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MEASUREMENTS OF ION-MOLECULE REACTIONS OF HE^+, H^+, AND HEH^+ WITH H_2 AND D_2

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Abstract

A drift tube-mass spectrometer apparatus has been used to determine the rate coefficient, energy dependence and product ions of the reaction $He^+ + H_2$. The total rate coefficient at 300 K is $(1.1 \pm 0.1) \times 10^{-13}$ cm^3/sec. The reaction proceeds principally ($\gtrsim 80\%$) by dissociative charge transfer to produce H^+, with the small remainder going by charge transfer to produce H_2^+ and by atom rearrangement to produce HeH^+. The rate coefficient increases slowly with increasing ion mean energy, reaching a value of 2.8×10^{-13} cm^3/sec at 0.18 eV. The corresponding reaction with deuterium, $He^+ + D_2$, exhibits a value $(5 \pm 1) \times 10^{-14}$ cm^3/sec at 300 K. The reaction rates for conversion of H^+ and HeH^+ to H_3^+ on collisions with H_2 molecules are found to agree well with results of previous investigations.

I. Introduction

The recent microwave occultation experiment carried out during the flyby of Jupiter by the Pioneer 10 spacecraft[1] has provided extensive observational data concerning the Jovian ionosphere which may be compared with theoretical models proposed by several authors[2-7]. Models of this kind take into account the physical and chemical properties of the neutral atmospheric constituents, the fluxes of ionizing radiation from the sun and the relevant atomic collision processes between the ions, electrons, and neutral constituents.

The present paper describes drift tube-mass spectrometer measurements of several ion-molecule reactions believed to be important in the hydrogen-helium upper atmosphere of Jupiter, in particular the reaction of He^+ ions with H_2 (and D_2) molecules to form H^+, HeH^+, and H_2^+ ions. Previously, only an upper limit for the rate of this reaction had been obtained from flowing afterglow studies[8]. Measurements of the three-body reaction of H^+ and the two-body reaction of HeH^+ with H_2 to form H_3^+ ions are also described.

II. Experimental Apparatus and Principle of Measurement

The measurements were carried out in the drift tube-mass spectrometer apparatus described in a recent publication[9]. The demands on the purity of the reactant gas (hydrogen) were more stringent here than in studies of faster ion-molecule reactions, since even very small amount of the common impurities found in commercially available hydrogen[10] cause rapid conversion of the highly reactive helium ion. For this reason some of the measurements were repeated in hydrogen that had been purified further by diffusion through a

heated palladium-silver alloy tube. The absence of significant amounts of background impurities in the apparatus was checked regularly by measuring the decay rate of He^+ ions in pure helium gas.

As in previous studies, the reaction rate coefficient is determined from the loss of the parent ion (He^+) as function of the parent ions' additional residence time[11] in the drift tube. In order to obtain the rate coefficient at above-thermal energies, the decay rate is measured as a function of E/p, the ratio of the drift electric field to the gas pressure. The ions' mean energy is derived from the measured drift velocity and Wannier's theoretical relationship[12].

III. Measurements

$He^+ + H_2$

The measurements were carried out in two parts; a determination of the He^+ loss rate in H_2, yielding the total rate coefficient, k_1, and an analysis of the product ions formed by the reaction to establish the relative contributions of the three exoergic branches,

$$He^+ + H_2 \longrightarrow \begin{cases} He + H^+ + H & (1a) \\ He + H_2^+ & (1b) \\ HeH^+ + H. & (1c) \end{cases}$$

The loss rate, $\nu = d(\ell n[He^+])/dt$, was found to depend linearly on the H_2 pressure over the measured range (0.2 to 1.1 Torr, see Fig. 1). The two body rate coefficient at 300 K is found to be $k_1 = (1.1 \pm 0.1) \times 10^{-13}$ cm^3/sec in purified H_2 (using the palladium-silver diffusion cell). The slightly higher rate constant observed

in unpurified hydrogen was attributed to a small nitrogen impurity in the commercial H_2. As a result of its greater molecular weight this impurity tends to build up in the differentially pumped drift cell by about a factor $[m_{N_2}/m_{H_2}]^{\frac{1}{2}} \sim 3.7$ over the $\sim$ 5 ppm contained in the supply tank.

