surface ionization experiments we were never able to detect H₂⁺ formation. This is as expected since H₂, having an I.P. of 15.6 eV, should not surface ionize on tungsten, whose work function is 4.58 eV. It was very surprising to observe that at high tungsten filament temperatures the production of H⁺ was observed, as shown in Fig. 11. At all stagnation pressures the onset temperature of the *m/e* = 1 ions is always about 400 °C greater than that of the *m/e* = 3 ions and the inflection point for *m/e* = 1 is always about 200 °C greater than that for *m/e* = 3. For the platinum filament (Fig. 13) the production of H⁺ is somewhat greater than the production of H₃⁺ with the onset and inflection temperatures being about the same for both. One explanation for this behavior is that the beam contains metastable hydrogen atoms which (due to high translation energy) do not decay by the time they exit the 1 kV/cm electric field (which serves to sweep ions out of the beam), and are surface ionized at the filament. Since the I.P. for H (*n* = 2) is about 3.4 eV an excited

TABLE V. Effective surface ionization potential for a platinum filament.

Pressure/Torr	Ionization potential/eV	
	H	H ₃
60	5.4	5.6
65	5.3	5.9
75	5.7	5.9

hydrogen atom would be expected to surface ionize readily. However, this explanation must be discarded since the Saha–Langmuir plots (Tables IV and V) show the ionization potential for H⁺ formation to be on the average 5.3 eV. However, this ionization potential compares well with the average ionization potential of 5.5 eV for H₃⁺ which is calculated from the 65 and 60 Torr results of Table V (leaving out the 75 Torr results because of the low signals) and the 80 Torr results of Table IV (which, as pointed out above, minimizes the effect of translational energy). This suggests that the H⁺ production is due to the presence of H₃ in the beam. One possible explanation is that these H⁺ ions are due to the dissociation of the H₃ molecule (not unlike dissociation of alkali halides on hot filaments^{73,74}). An interaction which might explain the production of H⁺ from H₃ is

Although this process is endoergic by about 5.0 eV (Fig. 4), that energy could be supplied by the translational energy of the H₃. Then in a second step the electronically excited H atom formed on the filament could ionize and desorb. However, if this is the correct mechanism, one would expect it to exhibit an ionization potential of 3.33 eV and not the observed 5.3 eV. The only other explanation for the generation of H⁺ is that in the surface ionization of H₃ to H₃⁺ some of the H₃⁺ which is now adsorbed on the surface dissociates to form H⁺ and H₂ before it has a chance to desorb as H₃⁺. This would then give H⁺ having the same effective ionization potential as H₃⁺ since they both originate from the same precursor, H₃. However, the dissociation of H₃⁺ to H⁺ and H₂ is endoergic by some 4.3 eV. The strength of the bond between H and a Pt surface is about 3.5 eV,⁷⁵ making the process H₃⁺ + 2Pt → H⁺ + 2Pt–H endoergic by 1.6 eV which could be supplied by the beam translational energy.

C. Photoionization

Figures 15 and 16 shows the preliminary results for this experiments. Curve (a) for the top panel of Fig. 15 shows the electron impact spectrum for a stagnation pressure of 100 Torr with the lamp off. As expected, the signal is virtually all due to H, but it is very weak due to the reduced temperature of the plasma characteristic of this stagnation pressure. Curve (b) of the same panel shows the photoionization mass spectrum (with the electron beam in the mass spectrometer ionizer turned off), corrected for a small amount of background (i.e., lamp off) signal. As can be seen, no photoionization is detected.

The bottom panel of Fig. 15 shows the effect of having the stagnation pressure reduced to 95 Torr. Curve (a) now

FIG. 14. Natural logarithm of the ionization efficiency (I_{eff}) plotted as a function of the inverse platinum filament temperature for the production of H⁺ and H₃⁺ ions, (a) stagnation pressure = 75 Torr, (b) stagnation pressure = 65 Torr, (c) stagnation pressure = 60 Torr. Lines represent a least-squares fit to the points.

