Evidence of Superelastic Electron Collisions from H_2^+ Studied by Dissociative Recombination Using an Ultracold Electron Beam from a Cooler Ring

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The dissociative recombination rate of H_2^+ was measured as a function of the storage time with an ultracold electron beam in a storage ring. The H_2^+ ions vibrationally relax with time, and almost reach the vibrational ground state at a time of 25 s after injection. The magnitude of the ground-state population after 25 s far exceeds that expected based on the initial ground-state population and its decay. This indicates the existence of a superelastic collision process, where electrons are scattered from excited molecular ions and gain energy by vibrational deexcitation.

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Atomic-physics research using ion-storage rings has made great progress since the early 1990s, especially concerning dissociative recombinations (DR) of molecular ions [1]. For molecular ions having permanent dipole moments, vibrationally cold ions are obtained simply by storing the excited ions for a time of 1 sec or less. Experiments using these ions, of which the vibrational quantum number is defined as $v = 0$, have enabled precise comparative studies between experiment and theory. However, those ions without dipole moments do not radiate infrared rays during storage, and their deexcitation would not be expected during a short storage time. This has been a difficulty in studying homonuclear diatomic molecular ions. The simplest molecular ion without a permanent dipole moment is H_2^+. The DR of H_2^+ has been studied with storage rings in Heidelberg [2], Stockholm [3,4], and Aarhus [5,6]. The population of the vibrational states varies according to the experimental conditions: The populations in Heidelberg and Stockholm are similar to each other, while the population in Aarhus is different. The vibrational deexcitation of infrared-inactive ions depends on both the intensity and quality of the electron beam as well as on the storage time. This is the reason why the populations are different among these storage rings. There are two possible mechanisms by which the vibrational distribution of the stored ions is affected during collisions using a low-energy electron beam. One is DR and the other is the vibrational deexcitation due to electron impact, which is called a superelastic collision (SEC):

$$H_2^+(v) + e(E_{\mathrm{rel}}) \rightarrow H_2^+(v - m) + e(E_{\mathrm{rel}} + \Delta E) \quad (m > 0, \Delta E > 0), \tag{1}$$

where v is the vibrational quantum number and E_{rel} is the relative energy between the electron and the ion. A SEC does not affect the circulating ion current, while DR decreases it. Although DR has been studied extensively both experimentally and theoretically, SEC has only been predicted theoretically [7,8], and so far there has been no experimental evidence [4]. It is theoretically predicted that the cross sections of SEC increase with a decrease in the electron energy, and even far exceeds those of DR in N_2^+ of $v = 1$ [7]. Experimentally, recent developments on the electron cooler have realized an electron temperature on the order of 1 meV by adiabatic electron beam expansion by a factor of 100 using a superconducting magnet [9]. This provides better experimental conditions for studying SEC.

An investigation was performed using the storage ring TARN II and its associated superconducting electron cooler [10]. The H_2^+ ions produced in a Penning ion source and accelerated to 15 MeV in a cyclotron were injected into the storage ring and merged with an electron beam. The stored ion beam had a $1/e$ lifetime of about 6 s at an average vacuum pressure of 1×10^{-10} mbar. The electron beam was produced from a cathode with a diameter of 5 mm in a strong magnetic field of 3.5 T, and then expanded to a diameter of 50 mm in a gradually decreasing field to 35 mT. Since the expansion factor was 100, the transverse electron temperature was expected to decrease to $\sim$1 meV from the initial thermal temperature of $\sim$0.1 eV. The electron density was 1.8×10^7 cm^{-3}.

The neutral atoms arise mainly from the following three reactions (R_g denotes a rest gas):

$$H_2^+ + R_g \rightarrow H + H^+ + R_g, \tag{2}$$

$$H_2^+ + e \rightarrow H + H^+ + e, \tag{3}$$

$$H_2^+ + e \rightarrow H + H. \tag{4}$$

Reaction (2) occurs around the entire storage ring, while (3) and (4) occur only in the electron cooler section.

