for energies near $\frac{3}{2}kT_e$.

It should be pointed out that although the analytical solutions have been found in these cases, for other applications perhaps more complex, the methods described in the text may be more satisfactory.

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Collision Processes Occurring in Decaying Plasmas Produced in Helium-Hydrogen Mixtures*

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The time dependence of the densities of He^+, He_2^+, H^+, H_2^+, H_3^+, HeH^+, and He_2H^+ ions was measured in the afterglow period of plasmas produced in helium containing 0.01, 0.02, and 0.1% hydrogen for total gas pressures varying from 1 to 10 Torr. The rate constant for the ionization of H_2 by $He(2\,^3S)$ was found to be 5.2×10^{-11} cm sec^{-1}. The studies resulted in the observation, for the first time, of the production of H_2^+ by mutual collisions between metastable hydrogen molecules. The radiative lifetime of these molecules was measured to be 2.7 ± 0.2 msec. The occurence of several other collision processes was also established. The mobility of H_3^+ in helium was determined to be $\mu_0 = 40 \pm 0.5$ cm^2 $(V\ sec)^{-1}$.

I. INTRODUCTION

In 1965, Oskam and Mittelstadt[1] published a study of the electron-density decay in helium-hydrogen mixtures after cessation of the discharge pulse. The electron density was measured using the microwave-cavity method. The measurements were performed over a total pressure range 1–32 Torr and a range of hydrogen concentrations 10^{-4}–1%. They measured an effective ambipolar diffusion coefficient D_a, which is defined as

$$(D_a p_0)_{\text{eff}} \equiv p_0 \Lambda^2/\tau_e, \tag{1}$$

where Λ is the characteristic diffusion length of the plasma container related to the fundamental diffusion mode, p_0 is the gas pressure reduced to 0 °C, and τ_e is the measured time constant of the exponential part of the electron-density decay curve.

For gas pressures between 4 and 32 Torr the effective ambipolar diffusion coefficient depended on the discharge-excitation pulse length and varied from $(D_a p_0)_{\text{eff}} = 1350$ to 1650 $cm^2\ sec^{-1}$ Torr. The larger value was obtained for the longest pulse length, which ranged from 0.01 to 5 msec. No satisfactory explanation was found for this behavior.

The only other afterglow studies in helium-hydrogen mixtures of which we are aware were performed by Adams *et al.*[2] using the flowing-afterglow method. They reported rate constants for reactions of He_2^+, HeH^+, HeH_2^+, and He_2H^+ with hydrogen. In order to determine the reasons for the unusual behavior of the effective ambipolar diffusion coefficient observed by Oskam and Mittelstadt, the present mass-spectrometer measurements were performed. In addition, it was believed that information could be obtained about the collision

processes responsible for the production of He_2H^+, an ion which was first reported by Veatch and Oskam.[3]

These studies have also resulted in the observation, for the first time, of the production of H_2^+ via the process

$$H_2^m(c\,^3\Pi_u,\ v=o)+H_2^m(c\,^3\Pi_u,\ v=o)\rightarrow H_2^+ + H_2(x)+e\,. \tag{2}$$

This metastable hydrogen molecule was first observed by Lichten[4] in a beam experiment. It has also been observed by others[5-8] in beam experiments, but the present study is the first to indicate that this metastable hydrogen molecule is present in a decaying hydrogen plasma. Process (2) for producing H_2^+ is analogous to the process which has been observed in decaying plasmas produced in nitrogen and helium-nitrogen mixtures.[9,10]

II. EXPERIMENTAL METHOD

The experimental tube used to study the time dependence of the ions during the afterglow period consists of a differentially pumped mass spectrometer which samples ions diffusing to the walls of a discharge tube. The mass spectrometer used is of the electric quadrupole type and has been described in detail elsewhere.[11]

The discharge region is a glass cylinder with metal endplates. One endplate is a molybdenum electrode, while the other is made of Kovar metal and contains a small hole (60 μ in diameter and 40 μ long) through which the ions effuse into the mass-spectrometer region.

