High-Resolution, Low-Energy Dissociative Recombination Spectrum of $^3HeH^+$

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We report the first high-resolution cross section measurements of dissociative recombination in $^3HeH^+$ for 0.05 meV $\leq E_{rel} \leq$ 300 meV. We used the electron cooling beam of the storage ring CRYRING, which now features $kT_\perp \sim 10$ meV. The experiment confirms the puzzlingly large low-energy rate measured previously and finds six heretofore unreported peaks at 34, 54, 113, 216, 250, and 284 meV. We remark on the utility of the Fourier transform to remove peak shifts and broadening due to the electron beam's thermal energy spread.

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Following the suggestion of Datz and Larsson [1], two ion storage ring experiments [2–5] have been carried out recently to measure dissociative recombination of HeH^+ ions:

$$HeH^+ + e \rightarrow HeH^* \rightarrow He + H\,.$$

In these experiments a high-quality electron beam was merged with circulating ions in one straight section of a storage ring. The production of neutral fragments was measured while a variable electron velocity offset was applied. Peaks appeared in the fragment yields when the relative energy exceeded 10 eV, but both experiments found more or less smoothly increasing yields as the relative energy was decreased below 1 eV, except for a tantalizing shoulder that appeared near 0.1 eV [3–5]. The resolution in these experiments was limited by the transverse electron temperature of $kT_\perp = 0.1$ eV. The present high-resolution experimental study of $^3HeH^+$ finds detailed structures in this region when colder electrons are used. In this work, an adiabatically expanding electron beam in a decreasing magnetic field [6,7], which reduces $kT_\perp$ to 0.01 eV, is used as far as we know for the first time in a study of dissociative recombination.

The absence of a favorable neutral-state curve crossing of the HeH^+ electronic ground state led to the suggestion that HeH^+ should recombine radiatively (i.e., with a relatively slow rate near $10^{-11}cm^3/s$). However, single-pass experiments found a much larger recombination rate [8] ($\sim 10^{-8}$ cm^3/s for $^4HeH^+$) and "window" resonances in the region below 1 eV. The storage ring experiments confirm the large recombination rate at very low relative energy. This larger-than-expected rate was difficult to reconcile with theory [9] because of the absence of curve crossings. These problems eventually led to new experiments and a reinterpretation of the single-pass data [10]. At the same time new theoretical efforts have clearly suggested that it is time to abandon the old picture of dissociative recombination completely relying on a curve crossing. A decisive step in this direction was recently taken when the first calculation of dissociative recombination driven by the nuclear-kinetic energy operator on adiabatic potential curves was performed [11]. The calculations were done for $^3HeH^+$ and showed that (i) the mechanism could account for a quite fast recombination and (ii) the indirect mechanism involving Rydberg states could *enhance* the cross section. These results are also important in the quest for sensible recombination mechanisms for polyatomic molecules (see, e.g., [11,12]).

The merged beam technique used in this experiment is identical to the one used to measure dissociative recombination of $^3HeH^+$, H_3^+, and D_2^+ ions at the heavy ion cooler storage ring CRYRING [4,13,14]. The main technical improvement in the present experiment is an innovative modification to the electron cooler or target [6,7], which lowered the transverse electron temperature by about 1 order of magnitude. The stored ions are cooled for 9 s after reaching full energy. This interval is long enough for excited vibrational levels to spontaneously decay [1].

Recently the CRYRING electron beam cathode and transport magnets have been modified to allow a tenfold expansion of the electron beam diameter prior to its injection into the main cooling solenoid. This adiabatic decompression of the beam results in a corresponding reduction in the transverse energy spread. Cooling force measurements [7] are consistent with a transverse temperature of 10 meV, about a factor of 10 lower than that used in our earlier work [4,14]. As a result of the associated improved cooling efficiency we could reduce the electron density by a factor of 2 thereby reducing spectral distortion due to the drag force as well as space-charge induced shifts in electron beam energy.