The variation of k_1 with the He^+ mean energy is shown in Fig. 2. A steady increase of k_1 with increasing ion mean energy is observed up to the maximum energy attained, $\sim$ 0.2 eV.

The analysis of the product channels of reaction (1) is complicated by the fact that all three of the expected product ions undergo secondary reaction with hydrogen. The reactions are:

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (2)$$

$$HeH^+ + H_2 \rightarrow He + H_3^+ \qquad (3)$$

$$H^+ + 2\,H_2 \rightarrow H_3^+ + H_2 \quad . \qquad (4)$$

Reaction (2) has been shown to be fast[13, 14] $k_2 = 1.4 \times 10^{-9}$ cm^3/sec at 300 K. The measured rates of reactions (3) and (4) are discussed later in this section.

At the relatively high H_2 pressures used in the measurements (0.05 Torr) one would therefore not expect to observe the primary products of (1b) and (1c) but only their secondary product, H_3^+, since the lifetimes of HeH^+ and H_2^+ (< 1 μsec at 0.05 Torr) are considerably shorter than the time of flight of ions through the drift tube ($\sim$ 1 msec). A drastic reduction of the H_2 pressure would have been required to make these lifetimes comparable to the ions' times of flight, which

unfortunately also would have reduced the number of ions produced in reaction (1) to below the detection limit.

The measurements were therefore restricted to observations of the primary product of branch (1a), H^+, (which has a lifetime of about 10 msec against three body conversion at 0.05 Torr) and the secondary product of branches (1b) and (1c), H_3^+. Both of these ions were observed in the experiment. Some of the observed "product" ions clearly were not produced by reaction (1) but arose from ion production in H_2 gas which reached the differentially pumped ion source. This contribution to the observed signal was separated from the signal of interest by carrying out the measurements in a mixture of helium and hydrogen. In this gas mixture the drift velocity of He^+ ions is considerably smaller than that of H_3^+ and H^+ ions, with the result that ions produced by reaction (1) have a longer transit time than those produced in the ion source.

It was concluded from these measurements that reaction (1) predominantly produces H^+ ions and that the sum of the reaction channels (1b) and (1c) accounts for less than 20% of the total rate coefficient. To arrive at this result, the contribution of reaction (4) to the observed H_3^+ signal was calculated from the measured H^+ signal, the rate constant k_4 and the H_2 density. The ratio of the remaining H_3^+ signal to the H^+ signal is then taken as the ratio $(k_{1b} + k_{1c})/k_{1a}$. Since there are experimental indications that our detection sensitivity for H^+ ions may be lower than that for H_3^+ ions, the actual contribution of reaction channels (1b) and (1c) to the total rate coefficient may be considerably lower than 20%.

$He^+ + D_2$

The total rate coefficient for the $He^+ + D_2$ reaction at 300 K was determined to be $(5 \pm 1) \times 10^{-14}$ cm^3/sec, roughly one half the value measured for $He^+ + H_2$. The reaction exhibited the pressure dependence expected for a two body process over the pressure range ~ 0.45 to 0.95 Torr (see Fig. 1). Since the deuterium was used without further purification, it is possible that this rate coefficient includes a ~ 20% contribution due to reactions with impurities, so that the actual rate coefficient may only be $\sim 4 \times 10^{-14}$ cm^3/sec.

As in the case of the light hydrogen isotope studies, the dominant product ion of this reaction appears to be the atomic ion D^+. The dependence of the rate coefficient on the ions' mean energy has not been studied.