The gas-handling system is analogous to that developed by Alpert.[12] The ultimate pressure was about 10^{-9} Torr following a system bakeout at 350 °C for a period of 24–36 h. The helium was purified by means of the cataphoretic segregation method.[13] The final cleaning of the discharge region was achieved by covering the discharge-tube wall with a molybdenum layer obtained from sputtering the discharge electrode. This cleaning process was continued until the impurity-ion signal was less than 0.5% of that of the dominant ion throughout the afterglow. This condition was necessary to achieve reproducibility of the data. The gas pressure was measured by a capacitance manometer which controlled a servo-operated valve to maintain a constant preset pressure in the discharge tube.

A block diagram of the measuring system is shown in Fig. 1. The discharge was produced by

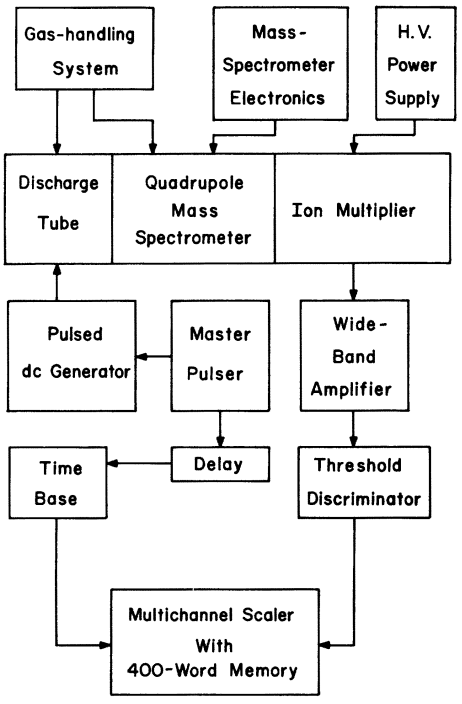

FIG. 1. Block diagram of measuring system.

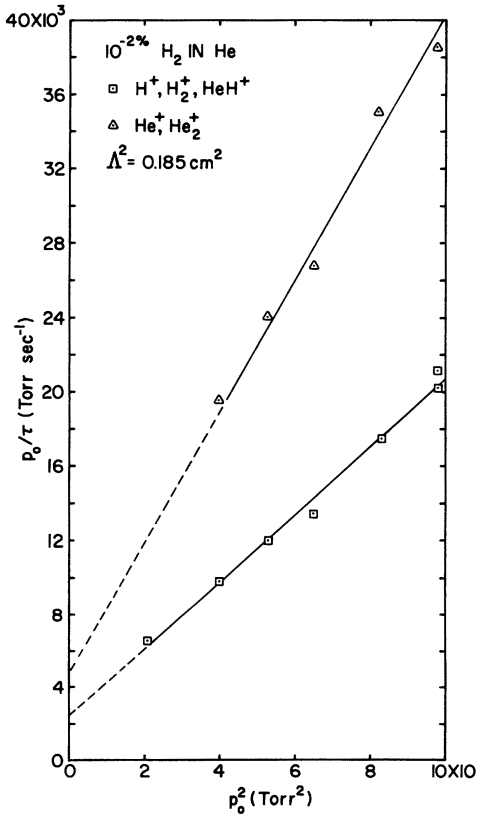

FIG. 2. Measured values of p_o/τ for H^+, H_2^+, He^+, HeH^+, and He_2^+ as a function of p_o^2 (gas temperature 300 °K).

a high-voltage dc pulse applied between the discharge-tube electrodes. The ions passing through the quadrupole mass spectrometer are detected by a 14-stage ion multiplier. The resulting anode pulses, each due to a single ion, are amplified by a wide-band amplifier and those above a minimum pulse height are selected by a discriminator in order to reduce the background count rate. The pulse from the discriminator are then fed into a multichannel scaler. The afterglow is divided into 100–400 equal-time intervals which have a minimum duration of 25 μsec. As the multichannel scaler advances from channel to channel, the number of pulses in the corresponding time intervals in the afterglow are recorded in the memory section. By accumulating the afterglow counts for a sufficient number of afterglow repetitions, a statistically significant number of counts can be recorded in each channel of the memory.

