PHYSICAL REVIEW A VOLUME 49, NUMBER 6 JUNE 1994

Dissociative recombination of HeH^+: A reexamination

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(Received 14 December 1993)

A high-energy-resolution study of the dissociative recombination of HeH^+ has been performed. A theoretical analysis has indicated that the recombination at low energy is due to the presence of a metastable triplet-state component of the ion beam.

PACS number(s): 34.80.Kw

INTRODUCTION

In a previous study [1], a large cross section was found for the dissociative recombination (DR) of HeH^+ at thermal energies. Numerous calculations [2–6] of the potential-energy curves for HeH and HeH^+ have shown, however, that the ground ($X\,^1\Sigma^+$) electronic state of HeH^+ does not have a suitable curve crossing with a repulsive neutral state through which the dissociative stabilization of the recombination could proceed. A second measurement of the recombination of HeH^+ using an ion-storage ring has recently been reported [7], and again a large cross section was found at low center-of-mass collision energies. This measurement also revealed the presence of a peak in the cross section in the vicinity of 20 eV. Recent theoretical calculations [8] of the elastic scattering of electrons from ground-state HeH^+ indicated the presence of resonances that coincide with the positions of resonances found in Ref. [1]. Given these developments, a decision was made to reexamine this process using our merged-beam apparatus at the University of Western Ontario. These measurements are described in this paper. We have, however, produced a reanalysis of these data that has indicated that the large cross sections observed arise not from the recombination of the ion ground state but in fact from a metastable triplet state of the ion. This explanation of the observed recombination was originally suggested by Michels [2].

EXPERIMENTAL TECHNIQUE

The present experiment has been formed using the MEIBE II merged-beam apparatus at the University of Western Ontario. The ions are formed in a high-pressure radio frequency ion source mounted in the terminal of a 400-keV Van de Graaff accelerator. The previous experiment employed a radio frequency trap ion source that delivered very small currents and, having an electron filament, was technically more difficult to operate in the Van de Graaf terminal. We have modified a conventional radio frequency ion source by decreasing the diameter of the extraction canal from 1 to 0.5 mm. This has allowed the source to be operated at higher pressures.[1] During the first series of measurements reported here, the source operated with a source gas consisting of 50% hydrogen, 50% helium at a pressure of between 20 and 30 m Torr. As seen below the recombination cross section and the positions of resonances obtained using ions derived from this source agree very closely with those obtained from the previous work.

Following acceleration, the ions are mass analyzed and injected into the merged-beam apparatus. Upon entering this apparatus, they are deflected twice to remove any neutrals formed in transit, and then they enter the interaction chamber. In this region, the electron beam is formed from an indirectly heated barium oxide cathode and merged with the ion beam using a trochoidal analyzer. After interacting over a distance of 8.6 cm, the electron beam is demerged from the ions and collected in a Faraday cup. The ion beam is electrostatically deflected into a second Faraday cup, while the neutrals pass on undeflected to a surface barrier detector. Other details of the apparatus have been published elsewhere [10] and the method for determination of the cross section is the same as in Ref. [1]. The merged-beam technique has the capability of very high center-of-mass energy resolution [10] provided low enough beam currents are employed to avoid space-charge effects, and electrostatic focusing effects are minimized in the interaction region. This is the case with this apparatus, and detailed studies have shown it to be capable of measuring very narrow resonant structures in cross sections [11,12].

HeH^+ ions undergo the processes

$$\begin{aligned}
&(a)\ HeH^+ + X \rightarrow He^+ + H + X\ ,\\
&(b)\ \rightarrow He + H^+ + X\ ,\\
&(c)\ \rightarrow He + H + X^+
\end{aligned}$$

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[1] This idea was first used by Knystautas and Lapointe [9] for the production of beams of multiply charged atomic ions from rf sources.

in collision with a background gas molecule X, and electron-ion dissociative recombination

(d) $e + HeH^+ \rightarrow He + H$

in collision with the electron beam. Neutrals arising from background gas collisions [(a),(b), and (c)] are separated from those formed by electron-ion interactions (d) by modulating the electron beam and counting the particles in and out of phase with the modulation. The difference in the two counts yields the true electron-ion signal.

