Electron-induced vibrational deexcitation of H$_2^+$

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Using the Coulomb explosion imaging method, the change of the relative population for the first six vibrational states of H$_2^+$ during the interaction with low-kinetic-energy electrons has been measured. A model based on rate coefficients for dissociative recombination and superelastic collision processes is developed to explain the time dependence of the relative vibrational populations. Using this model, we demonstrate that superelastic collisions with rate coefficients of $(1-4) \times 10^{-6}$ cm$^2$ s$^{-1}$ (about an order of magnitude higher than available theoretical predictions) can explain the observed electron-induced vibrational deexcitation of H$_2^+$.

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I. INTRODUCTION

In regions where charged particles play an important role, like astrophysical plasma, the interaction between slow electrons with molecular ions is of importance for the knowledge of the chemical composition of such environments. One of the most important reactions is the dissociative recombination (DR) [1], which for the simplest molecular ion H$_2^+$ in a ro-vibrational state $v,J$ is described schematically by (see Fig. 1)

$$\text{H}_2^+ (X^2\Sigma_g^+, v,J) + e^- (E) \rightarrow \text{H}_2^{**} \rightarrow \text{H}(n) + \text{H}(n'),$$

where $E$ is the electron energy, and H$_2^{**}$ is a neutral H$_2$ molecule in a doubly excited state. For low electron impact energies and low vibrational levels, the process occurs via the dissociative $^1\Sigma_g^+$ state [2]. The H$_2^{**}$($^1\Sigma_g^+$) state dissociates by crossing all the vibrational states of H$_2^+$ (see Fig. 1) as well as a series of Rydberg states of the neutral H$_2$ molecule.

The interaction between electrons and molecular ions does not lead always to dissociation. In fact, it has been theoretically demonstrated that one of the most important factors in calculating the DR cross section is the autoionization probability of the doubly excited state [3] that can also lead to changes in the vibrational population of the molecular ion. For electrons with low kinetic energy (below the first vibrational excitation threshold), only deexcitation is possible, and for H$_2^+$ such a process is depicted as

$$\text{H}_2^+ (v) + e^- (E) \rightarrow \text{H}_2^+ (v') + e^- (E + \Delta E) (v' < v, \Delta E > 0)$$

and is often called superelastic collision (SEC).

During the last 7 years, intense experimental and theoretical work has been done in the field of DR, mainly due to the advent of the new heavy-ion storage rings [4]. These rings have made it possible to produce beams of vibrationally cold molecular ions, which can be merged with a strong and cold electron beam. However, the method relies on the fact that the molecular ions cool radiatively to the ground vibrational state while being stored in the ring. Since a static dipole moment (relative to the center of mass) is required for such transitions to occur, the storage ring technique is not directly applicable to H$_2^+$ and other symmetric molecules.

On the other hand, HD$^+$ has been the subject of numerous experimental as well as theoretical studies. Based on the Born-Oppenheimer approximation, H$_2^+$ and HD$^+$ have the same electronic structure, and since HD$^+$ has a rather strong static dipole moment [5], the DR of vibrationally cold HD$^+$ could be studied in great detail using the heavy-ion storage

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FIG. 1. The ground state of H$_2^+$ and the $^1\Sigma_g^+$ dissociative state [29] of H$_2$ relevant for the low-energy electron collisions with H$_2^+ (v)$. 

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ring technique. The first such measurement on HD\(^+\) was carried out at the Test Storage Ring (TSR), Heidelberg, where cooling into the vibrational ground state within \(\sim 300 \text{ ms} \) was observed \cite{6}, in agreement with theoretical predictions by Amitay et al. \cite{5}. The DR cross section for vibrationally relaxed HD\(^+\) has been determined over a wide range of relative electron energies at several storage rings and is in good agreement with calculations based on the multichannel quantum-defect theory (MQDT) \cite{6-9}. The branching ratio into the different final Rydberg states corresponding to atomic states of H and D fragments has been measured using a three-dimensional fragment imaging technique and compared with calculations based on the Landau-Zener theory \cite{10}. It was found that for low electron energies, the final state was H(1\(s\)) + D(2\(l\)) [or D(1\(s\)) + H(2\(l\))] At higher electron energies an angular anisotropy, supposedly due to the symmetry of the involved states in the DR process, was found \cite{10,11}. A detailed study of the DR of HD\(^+\) in selected vibrational quantum states was also carried out by Amitay et al. \cite{12,13}. They measured simultaneously the vibrational population of the stored beam using the Coulomb explosion imaging (CEI) method and the DR product states with a two-dimensional imaging technique. With the help of this combination of techniques, they could provide the first state selected relative rate coefficients for DR. Recently, sharp thresholds in the DR cross section of vibrationally cold HD\(^+\) were observed and were related to the opening of new final atomic states. Such results are in contradiction to theoretical calculations, which assume that the low-energy (\(E < 2.5 \text{ eV}\)) total cross section can be calculated independently from the branching ratio \cite{14}.

DR measurements on H\(_2^+\) were carried out at CRYRING, Stockholm, for a range of relative electron energies from 0 to 20 eV \cite{15}. From the time and energy dependence of the DR rates, it was concluded that some vibrational cooling occurs in the ion beam when merged with the electron beam (at zero relative energy); this cooling was mainly attributed to very high recombination rates for high vibrational states, assumed to be destroyed by the electron interaction after a storage time of order 10 s. The SEC process, on the other hand was assumed to be too slow to influence the vibrational population of the H\(_2^+\) beam.