FIG. 15. Mass spectrum of molecular beam. (a) Electron impact mass spectrum, (b) background-corrected photoionization mass spectrum generated by irradiation of beam with mercury lamp. Smooth line indicates fit to data points. The stagnation pressure was set at 100 and 95 Torr as indicated.

shows the presence of some H_3 , through the intensities of all species are still small due to the plasma temperature which is still relatively low. The photoionization mass spectrum displayed in curve (b) now shows a distinct peak at $m/e = 3$, whose intensity is about 0.38 times that of the electron impact mass spectrum (a). Lowering the stagnation pressure further to 90 Torr (top panel of Fig. 16) results in stronger electron impact peak intensities as expected, due to the concomitant increase in the plasma temperature. The photoionization peak at $m/e = 3$ also increases, and the ratio of its intensity to that of the electron impact peak increases slightly to 0.42. Finally, decreasing the stagnation pressure to 80 Torr (bottom panel of Fig. 16) further increases the electron impact and photoionization peak intensities, the ratio of the $m/e = 3$ peaks now being about 0.5. The small increase in this ratio with decreasing stagnation pressure may be due to the fact that as the velocity of the H_3 species increases, the loss of the H_3^+ photoion, between the photoionization region and the mass spectrometer ionizer region (which are about 20 cm from one another), decreases. We interpret these results as indicating that we are indeed photoionizing metastable H_3 and the H_3^+ photocurrent is approximately proportional to the neutral metastable H_3 intensity. This is the first direct observation of photoionization of metastable H_3 .

As expected, no photoionization of H is seen at stagnation pressures of 100, 95, or 90 Torr. However, at 80 Torr

stagnation pressure a small photoionization peak at $m/e = 1$ is seen, having an intensity which is 6% of that of the corresponding electron impact peak. At first one might think that it is due to the presence of metastable H atoms in the beam. This interpretation would be consistent with its appearance at the higher plasma temperature. However, this cannot be the case since any metastable hydrogen atoms should have been quenched by the electric field in front of the photoionization chamber. As has been shown previously^{76,77} a field of 1000 V/cm lowers the lifetime of the $2s$ metastable state to about 5×10^{-9} s. For 8 eV hydrogen atoms traveling through the plates, which are about 1 cm long, they will remain in the field about 2.6×10^{-7} s. This corresponds to approximately 50 lifetimes of the $2s$ state; thus any metastable atoms should have relaxed by the time they have left the field. The presence of the small $m/e = 1$ photoionization mass peak cannot therefore be explained by involving the photoionization of metastable hydrogen atoms and must remain unexplained for the time being.

IV. SUMMARY AND CONCLUSIONS

We have investigated the scattering of a beam of neutral metastable $2p^2A_2'' H_3$ molecules at translational energies in the 0.1 to 10 eV range by Ar and propane, as well as their surface ionization and photoionization. The total scattering cross section of H_3 by Ar was shown to be about ten times larger than the corresponding H-Ar cross section, in keeping with the large size of the metastable H_3 molecule. The use

FIG. 16. Mass spectrum of molecular beam. (a) Electron impact mass spectrum, (b) background-corrected photoionization mass spectrum generated by irradiation of beam with mercury lamp. Smooth line indicates fit to data points. The stagnation pressure was set at 90 and 80 Torr as indicated.

of the larger propane molecule in place of Ar as a scattering partner results in a large increase in the total cross section for hydrogen atoms but not for H₃ in agreement with that interpretation. These results suggest that due to its large size and high internal and translational energies, this H₃ metastable molecule may be expected to exhibit unusual properties, especially in the area of reaction dynamics.

We were able to observe surface ionization of H₃ to H₃⁺ on both tungsten and platinum filaments. By measuring the production of H₃⁺ as a function of filament temperature we determined an effective ionization potential of H₃ and concluded that upon interaction with the metal surface the metastable 2p²A₂' state first decays to the 2p²E' state, which can then surface ionize to produce H₃⁺. This process is consistent with the small number of H₃⁺ ions which are formed, since the greater fraction of the H₃ which decay on the filament surface to the 2p²E' state dissociate to form H and H₂.