RESULTS

Measured cross sections for the dissociative recombination of HeH^+, over the energy range from 0.01 to 22 eV, are shown in Fig. 1. The low-energy region is shown with an expanded scale in Fig. 2. Comparison of these figures and the previous measurement [1] show that they are almost identical at low energies. The present results have more clearly defined resonant structures than demonstrated in the previous work, where the energy spacing used was larger and where the region above 0.1 eV was not investigated in detail. A peak is found in the vicinity of 20 eV, as in the case of the storage-ring measurements [7]. In fact, closer examination shows this to consist of a multiple-peaked structure (see Figs. 5 and 6).

Given the fact that there is no suitable curve crossing for ground-state HeH^+ ions, we decided to see if the low-energy results could possibly be explained in terms of the recombination of excited-state ions.[2] The lowest electronically excited states of HeH^+ arise from the atomic helium ion $He^+(1s)$ and the neutral hydrogen atom $H(1s)$. At $R=\infty$ the excitation energy is equal to the difference between the helium and hydrogen atomic ionization potentials: $I_{HE} - I_H = 10.98$ eV. The total two-electron spins of these states may be equal to 1 and 0, and so we have two energetically different states $a\ ^3\Sigma^+$ and $A\ ^1\Sigma^+$ which are degenerate at $R=\infty$. The energy curves of these states were calculated in Ref. 3. The potential-energy curves of both states are repulsive at small internuclear distances R, but weak attractive potential wells are created at large R by polarization and exchange forces (Fig. 3). The $a\ ^3\Sigma^+$ state has slightly more binding energy at all values of R than $a\ ^1\Sigma^+$.

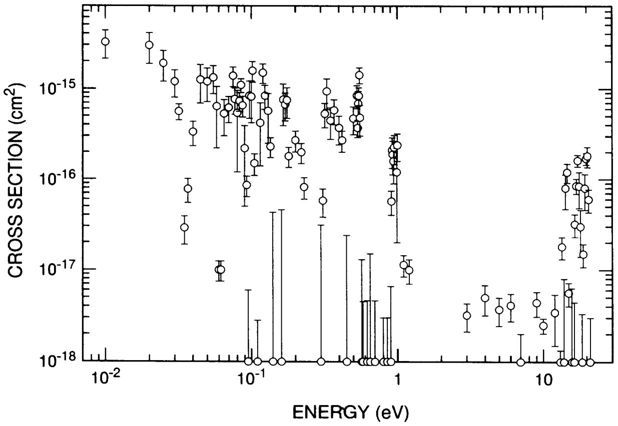

FIG. 1. Measured effective cross sections for the dissociative recombination of HeH^+ using a 50% H_2–50% He source gas. (The points that are shown to lie on the abscissa in fact refer to data where no recombination signal was observed).

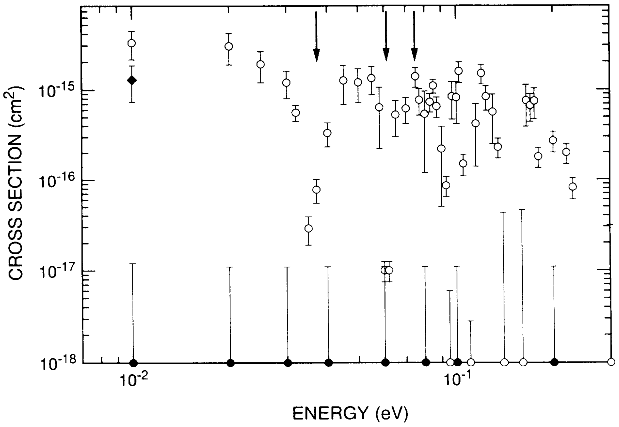

FIG. 2. The low-energy portion of Fig. 1 shown on an expanded scale. The energy separations between the excited and ground vibrational levels of the $a\ ^3\Sigma^+$ state are shown by the arrows. The solid circles are measurements taken with a $25\%H_2{:}25\%He{:}50\%O_2$ source gas. The solid diamond refers to a $37.5\%H_2{:}37.5\%He{:}25\%O_2$ gas mixture. Points lying on the abscissa represent data where no signal was observed.