Molecular ions that recombine with electrons dissociate rapidly into neutral atomic products. These are

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separated from the primary ion beam as it passes through a ring dipole magnet downstream from the electron target. Dissociative recombination produces a pair of He and H atoms which are counted as a single particle when they impinge nearly simultaneously on a surface barrier detector. The detector easily resolves the pair energetically from separate He and H atoms that result from rest-gas interactions.

The essence of the experiment is to measure, as a function of ion-electron relative energy, the yield of neutral He and H pairs produced per unit of stored ion current and per unit of electron current density. The ion current is measured with a current transformer, while the electron current is measured directly. The relative energy is deduced from the value of the electron power supply voltage at the cooling energy (when ion and electron mean velocities are matched) and at the detuning energy. Because of the thermal energy spread of the electron beam, the yield at each value of detuning energy E_d is proportional to the rate coefficient, $\alpha(E_d, T_\perp) = \langle \sigma(E_{\rm rel}) v_{\rm rel} \rangle$, where $T_\perp$ is the electron transverse temperature. The measured absolute recombination rate coefficient is plotted in Fig. 1. Excellent agreement exists between data taken for $v_e < v_i$ and data taken with $v_e > v_i$. The statistical errors are less than 3% except for a few points at the highest energy where the rate is low. Several new features stand out clearly in this spectrum. (The steep rise toward zero relative energy is an artifact due to the cooling force; during the 100 ms intervals when data are taken the relative energy can drift as much as 0.6 meV in the worst case.) The peaks above 10 meV relative energy are due to neutral Rydberg states which can be populated prior to dissociative recombination due to radial coupling [11]. Using least-squares techniques, we can find six peaks located

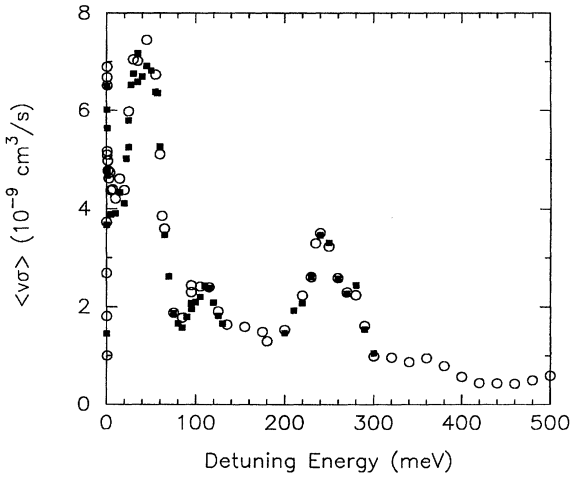

FIG. 1. Measured rate coefficient. The open symbols represent data taken with $v_e < v_i$ and the solid symbols represent data taken with $v_e > v_i$. The statistical error bars are smaller than the point symbols.

at 32, 51, 111, 211, 243, and 278 meV. Most of these peaks are probably blends made up of many unresolvable components. The relatively high density of points and their statistically small errors contrast with earlier single-pass experiments (see Ref. [15]) which obtained evidence for window resonances in the $^4HeH^+$ recombination spectrum [8]. Recent R-matrix calculations of the dissociative recombination of the electronic ground state of $^4HeH^+$ [16] have confirmed the window resonances in Ref. [8] and supplied additional support for the possibility of a quite large cross section in the absence of a curve crossing. The recent results from the single-pass experiment [10], in which it is claimed that the cross section for recombination of electronic ground state $^4HeH^+$ is vanishingly small, is in complete disagreement with [16]. It is also seemingly in variance with the result of the present work and the theoretical result in [11], but some caution should be exercised when making this comparison, since the single-pass data are for $^4HeH^+$, and our data and those in [11] are for $^3HeH^+$. A large isotope effect is expected and will significantly influence the resonances (including suppressing the cross section at resonances [17]).