The DR experiments [9] were performed by measuring the rate of H + H production between times T_i and T_f as a function of the electron acceleration voltage. Here, we refer to $[T_i - T_f]$ as the "time window." The injected ions were first stored and phase-space cooled until a time of T_i. After this period, the electron-acceleration voltage was stepped up (or down) to the measuring voltage, and then switched back and forth between the measuring voltages and the cooling voltage at a rate of 50 Hz in order to avoid an energy shift of the ions due to the drag force of the electrons.

The circulating ion current was measured by a new device using a SQUID (superconducting quantum interference device) [11]. The sensitivity of this device is 1 nA, which is about 3 orders of magnitude better than that of the usual dc current transformers. The absolute value of the rates was thus determined by using the ion and electron current as well as the geometrical size of the electron beam. Simultaneously with measurements of the stored beam current, the single neutral atoms emitted from the dissociative excitation were counted. At zero-collision energy, the main process is reaction (2), because the threshold energy (2.65 eV for $v = 0$) of the reaction (3) is much higher, and, hence, its rate is proportional to the ion beam current as long as the vacuum pressure does not change. The count rate was thus normalized to the beam current using a SQUID current-measuring device. The decay of the DR rate at the cooling energy ($E_{\mathrm{rel}} = 0$) was also measured with a multichannel scaler simultaneously with the rate from reaction (2) as a function of time.

Figure 1 shows the DR rate constants ($\langle v\sigma \rangle$) as a function of the storage time at the energy $E_{\mathrm{rel}} = 0$. The initial rise of the rate at a time less than 0.5 s reflects the phase-space cooling of the ion beam, where the ion temperature decreases because of electron cooling. The DR rate strongly decreases and stabilizes at a time longer than about 25 s. The DR cross sections at low energies depend greatly on the vibrational states [12]. Therefore, the variation of the rate with time is caused by a change in the population of the vibrationally excited states. The fact that the rate approaches a constant value suggests that the vibrational distribution of the ion beam becomes stationary. If the SEC process contributes to the results, the stationary distribution must consist of the vibrational ground state only, since the excitation is forbidden energetically. As demonstrated by an experiment at CRYRING [4], the change in the DR rate is caused by electron-ion collisions, and collisions with rest gas do not change the vibrational population. This was confirmed by comparing the DR rate of the delayed onset of the electron-cooler beam (10 s after ion injection). As can be seen in Fig. 1, the time dependence of the rate almost agrees between these curves. No change was also observed in the DR energy spectrum for the delayed start of the cooling electrons. Molecular ions can dissociate because of a motional electric field due to the dipole magnet passed by the ions. The present experimental condition provides an estimate of the maximum quantum ($v \sim 17$) which survive the dipole field according to Ref. [13]. There are two mechanisms (DR and SEC) which change the ion vibrational-state populations in electron-ion collisions at $E_{\mathrm{rel}} = 0$. The electron temperature is low enough to neglect the excitation process [inverse of Eq. (1)] at the cooler straight section.

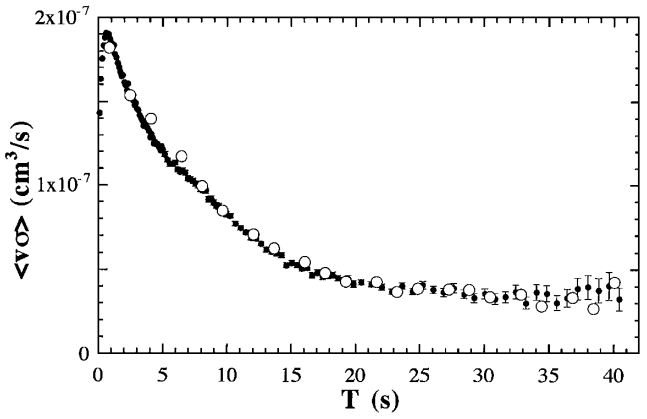

FIG. 1. Storage time dependence of the DR rate constants of H_2^+ at an electron collision energy of $E_{\mathrm{rel}} = 0$ eV. The data indicated by open circles show the rate measured with a 10 s delay of the electron cooling. The error bars indicate the statistical errors.