Since the $a\ ^3\Sigma^+$ state of HeH^+ has a total two-electron spin equal to unity ($S=1$), direct radiative transition to the ground $X\ ^1\Sigma^+$ state, which has $S=0$, is forbidden by the spin conservation rule. This transition may occur only by weak spin-orbit interaction, but to a first approximation the rate for this transition is zero for Σ states of

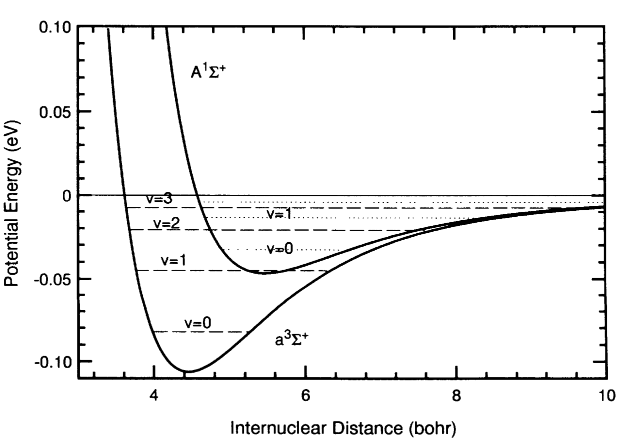

FIG. 3. The shallow potential wells of the $a\ ^3\Sigma^+$ and the $A\ ^1\Sigma^+$ states and their vibrational levels.

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[2] In Ref. [1], the dissociative excitation measurements seemed to indicate that the HeH^+ ions were in their ground electronic and vibrational states. We now believe that these results were a manifestation of a strong resonant process associated with the ground state, but that they did not preclude the existence of excited states in the beam.

diatomic molecules. The relativistic magnetic dipole transition is the predominant means of decay [13] of the $2\,^3S$ state of He. If this is also true for the $a\,^3\Sigma^+$ of HeH^+, the rate for this decay might be expected to be about a factor of 100 slower than for He($2\,^3S$, $\tau \sim 8000$ s) since the overlap between initial and final electronic wave functions is so poor. The transition $A\,^1\Sigma^+ \rightarrow X\,^1\Sigma^+$ is optically allowed, but may also be slow because of the poor overlap of the electronic wave functions of these two states. The transit time between the ion source and the interaction region is ~ 1.2 μs, and if the lifetime of the $A\,^1\Sigma^+$ state exceeds this, it may also be present in the ion beam. The existence of metastable excited ions in HeH^+ beams has already been established by Schopman and Los [14].

The degeneracy at $R=\infty$ of the triplet $a\,^3\Sigma^+$ and singlet $A\,^1\Sigma^+$ energies levels plays an important role for the recombination of the metastable molecular ion. Let us consider the neutral HeH** state (Fig. 4), which consists of the singlet $^1\Sigma^+$ molecular core and a Rydberg electron in a state $(n,1)$. In a zero-order approximation, the energy of the neutral HeH** complex E_0 may be written as the sum $E_0=E^1_+ + \epsilon(n,1)$, where E^1_+ is the energy of the core molecular ion in the singlet $^1\Sigma$ state, and the energy of the Rydberg electron $\epsilon(n,1)$ is equal to $-1/2n^2$, i.e.,

$$E_0=E^1_+ - 1/2n^2 \,.$$

These states can decay to produce the triplet $a\,^3\Sigma^+$ state, with the outgoing electron having a small kinetic energy if the internuclear separations are to the left of the stabilization points (Fig. 4). These states can also autoionize, leading to the release of a fast electron (~ 10 eV), leaving the ground molecular ion complex $\mathrm{He}(1s^2)+\mathrm{H}^+$ which dissociates. We can see from Fig. 4 that the energy levels with $n=7,8,\ldots,16$ cross the range of the ground vibrational level of the triplet molecular ion, i.e., the $a\,^3\Sigma^+$ state has many crossings suitable for DR. It should be noted the total spin of the system $e+\{\mathrm{HeH}^+, {}^3\Sigma\}$ may be equal to $\frac{3}{2}$ and $\frac{1}{2}$, and so the quartet states may also have crossings with the $a\,^3\Sigma^+$ state. The singlet state may also be present in the beam, but it will not contribute to the recombination. It is the term limit of the repulsive states that is shown in Fig. 4, and so there is no intersection with these states. A transition to the quartet manifold is not possible due to spin conservation.