The recombination rate coefficient shown in Fig. 1 arises through interactions with an electron beam that has the peculiar velocity distribution of an electron cooler. Of more general interest is the recombination cross section. When the longitudinal electron temperature is much less than the transverse temperature (it is negligible for the accelerated electron beam used here), the cross section $\sigma(E_{\rm rel})$ can be found from the measured rate coefficient $\alpha(E_d, T_\perp)$ by unfolding the integral

$$\alpha(E_d, T_\perp) = \int_0^\infty f(v_\perp) \sigma(E_{\rm rel}) v_{\rm rel} \, dv_\perp , \qquad (1)$$

where E_d is the relative energy of an ion and an electron moving with the mean laboratory energy of their respective beams, $f(v_\perp)$ is a two-dimensional Maxwell speed distribution, and $v_{\rm rel} = \sqrt{v_\perp^2 + v_d^2}$ is the relative velocity. The velocity spread of cooled ions is negligible compared with that of the electrons. If features in the spectrum are much broader than the electron and ion energy spreads, then the cross section can be unfolded simply by dividing the rate by the collision velocity. This condition does not hold at the lowest relative energies reached in this experiment, so a more sophisticated unfolding is warranted. When the rate integral is expressed in terms of energy instead of velocity,

$$\alpha(E_d, T_\perp) = \int_0^\infty f(E_\perp) \sigma(E_\perp + E_d) v_{\rm rel}(E_\perp + E_d) dE_\perp , \qquad (2)$$

it takes the form of a correlation integral. The electron energy distribution appropriate for this experiment is assumed to be

$$f(E_\perp) = \begin{cases} 0 & \text{if } E_\perp < 0, \\ \frac{1}{kT_\perp} \exp(-\frac{E_\perp}{kT_\perp}) & \text{if } E_\perp \geq 0. \end{cases} \qquad (3)$$

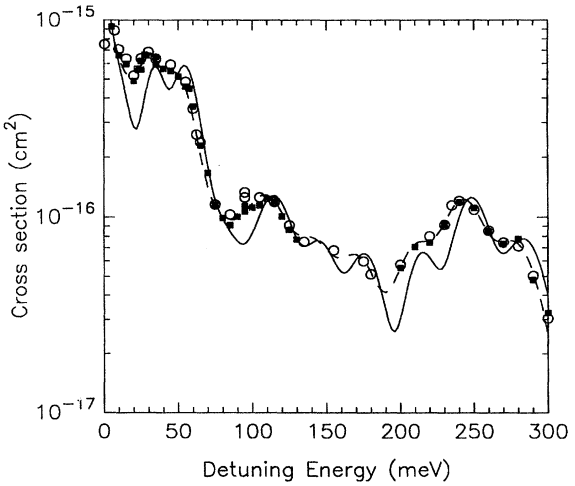

FIG. 2. Unfolded cross section. The solid line is the result of a fast Fourier transformation of the data, after fitting to a smooth curve by a nonlinear least-squares procedure over the interval from 10 to 300 meV. The dashed line is that fitted curve divided by the mean relative velocity v_d, and the symbols (see Fig. 1 for explanation) are the data points divided by v_d.

The measured rate can be unfolded by a numerical Fourier transform [18,19] to yield the cross section

$$\sigma(v_d) = \frac{1}{v_d}\mathcal{F}^{-1}\left(\frac{\mathcal{F}(\alpha)}{\mathcal{F}^*(f)}\right). \quad (4)$$

The result is shown in Fig. 2. The FFT is sensitive to noise in the data, so we chose to represent the data by a smooth curve obtained with a nonlinear least-squares procedure. For comparison the simplified estimate $\sigma = \alpha/v_d$ is also shown. The thermal spread of the electrons produces a shift of peak positions in addition to a broadening. This is illustrated in Table I. The uncertainty in the peak positions is estimated to be less than 1 meV. It is interesting to note that when the FFT is applied to our older, lower resolution ($kT_\perp = 100$ meV) spectrum [3,4], most of the same features appear. It should be emphasized that this procedure does not find structures in the cross section that are not evident in the rate coefficient. It does, however, remove the broadening and centroid shifts caused by the electron thermal spread, so that the positions of structures in the cross section can be more precisely measured.

TABLE I. Centroids of resonances (meV).