In order to study the population of the vibrational states, DR cross sections were measured at different time windows while changing the electron energy in small steps. The results are shown in Fig. 2. At low energies of less than 1 eV, the spectra are dominated by capture to the doubly excited $(2p\sigma_u)^2\,{}^1\Sigma_g^+$ state. The broad structure, ranging from 2–23 eV, can be ascribed to the core-excited Rydberg states [14]. The low-energy bump corresponds to the states converging to the first excited ion core $(2p\sigma_u)^2\Sigma_u^+$. The higher bump originates in many core-excited Rydberg manifolds. The structure changes with time windows: With an increase in T_i, bumps are separated more clearly and the peaks of the bumps shift to higher energies. The peak cross section at about 9 eV for a time window of [25–26.5 s] is $\sim 5 \times 10^{-17}$ cm^2, which is smaller than the other data [3,6] so far reported, and comparable with the cross sections of HD^+ DR at the corresponding energies [6].

In order to estimate the relative populations of the vibrational levels, we calculated the energy dependence of the DR cross sections for various vibrational states. We adopted a method used for a previous study [15] after extending it so as to take into account the "closed dissociative channel" [9]. The condition of the calculation is also basically the same as in the previous calculation, where five symmetries ($^1\Sigma_g$, $^1\Pi_g$, $^1\Pi_u$, $^3\Pi_g$, $^3\Pi_u$) of two-electron excited states $(2p\sigma_u)(nl\lambda)$ $(n \geq 2)$ are included,

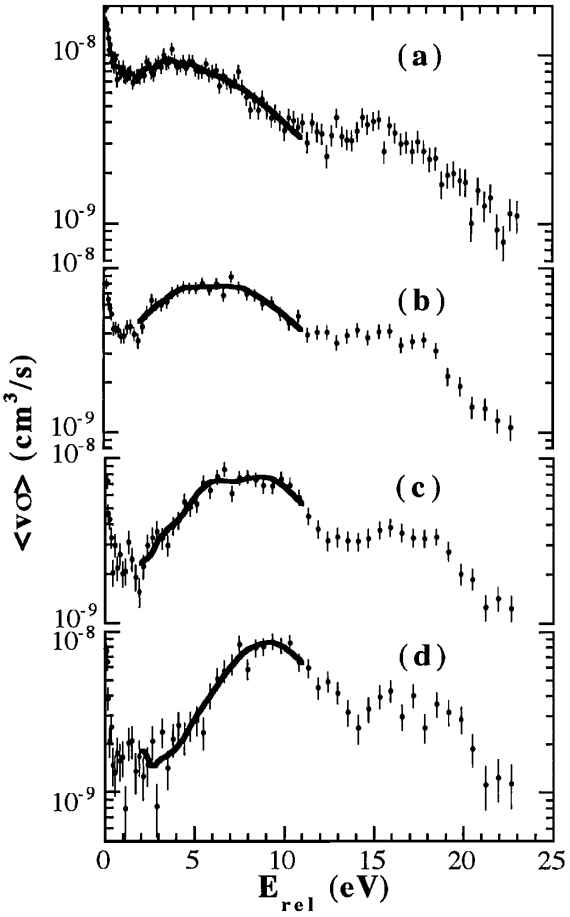

FIG. 2. DR rate constants of H_2^+ as a function of the collision energy (E_{rel}) for the different time windows of (*a*) [2–2.5 s], (*b*) [5–5.5 s], (*c*) [10–11 s], and (*d*) [25–26.5 s]. The curves represent fits of the theoretical curves to the data.