III. RELEVANT AFTERGLOW PROCESSES

During the studies it was found that the ionization process (2) has to be considered when discussing the properties of the decaying plasmas produced in helium-hydrogen mixtures.

The presence of helium triplet metastable atoms during the decay period results in the production of H_2^+, HeH^+, and H^+ ions by the Penning processes

$$He^m + H_2 \rightarrow H_2^+ + He + e \quad (3a)$$

$$\rightarrow HeH^+ + H + e \quad (3b)$$

$$\rightarrow H^+ + H + He + e\,. \quad (3c)$$

They can also produce He^+ ions by the ionization process

$$He^m + He^m \rightarrow He^+ + He + e, \quad (4)$$

while the He^+ ions are converted into He_2^+ ions by

$$He^+ + 2He \rightarrow He_2^+ + He. \quad (5)$$

Processes (4) and (5) have been found to influence the properties of afterglows produced in helium and in helium containing a small amount of neon atoms.[14]

The He_2^+ ions, but not the He^+ ions, produced during the discharge-pulse and plasma-decay period produce H^+, H_2^+, HeH^+, and He_2H^+ as a consequence of the process[15]

$$He_2^+ + H_2 \rightarrow H^+ + H + 2He \quad (6a)$$

$$\rightarrow H_2^+ + 2He \quad (6b)$$

$$\rightarrow HeH^+ + H + He \quad (6c)$$

$$\rightarrow He_2H^+ + H\,. \quad (6d)$$

These reactions have been observed by Aquilanti *et al.*,[16] and the total reaction-rate constant for processes (6a)–(6d) has been measured by Adams *et al.*[2] to be 5.3×10^{-10} cm^3 sec^{-1} at 200 °K.

In addition to processes (3b) and (6c), HeH^+ can be produced by

$$H_2^+ + He \rightarrow HeH^+ + H\,. \quad (7)$$

According to Chupka and Russell,[17] who performed photoionization measurements in helium-hydrogen mixtures, the H_2^+ ions in process (7) must be at least in the third vibrational level, which is about 0.8 eV above $v=0$. The HeH^+ ions may be lost by the processes

$$HeH^+ + H_2 \rightarrow H_3^+ + He \quad (8)$$

and

$$HeH^+ + 2He \rightarrow He_2H^+ + He\,. \quad (9)$$

The production of Ar_2H^+ by a process analogous to (9) has been postulated by Fehsenfeld *et al.*[18] in

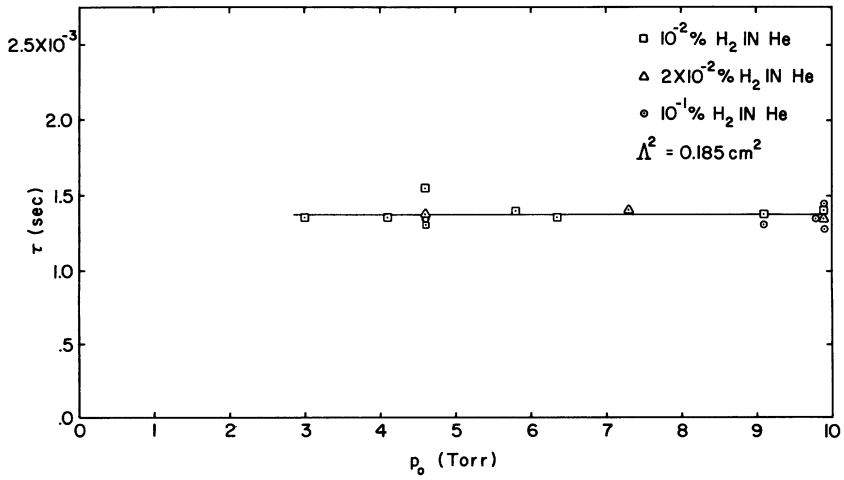

FIG. 3. Measured values of the time constant related to the final decay rate of H_2^+ ions as a function of total gas pressure for various hydrogen concentrations and short discharge pulse lengths.

connection with measurements in argon-hydrogen mixtures. However, there does not exist direct evidence for the occurrence of reaction (9).