HeH^+ and $H^+ + H_2$

In the course of these measurements the two-body conversion of HeH^+ to H_3^+ on collisions with H_2, reaction (3), was observed to occur with a rate coefficient $k_3 \gtrsim 10^{-9}$ cm^3/sec at 300 K, in agreement with the results of recent measurements[14, 15]. In the present experiment the HeH^+ ions were apparently produced from metastable helium atoms through the reaction $He^M + H_2 \rightarrow HeH^+ + H + e$. Our results are given as a lower bound because the observed loss of HeH^+ was slightly compensated by a resupply reaction involving the small fraction of He_2^+ ions produced in the ion source; viz. $He_2^+ + H_2 \rightarrow HeH^+ + He + H$.

The three-body conversion of H^+ to H_3^+, reaction (4), was observed to occur with a rate coefficient $(3.1 \pm 0.15) \times 10^{-29}$ cm^6/sec at 300 K, in good agreement with previous determinations[16].

Discussion

The reaction of He^+ with H_2 has not been previously observed in laboratory measurements. An upper limit for its rate coefficient, however, was given by Fehsenfeld et al[8], who concluded from measurements in a flowing afterglow system that the rate coefficient at 300 K was less than or the order of 10^{-13} cm^3/sec, very close to the value $k = (1.1 \pm 0.1) \times 10^{-13}$ cm^3/sec measured in the present experiment. The present studies also indicate that a majority or all of the reaction at low energies goes to formation of H^+ by dissociative charge transfer, reaction (1a).

Dissociative charge transfer may occur if one of the H_2 (1σ) electrons is captured into the 1s state of He and the second H_2 (1σ) electron is simultaneously excited into the repulsive $1\sigma_u$ state of H_2^+ or into the attractive $1\sigma_g$ state above the dissociation limit (see Fig. 3, which shows the relevant potential energy curves for H_2 and H_2^+). Charge transfer, in general, is a fast process only if the initial and final states are nearly resonant in energy; in the $He^+ - H_2$ system this condition occurs only for two H-H internuclear separations R_1^* and R_o^*, both of which are quite different from the equilibrium separation in the H_2 molecule. Thus, if distortion of the H_2 molecule during the collision with He^+ is neglected, one would expect the overlap between the ground state H_2 wave function and that of the H_2^+ (σ_u) or (σ_g) state to be small at energy resonance, leading to a small rate coefficient for dissociative charge transfer.

However, estimates of the overlap integral based on the usual approximations to the wave functions (delta functions at R_1^* and R_o^* for the H_2^+ states and a gaussian function for the H_2 ground vibrational state) lead to prediction of a rate constant many orders of magnitude

smaller than that observed. In this case one must also consider possible contributions to the overlap integral from the Franck-Condon region (cross hatched area in Fig. 3) where the H_2^+ (σ_g) wave function oscillates rapidly. If the cancellation between the various parts of this oscillatory wave function as it overlaps the gaussian ground state wave function is incomplete, the finite contribution to the overlap integral may be sufficient to account for the observed, slow charge transfer rate.

Finally, the fact that the $He^+ + D_2$ rate coefficient is approximately one half that of $He^+ + H_2$ is in the proper direction for an isotope effect in which the more compact D_2 ground state wave function has a smaller overlap with the "delta function" D_2^+ wave functions at the energy resonant points R_1^* and R_0^*. However, the observed difference between the D_2 and H_2 rates is far smaller than would be expected if the delta function representation of the H_2^+ and D_2^+ states were adequate, again suggesting that contributions to the overlap integral from the D_2^+ (σ_g) state in the Franck-Condon region must be considered.

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Figure Captions

Fig. 1 Observed He^+ loss rate ν as a function of the H_2 and D_2 pressures. The open circles and squares refer to measurements in "research grade" H_2 and D_2, the crosses to measurements in H_2 which had been further purified by diffusion through palladium-silver alloy.

Fig. 2 Total rate coefficient k_1 for the reaction $He^+ + H_2$ as a function of E/p and of the He^+ mean energy (laboratory frame). The solid data point at E/p = 0 represents an average of 20 points with an rms deviation of $\sim$ 10%.