$\langle\sigma v_{\rm rel}\rangle$	σ
32	34
51	54
111	113
211	216
243	250
278	284

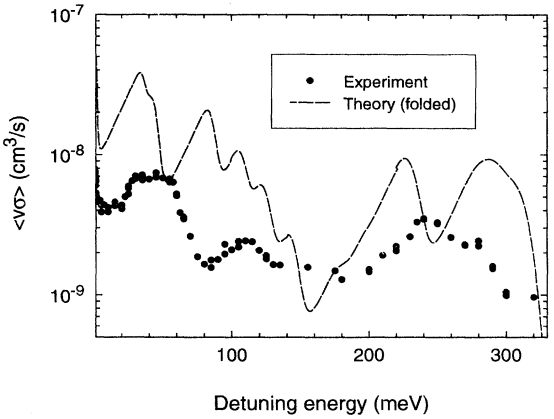

FIG. 3. Comparison of the measured rate coefficient with the folded theoretical cross section [11].

A recent calculation by Guberman [11] for recombination from the ground state of $^3HeH^+$ contains many neutral Rydberg resonances in this energy region. Even with the low electron temperatures used here, it is not possible to isolate those individual resonances. Figure 3 shows a comparison of our measured rates (i.e., from Fig. 1) with a folding of Guberman's cross section over the electron energy distribution appropriate to our beam. The comparison reflects the "state of the art" in the field of dissociative recombination in small molecules without curve crossings. Both curves indicate a large cross section at low energies, which tends to support the radial coupling mechanism behind the theory and an enhancement of the cross section (instead of a "window") at the resonance positions. The initial state in Guberman's calculations is the ionic $^1\Sigma^+$. It has been shown elsewhere [10] that the large $^4HeH^+$ cross section observed at the lowest relative energies, which cannot be explained by curve crossings between the ionic ground state and dissociating states of the neutral molecule, is actually due to a contaminant in the ion beam, the $a^3\Sigma^+$ state, for which curve crossings do occur. In our earlier $^3HeH^+$ experiment [4], run under the same ion source conditions as the present one, we observed structure, in the much higher relative energy range 10 to 30 eV where isotope effects are expected to be negligible, which resemble those in Fig. 6 of [10], taken with no triplets in the $^4HeH^+$ beam, but which do not match the peaks in Fig. 5 of [10], taken with triplets in the beam. We do not have justification to invoke the presence of the fragile metastable excited triplet state to explain the rate that we observe. Systematic effects such as triplet-state contamination found when using lower energy accelerated ions [10] need not appear for higher energy stored ions. To begin with, the very long path lengths (hundreds of thousands of km) in storage ring experiments—compared

with path lengths of less than 10 m in a single-pass experiment—provide ample opportunity for collisional destruction of triplet states in the rest gas during the electron cooling phase of the data cycle. Furthermore, we have made estimates that indicate that triplet vibrational levels with $v > 1$ are dissociated by the 40 MV/m motional electric fields of the storage ring dipoles. In addition, the storage ring experiment reported by Tanabe *et al.* [5] includes crude measurements of the fragment kinetic energies which are of the right value for ground-state recombination and are too large for triplet-state recombination. This issue has been discussed further elsewhere [4,5]. The exact positions of resonances and hence their interference effects depend on the locations of isotopic-mass-dependent vibrational levels of the neutral Rydberg states as well as of the ground-state ion. So a possible explanation for the apparent absence of a low-energy cross section for ground-state $^4HeH^+$ is a strong isotope effect.

In conclusion, we have found resonance peaks in the cross section for dissociative recombination of $^3HeH^+$ ions in the region below 0.5 eV relative energy that are of obvious statistical significance. The spectrum is symmetric about zero relative velocity. Both the large low-energy cross section and the resonance peaks are strong evidence for the radial coupling mechanism of Guberman, which involves a breakdown of the Born-Oppenheimer approximation. This mechanism is operable in the absence of molecular curve crossings.

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[19] We have used the Microsoft Corporation spreadsheet *Excel, Version 4.0,* which has a built-in FFT.