We also observe the formation of H⁺ by surface ionization but are unable to completely explain this observation. Further experiments are necessary to elucidate the mechanism of this process. By velocity selecting the H₃ beam, one should be able to observe the effect of translational energy on surface ionization efficiency and gain insight into the mechanism which generates H⁺.

Lastly, we observe the production of H₃⁺ when the beam is irradiated with the light from a high pressure mercury lamp. This is the first direct observation of photoionization of metastable H₃.

APPENDIX A: POSSIBLE ALTERNATIVE ORIGINS OF DETECTED H₃

Because of our interpretation of the *m/e* = 3 mass spectral peak as due to an H₃ metastable, it is necessary that any other mechanisms which could account for that peak be ruled out. As a result, a number of potential candidates have been considered.

1. Ion-molecule reactions

One possible explanation for the observation of a *m/e* = 3 signal could be a reaction which produces H₃⁺ ions in the mass spectrometer ionizer by a mechanism other than electron impact ionization of neutral H₃. Since in this region a large number of ions as well as electronically excited species are produced, it is not unreasonable to consider that they might react with neutral molecules in the beam to form H₃⁺ which would then be extracted and detected by the mass spectrometer. Ion-neutral reactions tend to have large cross sections (~100 Å²)^{58b} and therefore could contribute to the observed signal.

The most likely ion-molecule reaction which may occur in the ionizer and produce H₃⁺ ion is

Rate constants for this reaction have been experimentally^{78,79} measured as well as calculated⁸⁰ as a function of energy for thermal energies and lie in the range (6 to 20) × 10⁻¹⁰ cm³ s⁻¹. From these results, thermal cross section can be

obtained which can be extrapolated to higher energies since they are known to be inversely proportional to the relative velocity of the reagents.^{80,81} At a laboratory H₂ translational energy of 8 eV this cross section is estimated to be 6.6 Å². Using this value we conclude that only 0.004% of the observed H₃⁺ mass peak intensity could be due to process Eq. (A1). Even if a significant fraction of the H₂ molecules have an energy as low as 1 eV (which is very unlikely in view of the high temperature of the arc discharge), this figure would be about 0.01%, which is still very small. As a result, it can be concluded that this process contributes negligibly to the observed signal.

Since an electron current can trap positive ions in the ionizing region of the mass spectrometer such a trapping could amplify the likelihood of process (A1). However, the ratio of the *m/e* = 3 to *m/e* = 1 peak intensities did not vary with electron current over the range 30 to 130 μA. Thus ion-molecule reactions may be ruled out as the cause of our observed *m/e* = 3 signal. As an independent confirmation of this conclusion, we doubled the background pressure of the mass spectrometer detector by introducing D₂ into it. No increase in the size of the ac peaks at *m/e* = 4 or 5 was detected, with the electron bombardment ionizer on, when the arc discharge H/H₃ beam, modulated at 150 Hz by a chopper, was sent into the detector. This indicates that no DH₂⁺ or D₂H⁺ is formed by reaction of H₂⁺ ions resulting from electron bombardment of beam molecules, with background D₂.

2. Three-body recombination processes

Recombination process of the type

which are possible at sufficiently high pressures, can be ruled out. The pressure in the mass spectrometer ionizer region is of the order of 10⁻⁵ Torr, resulting in a number density of 3.5 × 10¹² molecules cm⁻³. It is difficult to calculate the number of triple collisions that occur in a gas, but a fairly good estimate should be obtained by equating the ratio of triple collisions *Z*₁₂₃ to binary ones *Z*₁₂ to the ratio of the molecular diameter *d* to the mean free path.⁸² Under our conditions *d* ~ 10⁻⁸ cm and λ ~ 760 cm, *Z*₁₂₃/*Z*₁₂ results in a ratio of the order of 10⁻¹¹. This crude calculation shows that at the pressures at which our mass spectrometer detector is operated three-body processes are highly unlikely.