The He_2H^+ ions are produced by processes (6d) and (9) and are lost by

$$He_2H^+ + H_2 \rightarrow H_3^+ + 2He . \quad (10)$$

The rate constant for this process has been measured by Adams *et al.*[2] at temperature of 200 °K.

Two more collision processes have to be considered. These are

$$H^+ + H_2 + He \rightarrow H_3^+ + H \quad (11)$$

and

$$H_2^+ + H_2 \rightarrow H_3^+ + H . \quad (12)$$

The reaction rate for process (12) is quite large.[19]

In order to calculate the time dependences of the number densities of the particles governing the decay properties of plasmas produced in helium-hydrogen mixtures, the continuity equation for each of the active particles [He^m ($2\,^3S$), He^+, He_2^+, $H_2^m(c\,^3\pi_u, v=0)$, H^+, H_2^+, H_3^+, HeH^+, He_2H^+] has to be solved. The solutions of the continuity equations are rather simple functions if the experimental conditions are chosen such that the loss processes are mainly diffusion towards the walls of the plasma container and/or linear volume-loss processes.

For particles which are not produced during the decay period, the time dependence of the fundamental mode is a single exponential function. The relevant time constant is directly related to the loss processes of the particle. If the particle is also produced during the decay period, its time dependence is given by the sum of exponential functions having different time constants.[20] One time constant is related to the loss processes of the particle, while the other (others) describes (describe) the loss of the producing particles. The final decay of the particles will be determined by the largest time constant.

It can easily be shown that the time constant τ, related to the loss processes of any particle, is, for the assumptions made, given by[20]

$$1/\tau = D/\Lambda^2 + \nu . \quad (13)$$

Here, D is the diffusion coefficient of the particle (ambipolar diffusion coefficient D_a for charged particles), Λ is the fundamental characteristic diffusion length of the plasma container, and ν is the volume-destruction frequency of the particle considered.

The ion signal measured by the mass spectrometer gives information about the time dependence of the ion density inside the plasma only if the density gradient at the plasma boundary is independent of time. This means that the density distribution of the ions has to be very close to the fundamental diffusion-mode distribution. Oskam[20] derived requirements with respect to the time in the afterglow period as well as the decrease in the magnitude of the fundamental mode distribution, after which the influence of higher diffusion modes on the measurements can be neglected for particles lost by diffusion only. If, however, the particles disappear by a combination of diffusion loss and volume loss, the required decrease in the density of the particles involved can be shown to be considerably larger than the required decrease for loss by diffusion only. Thus it is essential that the discharge excitation produces a charged-particle distribution close to a fundamental-mode distribution.

IV. RESULTS AND DISCUSSION

The time dependence of the ion densities in the afterglow period was measured in plasmas produced in helium containing 0.1, 0.02, and 0.01% hydrogen for total reduced gas pressures varying from 1 to 10 Torr. The gas temperature was 300 °K and the duration of the discharge pulse varied from 0.05 to 10.0 msec, applied at usually 64-msec intervals.

It was observed that the shorter the pulse length, the greater were the effects on the plasma decay properties of the metastable hydrogen molecules through process (2). By increasing the discharge pulse length to 5 or 10 msec, the influence of process (2) on the plasma decay was greatly reduced. Thus it was possible to have another variable in the analysis of the data.

The dominant ion in the afterglow was, in general, H_3^+, except for some of the lowest pressures used. Also present were H^+, H_2^+, He^+, HeH^+, He_2^+, and He_2H^+, but in smaller amounts. The ion HeH_2^+ observed by Adams *et al.*[2] at a gas temperature of 200 °K was not detected.

The large number of possible processes in a decaying plasma consisting of seven different positive ions and two types of metastable particles makes the interpretation of the data quite complicated. All the ion conversion processes, however, eventually lead to the stable ion of lowest energy H_3^+. Owing to the large reaction-rate constants of these conversion processes, the decay rates of most ions were found to be determined by their rates of production by metastable particles. Thus in most cases it will only be possible to determine some of the processes involved and to obtain information about the loss rates of the metastable particles.