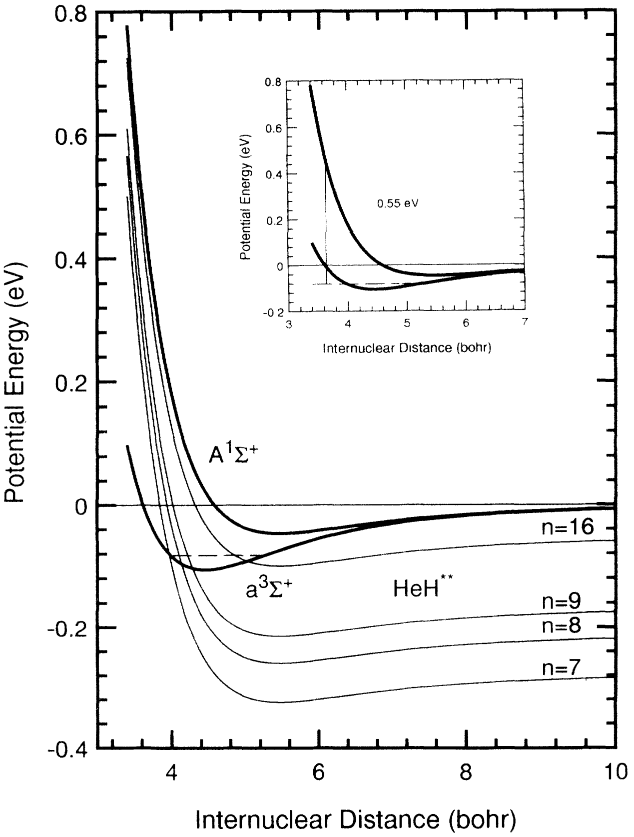

FIG. 4. Schematic diagram of the curve crossings suitable for recombination of the $\mathrm{HeH}^+\,a^3\Sigma^+$ state. The insertion shows the reason for the recombination cross section going to zero above 0.55 eV.

In order to see if there is any evidence of the $a\,^3\Sigma^+$ state contributing to the recombination, it was decided to calculate the vibrational levels of this state. To do this one must solve the Schrödinger wave equation

$$\frac{d^2\phi}{dR^2}+\frac{2\mu}{h^2}[E-V(R)]\phi=0 \,, \qquad (1)$$

where V represents the potentials shown in Fig. 3; μ is the reduced mass of the molecular ion: $\mu=M_1M_2/(M_1+M_2)$; and ϕ is the wave function of the vibrational motion. In the semiclassical approximation these levels may be determined by means of the Bohr-Sommerfeld quantization rule:

$$\int_{R_1}^{R_2}\{2\mu[E-V(R)]\}dR=\pi h(v+1/2) \,, \qquad (2)$$

where v ($=0,1,2,\ldots$) is the vibrational quantum number, and R_1 and R_2 are the turning points. In order to estimate the total number of vibrational levels supported in a given well, let us consider $E=0$ in (2) and compute the integral in the range $R_e<R<\infty$, where R_e ($=4.5a_0$) is the equilibrium point of the potential well. In this range, the potential $V(R)$ may be represented as the polarization potential $V(R)\approx -\alpha/2R^4$, where $\alpha=4.5$ is the polarizability (in atomic units) of the hydrogen atom in the ground state. From this calculation, we have obtained

$$N_{\mathrm{max}}=v_{\mathrm{max}}+1$$

for the maximum number N_{max} of vibrational levels, where

$$v_{\mathrm{max}}=\frac{\sqrt{\mu\alpha}}{\pi R_e}-\frac{1}{2} \,.$$

The values of N_{max} for $a\,^3\Sigma^+$ are given in Table I for all the isotopomers of HeH^+ and in Table II for the $A\,^1\Sigma^+$ state of $^4\mathrm{HeH}^+$.

The energies of the vibrational levels were determined quantum mechanically by solving Eq. (1) as the usual eigenvalue problem. The problem was also approached

TABLE I. Energies E_v of the vibrational levels of the $a\ ^3\Sigma^+$ state of HeH^+ [in eV with respect to the $He^+(1s)+H(1s)$ dissociation limit] are listed.

v	$^4HeH^+$		$^3HeH^+$	
	Quasi-classical	Quantal	Quasi-classical	Quantal
0	−0.0823	−0.0823	−0.0815	−0.0815
1	−0.0451	−0.0451	−0.0435	−0.0436
2	−0.0209	−0.0208	−0.0194	−0.0194
3	−0.0075	−0.0075	−0.0065	−0.0065
N_{max}	5	5	5	5
	$^4HeD^+$		$^3HeD^+$	
0	−0.0873	−0.0873	−0.0864	−0.0864
1	−0.0562	−0.0562	−0.0540	−0.0540
2	−0.0330	−0.0330	−0.0305	−0.0305
3	−0.0172	−0.0172	−0.0150	−0.0150
4	−0.0077	−0.0076	−0.0057	−0.0065
N_{max}	7	7	7	7

semiclassically. The integral in (2) was calculated numerically as a function of energy E and the levels were determined as roots of Eq. (2). The results for the $a\ ^3\Sigma^+$ and $A\ ^1\Sigma^+$ states are given in Tables I and II. It was found that semiclassical and quantum-mechanical approximations give the same results. The reason for this is that the potential V and its gradient in (1) are small and therefore the semiclassical approximation is excellent in the case of the $a\ ^3\Sigma^+$ molecular state.