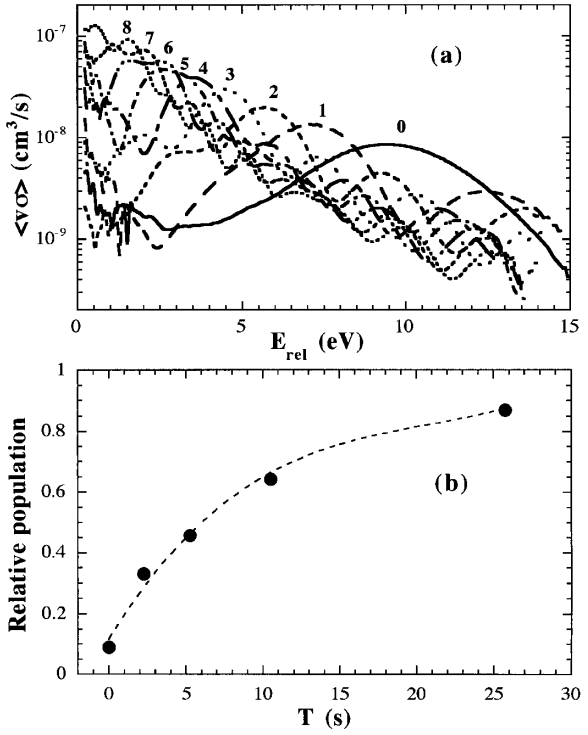

FIG. 3. (a) Calculated DR rate constants of H_2^+ as a function of the collision energy (E_{rel}) for different vibrationally excited states. (b) The relative population of the vibrational ground state as a function of the storage time, deduced by a fitting, except for $T = 0$ (see text).

and both the rotational motion and the indirect process are neglected. The calculated rate constant ($\langle v\sigma \rangle$) convoluted with a Gaussian of 0.1 eV half-width is shown in Fig. 3(a). The value of half-width was roughly estimated using the formula given in Eq. (15) of Ref. [1]. The populations were determined by a least-squares fit of the calculated curves for $v = 0$–8 to the experimental spectra for each time window in the energy range of 2–11 eV. In order to avoid the effect from the higher energy bump, the maximum energy was terminated at 11 eV. The fitted curves are shown in Fig. 2 together with the data; the relative population of the vibrational ground state is shown in Fig. 3(b). The population at $T = 0$ is that determined by the Franck-Condon overlap between the vibrational ground state of H_2 and the various vibrational levels of H_2^+ [16], which is expected in the electron-impact ionization of H_2 molecules in the vibrational ground state. This population agrees approximately with the extrapolated value of the present data to $T = 0$. The population of the vibrational ground state increases with storage time and reaches about 90% after 25 s. In the electron-cooling section, the electrons travel parallel to the ions over the ~1.5 m interaction region. In this region, the relative velocities are dominated only by the electron temperature at $E_{rel} = 0$. In the toroidal region where the electron and ion beams merge and separate, the relative energies increase, even at zero relative energy in the straight cooling region. Thus, collisional excitation may be non-negligible at the energies encountered in the toroidal region. This causes vibrational heating, and is partly responsible for the mixing of components other than the vibrational ground state. The same can be said during DR measurements within the time window where the relative energy is large. In the toroidal region, the dissociative excitation by electrons [Eq. (3)] is non-negligible because of increasing collision energy. The cross sections of this process increase with energy up to about 10 eV, and also with increasing vibrational quantum numbers, as observed experimentally [6]. Therefore, the toroidal region also partly contributes to the removal of highly excited vibrational states.

The fact that ions are almost in their vibrational ground states after 25 s was also confirmed by measuring the kinetic energy released in the DR at zero energy using a technique of a two-dimensional fragment imaging [2]. The released energy was in good agreement with the $v = 0$ state.