The first step in one sequence of processes is the production of He^+ ions by a collision between

two $He(2\,^3S)$ atoms, i.e., process (4). This means that the measured decay rate of the number density of He^+ ions will be twice as large as the decay rate of the $He(2\,^3S)$ number density. Since He_2^+ ions are produced from He^+ ions via process (5), the time dependence of the number density of He_2^+ ions during the decay period will be the same as that of the He^+ ions, provided the rate of loss of He_2^+ is larger than its production rate. The He_2^+ ions in turn produce hydrogen ions via process (6).

Another ionization process occurring during the decay period of plasmas produced in helium-hydrogen mixtures is the production of hydrogen ions by metastable helium atoms via the Penning process (3). The decay properties of ions produced by this process will be the same as those of the metastable helium atoms, provided the loss rate of the ions is larger than their rate of production.

In a helium-hydrogen mixture, the loss rate of $He(2\,^3S)$ metastable atoms is determined by the Penning process (3) and diffusion to the walls of the plasma container. In Fig. 2 is plotted p_0/τ for the ions He^+, He_2^+, H^+, H_2^+, and HeH^+ as a function of p_0^2. The straight line for the p_0/τ values of H^+, H_2^+, and HeH^+ can be represented by

$$p_0/\tau = D_m p_0/\Lambda^2 + C_3 r p_0^2 , \tag{14}$$

while these values for He^+ and He_2^+ can be represented by

$$p_0/\tau = 2(D_m p_0/\Lambda^2 + C_3 r p_0^2), \tag{15}$$

where $r = p_0(H_2)/p_0(He)$.