If we compare the energy differences ΔE_{0v} between the calculated 0 and v vibrational levels,

$$\Delta E_{01}=0.0372 \text{ eV} , \quad \Delta E_{02}=0.0612 \text{ eV} , \quad \Delta E_{03}=0.0748 \text{ eV} , \tag{3}$$

(indicated by the arrows in Fig. 2), we see that these values are in excellent agreement with the positions of the experimental resonances. This agreement suggests that the recombination observed in this experiment is actually associated with the metastable $a\ ^3\Sigma^+$ state, the resonances arising from competition between the recombination and vibrational excitation [12,15–17]. Furthermore, the large depth of the resonances indicates that the ions were predominantly in the $v=0$ level of this state.

The disappearance of the cross section in the energy range between 0.55 and 0.90 eV may be explained by examination of Fig. 4. It can be seen that transitions from the initial ion state to the repulsive dissociating states can occur for center-of-mass energies less than 0.55 eV but not for higher energies. The 20-eV energy peak in the cross section may be explained in terms of electron capture from the ground state of the HeH^+ ion to a repulsive doubly excited state such as those illustrated in Fig. 4. The reasons for the dips between 0.09 and 0.55 eV and for the peak between 0.9 and 1.2 eV are not clear, and are perhaps associated with some other excited ion state or recombination process. Initial calculations show that the positions of these resonances correlate with transitions involving the second triplet state of HeH^+. In the earlier studies of Yousif and Mitchell [1], the dissociative excitation results gave an indication that this state was populated under low-pressure source conditions. It is not clear, however, how this state can survive passage from the source to the collision region, for it can make radiative transitions to the first triplet state. A more careful examination of the effects of rotational excitation on the lifetime of this state is currently underway to see whether this might be a reason for its survival into the interaction region. The results of this study will be published later, and a discussion of the associated resonances will be deferred until then.

TABLE II. Energies E_v (eV) of the vibrational levels of the $A\ ^1\Sigma^+$ state of $^4HeH^+$.

v	E_v
0	−0.0327
1	−0.0135
2	−0.0041
3	−0.0008
4	N_{max}

Having obtained convincing theoretical evidence for the hypothesis that the recombination observed at low energies was actually associated with the $a\ ^3\Sigma^+$ state of the ion, a method was sought for experimental verification of this hypothesis. One way to remove spin-forbidden metastable states from an ion beam is to introduce oxygen into the ion source. Oxygen has a lone pair of electrons, and electron exchange reactions can occur between the O_2 molecule and the ion resulting in the quenching of the excited states [18]. This technique had been demonstrated by us in previous studies of CH^+ recombination [19]. In that case it was found that addition of oxygen to the source gas resulted in the decrease of the CH^+ recombination cross section because the original ion beam contained a fraction of the ions in the $^3\Pi$ excited state.

The results shown in Fig. 1 were taken using a 50% H_2:50%He gas mixture in the ion source. When this was replaced with a 25%H_2:25%He:50%O_2 mixture, the low energy cross sections were found to decrease to undetectable levels, as shown by the solid circles in Fig. 2. (A single data point at 0.01 eV, taken with a 37.5%H_2:37.5%He:25%O_2 gas mixture is also shown, indicating the effect of changing oxygen concentration). This is regarded as convincing proof that the signal observed was in fact due to the recombination of the $a\ ^3\Sigma^+$ state of HeH^+ and not to the ground singlet state. Further evidence for the presence of a large excited-state component in the ion beam is provided by the change in the 20-eV peak with the addition of oxygen to the source. This is illustrated in Figs. 5 and 6, where it is seen that these peaks are enhanced by about a factor of 2 by the use of oxygen. The 20-eV peak structure is due to recombination arising from transitions from the ground state of HeH^+ to upper, dissociating, neutral Rydberg states such as those shown in Fig. 4. If a substantial fraction of the beam is excited, then a large enhancement of this cross