Fig. 3 Potential energy as a function of internuclear separation R for the relevant states of H_2 and H_2^+ involved in dissociative charge transfer. The cross-hatched area indicates the Franck-Condon region of the H_2 molecule in the ground vibrational state. The horizontal dashed line is at the ionization energy of He^+, indicating the energy resonant points for the dissociative charge transfer process.

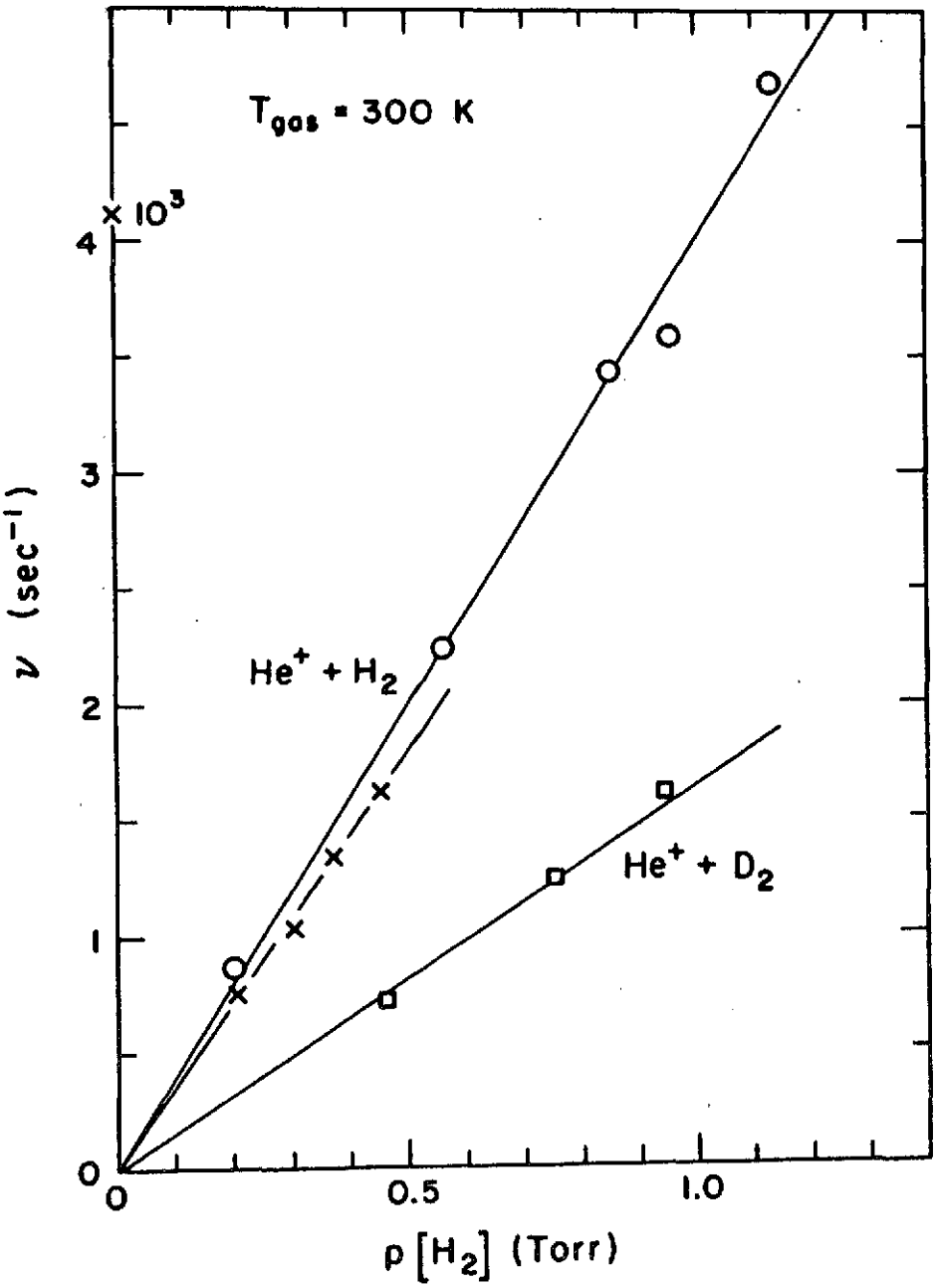

Figure 1

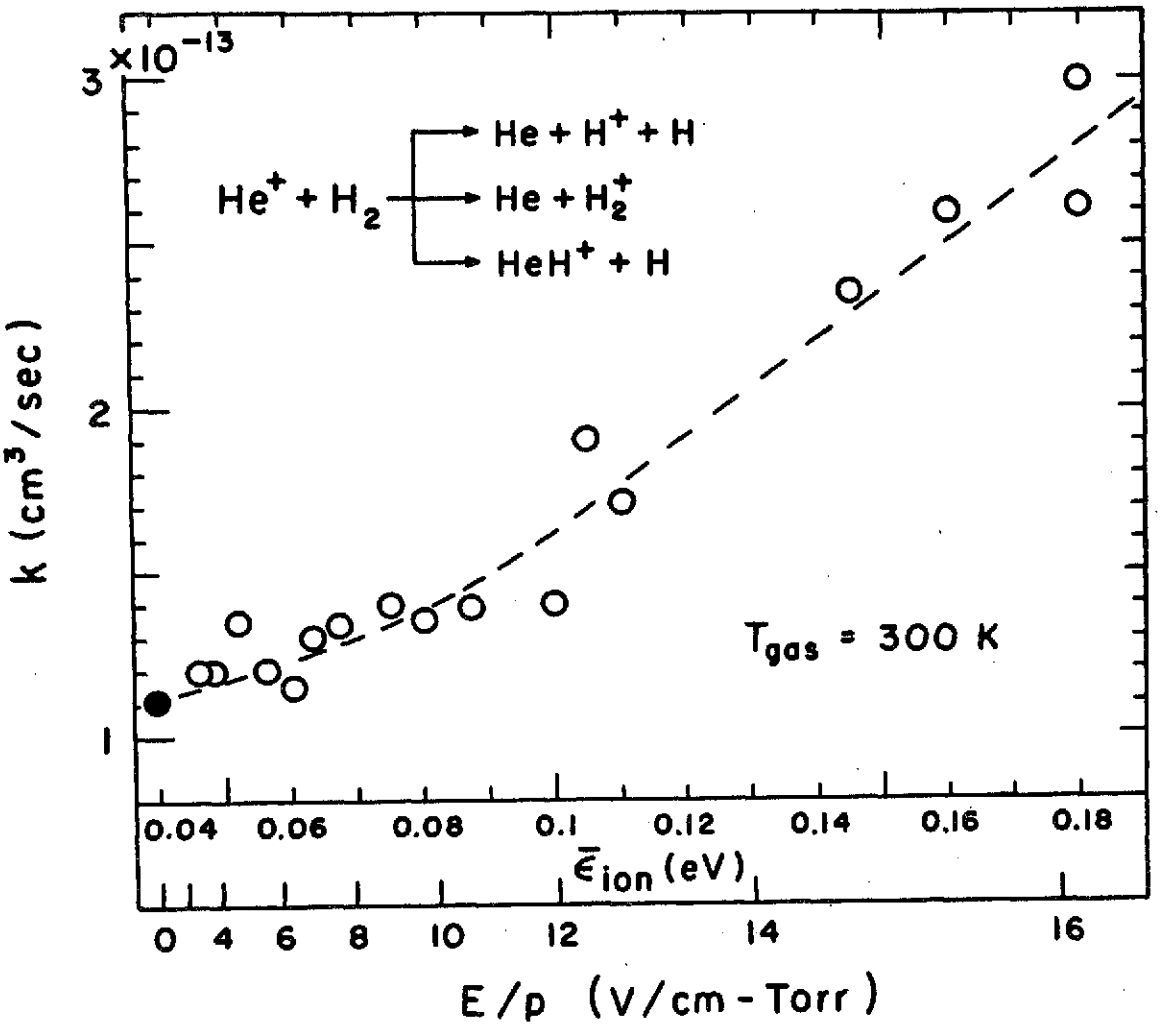
3 ×10⁻¹³
2
1
k (cm³/sec)
He⁺ + H₂
He + H⁺ + H
He + H₂⁺
HeH⁺ + H
T_gas = 300 K
0.04 0.06 0.08 0.1 0.12 0.14 0.16 0.18
ε̄ ion (eV)
0 4 6 8 10 12 14 16
E/p (V/cm - Torr)