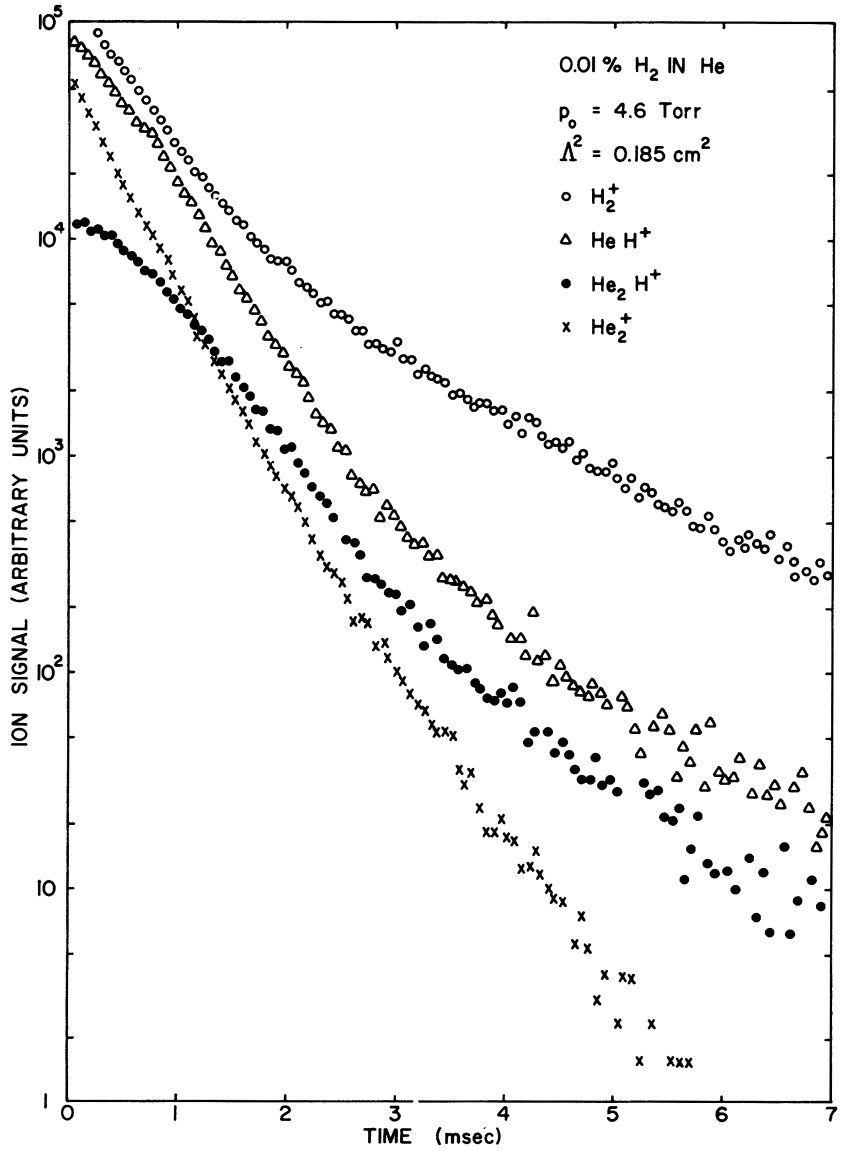

FIG. 4. Time dependences of the number densities of H_2^+, HeH^+, He_2^+, and He_2H^+ ions for short discharge pulse lengths.

The evaluation of the constant C_3 yields $C_3 = 1.8\times10^6$ (Torr sec)$^{-1}$, which corresponds to a reaction-rate constant for the Penning process (3) equal to $k_3 = 5.2\times10^{-11}$ cm^3 sec^{-1}. This value is in excellent agreement with the value reported by Sholette and Muschlitz[21] and by Marshall,[22] but is somewhat larger than the value of 3.18×10^{-11} cm^3 sec^{-1} obtained by Schmeltekopf and Fehsenfeld.[23] The value for the diffusion coefficient of He ($2\,^3S$) in helium follows from the intercepts of the straight lines in Fig. 2 at $p_0^2 = 0$. Its value was found to be given by $D_m p_0 = 460$ cm^2 sec^{-1} Torr and is also in excellent agreement with previously published values.[24]

The measured decay curves for H^+, H_2^+, and HeH^+ exhibited a time constant related both to the direct production of these ions by metastable helium atoms via process (3) and to production via the sequence of processes (4)–(6). From energy considerations it follows that H^+ and H_2^+ cannot be produced by HeH^+, while H_2^+ and H^+ cannot produce each other. Thus, it is possible to conclude that processes (3a), (3c), (6a), and (6b) definitively occur. However, nothing can be concluded about the occurrence of processes (3b), (6c), and (6d), because of the possibility that the decay properties of HeH^+ and He_2H^+ ions are governed by their production by H^+ and HeH^+ ions, respectively.

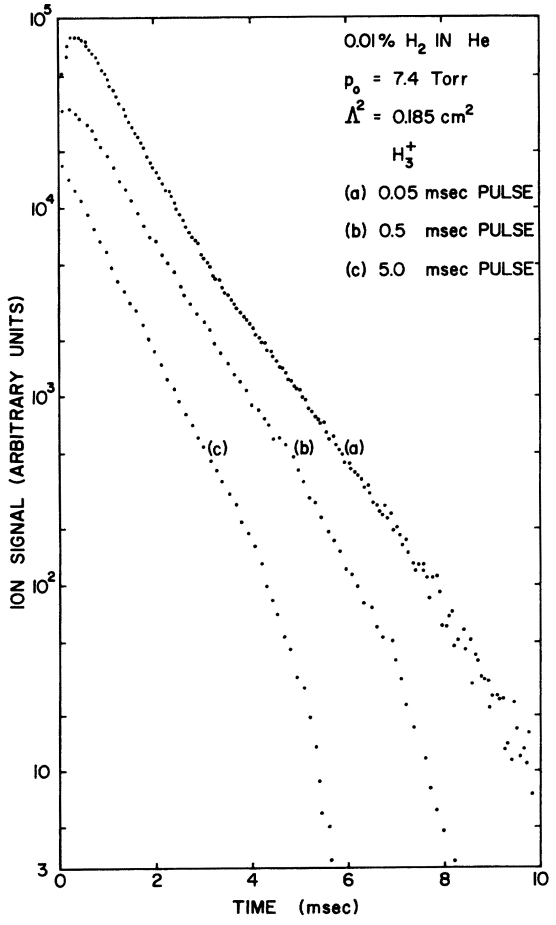

FIG. 5. Time dependence of the number density of H_3^+ ions for three different discharge pulse lengths.