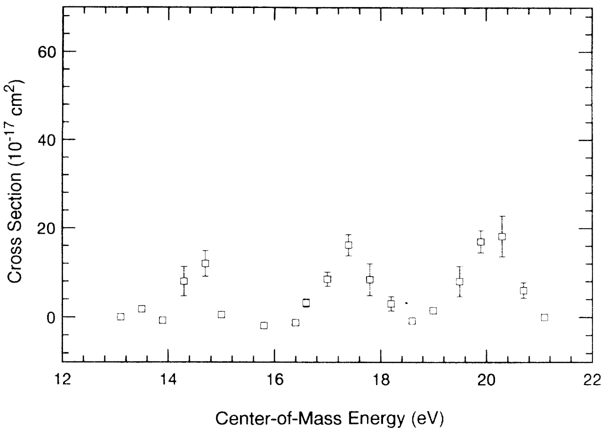

FIG. 5. The high-energy portion of Fig. 1 shown on an expanded scale. The source gas was 50%H_2:50%He.

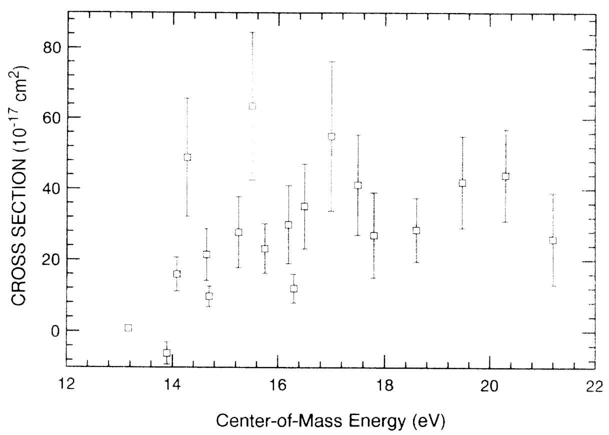

FIG. 6. High-energy results obtained when the 50%H_2:50%He source gas was replaced with a 25%H_2:25%He:50%O_2 mixture.

section would be expected when the excited states were quenched. The fact that there is an enhancement by about a factor of 2 suggests that perhaps 50% of the beam used for the original measurements consisted of ions in excited states. This would mean that the low-energy cross sections shown in Figs. 1 and 2 should actually be multiplied by a factor of 2, since they arise from this excited-state component.

DISCUSSION

When the original measurements of HeH^+ recombination made by Yousif and Mitchell [1], it was a surprise to find that the measured cross section was so large given that there did not seem to be any obvious mechanism through which the recombination should proceed rapidly. The present work provides an explanation for this, based upon the recombination of excited-state ions that is supported by both theoretical modeling and experimental observation. Having said that, it should be noted that there has been a recent theoretical study by Sarpal, Tennyson, and Morgan [20] of the dissociative recombination of ground-state HeH^+ ions that agrees well with the earlier results of Yousif and Mitchell. This calculation invoked indirect recombination through the neutral Rydberg manifold lying below the HeH^+ ground state. Clearly there is a serious discrepancy here, and further work will have to be done to understand this problem.

HeH^+ is of course not the only species whose recombination has been the subject of controversy. H_3^+ also displays a rapid recombination rate despite the absence of a suitably placed curve crossing through which direct recombination might proceed. Bates [21] has recently discussed the theoretical situation and proposed a multistep mechanism through which this process proceeds. A suggestion was made to the current authors [22] to investigate the effect of oxygen addition to the source gas on our measurements of H_3^+ recombination [23]. This ion is believed to have a stable triplet excited state, ${}^3\Sigma_u^+$, although this is in a linear configuration as opposed to the equilateral geometry of the ground state [24]. This experiment was performed, but it was found that the addition of oxygen to the ion source produced no change in the measured cross section. This suggests, therefore, that the observed large recombination rate for H_3^+ cannot be explained as arising from an excited ion species.

Note added in proof. T. Tanabe *et al.* [Phys. Rev. A **49**, R1531 (1994)] have recently reported no change in measured HeH^+ recombination cross sections when 9–19 % oxygen was added to the source gas. As seen from Fig. 2, these concentrations are too low to greatly affect the triplet-state component.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of the Canadian Natural Sciences and Engineering Research Council and the United States Air Force Office of Scientific Research. M.C. would also like to thank the Center for Chemical Physics at the University of Western Ontario for support. The collaboration of A.C. was made possible by a NATO Exchange Program grant.

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