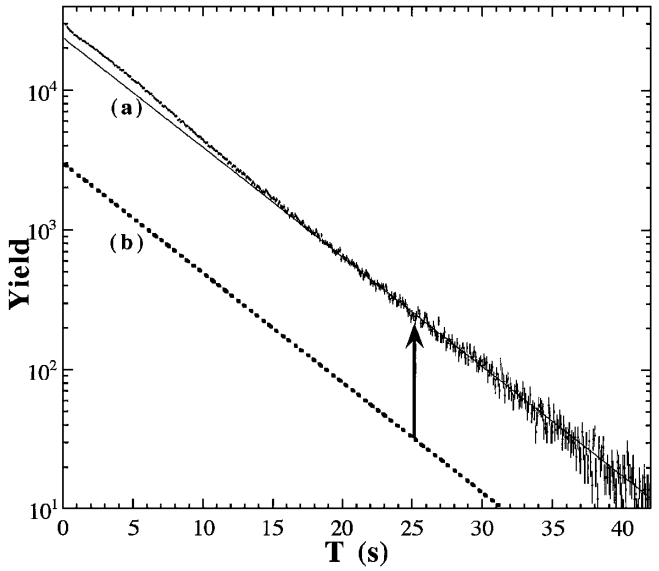

FIG. 4. Yield of single-H events after injection at the collision energy of $E_{\mathrm{rel}} = 0$ eV. The yield is proportional to the number of stored ions. The lines are described in the text.

Using the vibrational distribution shown in Fig. 3(b), we show hereafter the large contribution of the SEC to the vibrational quenching process. We define $N_v(t)$, which is the number of the stored particles with a vibrational quantum number of v at a time t after injection. If we consider only the DR process in the electron-ion collision, the function $N_v(t)$ has an exponential form according to the relation $N_v(t) = N_v^0 \exp(-R_v t)$, where R_v is the total destruction rate in the entire storage ring and N_v^0 is the number of stored particles at a time of $t = 0$. R_v is given by $R_v = 1/\tau_R + 1/\tau_v$, where τ_R and τ_v are the beam lifetimes due to collisions with the residual gas and the DR in the electron-ion collisions, respectively. As described previously, collisions with the residual gas do not change the populations of the vibrational states, and τ_R is almost independent of the vibrational quantum number. τ_v is also given by $1/\tau_v = (l/L)\rho_e \langle v\sigma \rangle_v$, where l is the length of the cooling section, L is the circumference of the ring, and ρ_e is the electron density. Figure 4 represents the rate of single-H events recorded with a multichannel scaler at the cooling energy ($E_{\mathrm{rel}} = 0$), which is due mainly to collisions with residual gas, and is proportional to the number of stored particles. Since the beam initially consists of many vibrationally excited states, and the lifetime due to the DR depends on the vibrational states, the data must follow multiexponential decay. However, at a storage time longer than 25 s, almost all ions are in the vibrational ground state, as has been discussed and, hence, one can expect approximately single exponential decay. The value of $R_{v=0}$ was determined to be 0.18 s^{-1} from the data over 25 s [line (*a*) in Fig. 4]. On the other hand, since the population of the $v = 0$ component at $T = 0$ was estimated to be about 10% of the total stored particles (N^0_{total}) from Fig. 3(b), the $v = 0$ component should follow the decay line given by $(1/10)N^0_{\mathrm{total}} \exp(-R_{v=0}t)$, as shown in Fig. 4 [line (*b*)], if we neglect the SEC process. Actually, at the 25-s storage time, the experimental data are about a factor of 8 higher than the value expected from line (*b*), as indicated by the arrow in the figure. This means that the ground-state population increased during storage. This is clear evidence of the SEC in which the vibrationally excited states transform into states with a lower vibrational quantum number towards the ground state.

This experiment also demonstrated that H_2^+ ions can be obtained in their vibrational ground states. The same can be applied to other non-IR-active ions in the storage rings.

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