For short discharge pulse lengths it was observed that the final decay rate of the density of H_2^+ ions was smaller than the rates associated with any known loss or production process of these ions. The same small rate of loss was observed for other ions, but H_2^+ was energetically the highest of the ions exhibiting this behavior. It is therefore plausible to assume that an as yet unknown production process of H_2^+ ions occurs, while these ions produce the other observed ions via processes mentioned in Sec. III. The only possible explanation of the data is the production of H_2^+ ions through collisions between two $H_2(c\,^3\Pi_u, v=0)$ metastable molecules, i.e., via process (2).[25]

The measured time constants related to the final decay rate of H_2^+ ions as a function of total gas pressure as well as hydrogen concentration are given in Fig. 3. These data show that the time constant is independent of helium pressure and hydrogen concentration. This means that the rate of diffusion loss as well as the rate of volume loss of $H_2(c\,^3\Pi_u, v=0)$ by collisions with hydrogen and helium are negligible in the range of experimental conditions used. Thus the loss of $H_2(c\,^3\Pi_u, v=0)$ is governed by its radiative lifetime τ_r. Taking into account that τ_r is measured through the time constant of H_2^+ produced via process (2), the radiative lifetime is found to be $\tau_r = 2.7\pm0.2$ msec. This value is larger than the value of 1.0 ± 0.1 msec measured by Johnson[26] using the time-of-flight technique and the theoretically calculated value of $1.0^{+1}_{-0.5}$ msec reported by Freis and Hiskes.[27]

From the data shown in Fig. 3 upper limits of the deactivation of $H_2(c\,^3\Pi_u, v=0)$ by two-body collisions with helium atoms or by hydrogen molecules were estimated to be smaller than 10^{-16} and 10^{-13} cm^3 sec^{-1}, respectively. The phenomenon of diffusion suppression of $H_2(c\,^3\Pi_u, v=0)$ is not completely surprising, since the same phenomenon has been found for $N_2(a'\,^1\Sigma_u^-)$ by Lund and Oskam[9] in nitrogen afterglows.

Figure 4 shows the time dependences of the number densities of H_2^+, HeH^+, He_2H^+, and He_2^+ ions under conditions where the final decay rate of H_2^+ is determined by metastable hydrogen molecules via process (2). The decay rate of the HeH^+ ion during the later part of the decay period is the same as that of the H_2^+ ion. This indicates that

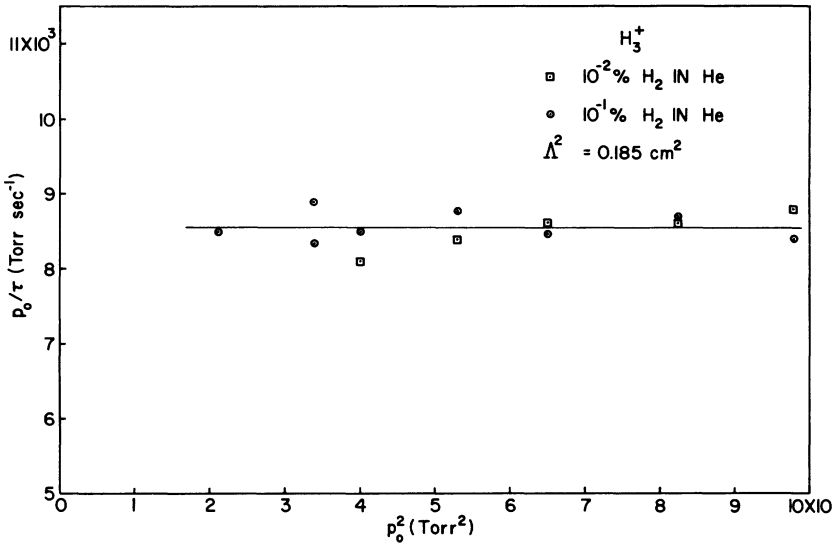

FIG. 6. Measured values of p_0/τ for H_3^+ as a function of pressure for long discharge pulse lengths.

the HeH^+ ion is produced by vibrationally excited H_2^+ ions via process (7). Moreover, the time dependence of the He_2H^+ ions is closely the same as that of HeH^+, which shows that the He_2H^+ ions present in the decaying plasma are produced at least in part by process (9). The time dependence of the density of He_2^+ is also given in Fig. 4 to show that it does exhibit a different time dependence. However, this does not exclude the possibility of the production of He_2H^+ ions via process (6d).