3. Excited atom-molecule reactions

Since electronically excited H atoms can be formed in the mass spectrometer ionizer by electron bombardment of H atoms,⁸³ the reactions of these species with H₂ is another candidate for production of H₃⁺

For this process to account for 10% of our observed H₃⁺ signal it should have a cross section of about 1200 Å², which is unrealistically high. Furthermore, the lack of the increase of the *m/e* = 5 peak when D₂ was introduced in the mass

spectrometer [as described in the discussion of process (A1)] confirms that Eq. (A4) does not contribute significantly to the observed H_3^+ signal.

APPENDIX B: LIFETIME OF HIGH-LYING RYDBERG STATES

We examine here the possibility that the observed metastable H_3 is due to excited electronic states other than the $2p^2A_2''$ state. In recent years there has been an increase in the number of studies of atoms⁸⁴⁻⁸⁷ in which the valence electron is excited to a state of high n (the principle quantum number). In these Rydberg states the electron is very weakly bound. Simple Bohr theory indicates that for $n = 25$ the mean radius is approximately 500 Å and the ionization energy of the excited electron is only 20 meV. In thermal collisions such atoms can ionize or change their state. However, in a collisionless environment they are relatively long lived. Quantum mechanical treatments^{87,88} for excited H atoms show that for $n = 25$ the radiative lifetime can be anywhere from 3 to 500 μ s depending on the value of the orbital angular momentum quantum number l . These long lifetimes are a consequence of poor overlap between the wave functions of the excited state and the ground or lower excited states.

Due to these lifetimes the possibility exists that the H_3 we have observed is not in the $2p^2A_2''$ state as we proposed but some higher-lying Rydberg state. To rule this out it is necessary to analyze the ability of these higher states to survive field ionization when traversing the ion deflection plates.

When an atom is in a high Rydberg state it may be described to a good approximation as an ionic core with a single electron sufficiently far away from the core to be described by the single particle Hamiltonian⁸⁹

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r). \quad (B1)$$

In the presence of a constant electric field E , which is taken to lie along the z axis, a zE term must be added to the right-hand side of this equation. This field not only will perturb the atomic energy levels (Stark effect) but will cause a local potential maximum to appear on the "down-field" side of the atom. Therefore, in the presence of such an electric field there are no true stationary states and the electron will have a finite probability of tunneling through this potential barrier to the outside. As the field increases the barrier becomes lower and narrower, thereby increasing the probability that the electron will be emitted. The penetrability of this barrier was first calculated by Lanczos⁹⁰ and this result has since been extended by many workers.⁹¹⁻⁹⁷ If this simple hydrogenic model is assumed to hold for neutral atoms in general, then all Rydberg states with a principal quantum number greater than the critical value

$$n_c \approx 24[E(\text{kV/cm})]^{-1/4} \quad (B2)$$

are field ionized, in a field of intensity E . This has been experimentally verified,⁹⁷⁻⁹⁹ and the hydrogenic theory provides a good model of highly excited Rydberg states in other species such as rare gases and alkali atoms.

Assuming this theory to be valid for the Rydberg states of H_3 , the 1 kV/cm field used in the present experiments can

be expected to field ionize any H_3 with $n \geq 25$ and deflect the ions generated in this manner. We therefore expect that the species which we are detecting are not in highly excited Rydberg states.

With quenching of high Rydberg states accomplished by field ionization we still need to rule out the possibility of lower-lying Rydberg states. To do this it suffices to examine the radiative lifetimes for states with $n \leq 25$. As calculated from equations listed in Bethe and Salpeter,⁸⁷ as well as experimental data from Stebbings⁹⁷ and Allen,¹⁰⁰ such states should have radiative lifetimes less than 10 μ s. The Rydberg states of H_3 are expected to display a similar behavior and to have radiatively decayed before reaching the mass spectrometer detector in our apparatus, for states whose downward transitions are not optically forbidden. However, the results in Sec. III A suggest that some H_3 may nevertheless be in higher Rydberg states than the $2p^2A_2''$ one.

From this analysis and the discussion in Sec. II A we can conclude that the metastable we observe is not predominantly a high lying Rydberg one and is most likely to a major extent the $2p^2A_2''$ state.

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