Figure 2

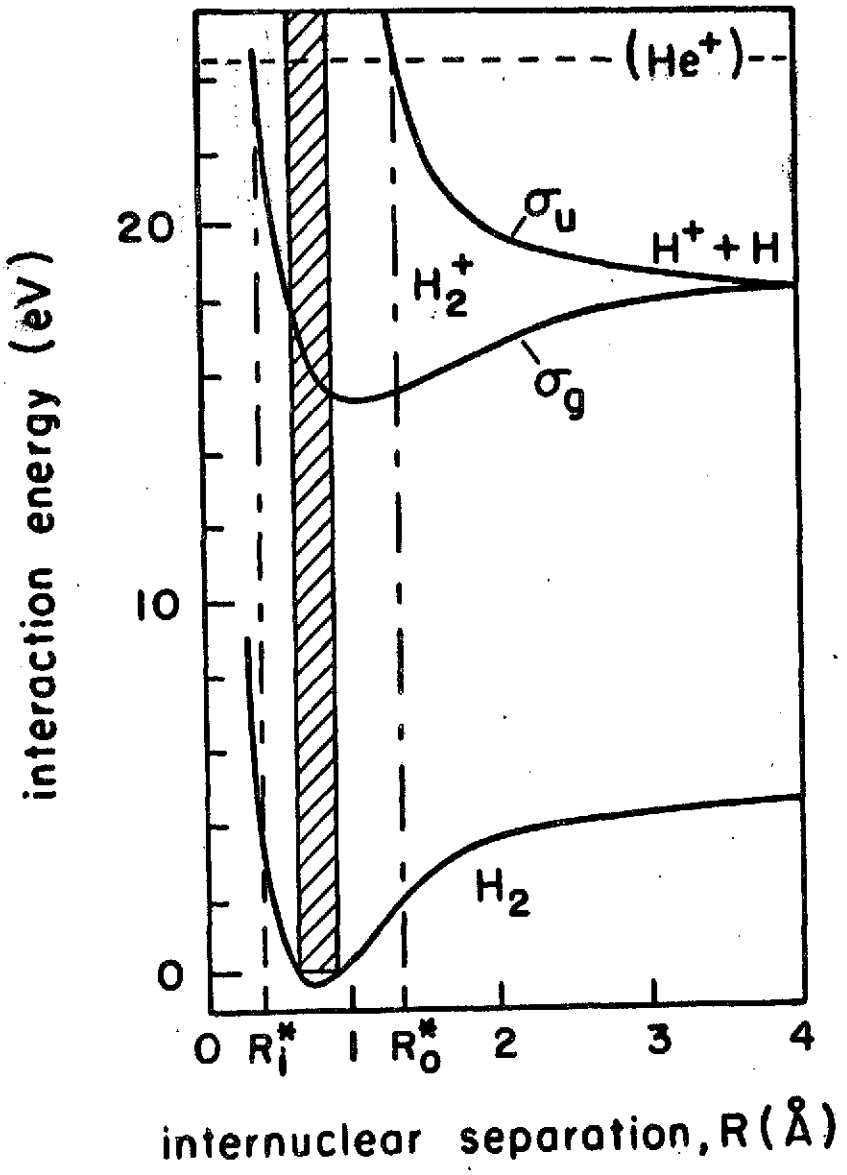
(He+)
σu
H+ + H
H2+
σg
H2
20
10
0
0
R1*
1
R0*
2
3
4
interaction energy (eV)
internuclear separation, R (Å)

Figure 3