Figure 5 shows the measured time dependence of H_3^+ ions for three different discharge pulse lengths. As mentioned previously, the influence of the production of H_2^+ ions via process (2) on the plasma decay properties was largest for the shortest pulse lengths. Since H_3^+ ions are produced directly through process (12) and indirectly via several other processes, it can be expected that the measured decay of H_3^+ ions will depend on discharge pulse length. The shortest discharge pulse length should result in the smallest decay rate of H_3^+ ions. This explains the observed apparent change in the effective diffusion coefficient of H_3^+ ions as reported by Oskam and Mittelstadt.[1] The increase in the decay rate during the late afterglow (Fig. 5) is due to the transition from ambipolar diffusion to free diffusion, which has been observed previously.

In order to determine the ambipolar diffusion coefficient of H_3^+ ions in helium, it was necessary to use discharge pulse lengths long enough to ensure that the decay rate was determined solely by loss processes of H_3^+. The measured values of p_0/τ are shown in Fig. 6 as a function of helium pressure for two hydrogen concentrations. The p_0/τ values are independent of pressure, which shows that under these conditions the loss of H_3^+ is governed by ambipolar diffusion. The measured ambipolar diffusion coefficient is given by $D_a p_0 = 1570 \pm 20$ cm^2 sec^{-1} Torr for a gas temperature of 300 °K. The corresponding mobility of H_3^+ in helium is $\mu_0 = 40 \pm 0.5$ cm^2 (V sec)$^{-1}$, which is in excellent agreement with the upper limit reported by Oskam and Mittelstadt.[1]

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Temperature-Dependent Phase Memory of Ruby Determined by Self-Induced Transparency*

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A computer simulation of recent self-induced-transparency experiments in ruby demonstrates the general appropriateness of a previously derived two-level model for a wide range of attenuator temperatures. The only significant deviation is a sharper rise in the experimental delay curve. The temperature dependence of the homogeneous phase relaxation T_2' was introduced by including a "direct" phonon transition process in our program. The parameters for best fit provide $T'_2 \simeq 50$ nsec for $T \simeq 0$ °K, which emphasizes the importance of phase-memory effects in low-temperature atomic-coherence experiments in ruby.

The self-induced-transparency (SIT) effect was first observed in a cryogenically cooled ruby attenuator.[1,2] Similar effects have been observed in rubidium vapor[3] and SF_6,[4] and compared with theoretical calculations for those materials.[3,5] Recent experiments[6-8] provide sufficient quantitative data on SIT in ruby as a function of attenuator temperature to permit a quantitative comparison with theory. Such a comparison provides information on phase relaxation in ruby, which is unattainable through standard optical techniques.

A model for SIT in ruby has been developed in which an ensemble of two-level atomic systems is subjected to both homogeneous ($T_2' \neq \infty$) and inhomogeneous ($T_2^* \neq \infty$) broadening.[9] The latter represents the effects of local crystal strains and is virtually temperature independent: the former is owing to transitions involving phonons, and thus depends markedly on temperature.[10] At low temperatures (below 77 °K), inhomogeneous broadening predominates which encourages the belief that "it is not possible to determine optically which phonon processes are important at low temperatures"[10]; however, the sensitivity of optical atomic coherence effects (SIT, photon echo, etc.) to finite phase-memory times (T_2') provides a fortunate exception. For example, the SIT pulse delay has been shown to be extremely sensitive to variations in the temperature (experimental study[6]), or the T_2' (theoretical study[9]) of the attenuator. In particular, the maximum pulse delay t_D (max) is not expected to exceed T_2'. Similar effects have been observed in photon-echo experiments,[11,12] although these require the application of external magnetic fields.

This paper reports a computer simulation of the ruby SIT experiment described in Refs. 6 and 7. In those studies, a ruby attenuator with a 45-db linear absorption at 4 °K was exposed to pulses of coherent radiation with a full width at half-maximum of the light intensity of 30 nsec. In the theoretical calculation, the pulse, which is taken to be