Andersen et al. \cite{7} have used photodissociation to prepare an H\(_2^+\) beam primarily in the vibrational states \(v = 0\) and 1 at the Aarhus Storage Ring, Denmark (ASTRID). Applying imaging technique \cite{11}, they obtained some information about the vibrational distribution of H\(_2^+\) and the product states of the DR. Both experiments at CRYRING and ASTRID showed a tendency of the H\(_2^+\) DR cross section to become larger for a vibrationally excited beam and the absence of dissociation into the H\((n=1) + H(n=1)\) channel, in agreement with the observation for HD\(^+\) \cite{11}.

The first experimental evidence for SEC processes was recently found for H\(_2^+\) at the TARN II storage ring \cite{16}. Vibrational deexcitation was observed when the molecular ion beam was merged with the electron beam, and the authors demonstrated that both DR of high vibrational states as well as SEC are responsible for the change in the vibrational population of the stored beam, a conclusion somewhat in disagreement to that drawn from the CRYRING experiment \cite{15}. Although Tanabe et al. \cite{16} were able to clearly demonstrate the existence of SEC, a direct comparison with the theoretical values was not possible, because the vibrational distribution of the stored ion beam could not be uniquely determined.

Theoretically, an extensive description of the DR process for HD\(^+\) and H\(_2^+\) using MQDT \cite{17} has been performed. Based on this theory, Nakashima et al. \cite{3} have calculated the cross section for the DR of H\(_2^+\), HD\(^+\), and D\(_2^+\) for collisions with slow electrons (0.02 eV \(\leq E \leq 1.00 \text{ eV}\)) and demonstrated the strong dependence of the cross section on the initial vibrational state. Later on, Takagi \cite{18} incorporated the molecular rotation in the MQDT and calculated the DR cross section of H\(_2^+\) for \(E \approx 10 \text{ eV}\). Schneider et al. \cite{2} have performed a very comprehensive calculation for the DR of HD\(^+\) and demonstrated good agreement with existing data for the cross section over a wide range of energy. Both Takagi’s and Schneider’s calculations were also able to reproduce the so-called window (Rydberg) resonances due to the indirect DR process \cite{19}.

On the other hand, theoretical calculations for SEC processes are rather scarce. Nakashima et al. \cite{3} have calculated the singlet scattering \(d\)-wave partial cross sections for vibrational excitation and deexcitation of H\(_2^+\) for the vibrational states \(v = 0, 1\), and \(2\) with 0.02 eV and 1.0 eV, using the MQDT method. For the deexcitation process, the dominant cross sections are found to be for transitions with \(\Delta v = -1\). All the cross sections were found to be smaller than the DR cross sections for the same initial vibrational states. Rate coefficients for the deexcitation processes were not calculated by Nakashima et al., but can be estimated by comparing them to the DR rate coefficients and cross sections published in the same paper, and we estimate them to be in the range of \(7 \times 10^{-9} \text{ to } 7 \times 10^{-8} \text{ cm}^3 \text{s}^{-1}\) for the various vibrational states. Sarpal and Tennyson \cite{20} have calculated the rate coefficients for the vibrational excitation and deexcitation of H\(_2^+\) with low-energy electrons. The calculation was carried out for the first three vibrational states using \(R\)-matrix theory and the deexcitation rate coefficients were found to be \(8.5 \times 10^{-8} \text{ cm}^3 \text{s}^{-1}\) for the \(v = 1 \rightarrow 0\) transition and \(2.0 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}\) for the \(v = 2 \rightarrow 1\) transition. The rate coefficient for the \(v = 2 \rightarrow 0\) transition was found to be smaller by an order of magnitude (all numbers are given for thermal electrons with a temperature of \(T = 100 \text{ K}\)). The calculation made by Sarpal and Tennyson \cite{20} was performed entirely within the adiabatic nuclei approximation, which ignores the autoionizing states involved both in the direct DR (i.e., mainly the \(^1\Sigma^+_g\) state, see Fig. 1) and indirect DR. As pointed out above, there are no quantitative comparisons with experimental results for the SEC processes.

In this paper, we present results for vibrational populations in H\(_2^+\) during the interaction with slow electrons. Using the CEI technique, rates of vibrational deexcitation are derived and the results compared to the predicted effects of DR and SEC. In this context, we demonstrate that the SEC processes are the dominant factors for explaining the deexcitation of the H\(_2^+\) molecular ions. Comparison with a simple model describing the time dependence of the vibra...
tional population based on the theoretical rate coefficients is
presented, and it is demonstrated that the existing theoretical
rate coefficients for the SEC are too small to explain the time
dependence of the vibrational population.

II. EXPERIMENTAL SETUP

A. The heavy-ion storage ring TSR

The experiment presented here was performed at the heavy-ion storage ring TSR located at the Max-Planck-Institut für Kernphysik, Heidelberg, Germany. The ring, shown in Fig. 2, has a circumference of 55.4 m and consists of different steering and focusing magnets allowing one to store ions with a magnetic rigidity of up to 1.5 Tm. The H$_2^+$ ions were produced by direct electron-impact ionization of neutral H$_2$ in a Penning ion source, accelerated to $E_i$ = 1 MeV by a Van de Graaff accelerator and injected into the storage ring. Approximately 10$^7$ ions were stored after each injection and the mean storage lifetime was about 10 s at a vacuum of about 5 x 10$^{-11}$ mbar. The ions were merged with the electron cooler beam over a length of 1.5 m. The diameter of the electron beam was about 3.5 cm and the electron density 6.1 x 10$^6$ cm$^{-3}$. The transversal and longitudinal temperatures were $kT_\perp$ ~ 12 meV and $kT_\parallel$ ~ 0.1 meV, respectively. Along the whole experiment, the velocity of the electron beam was set very close to that of the injected ion beam. Hence, the electron-ion collisions occurred at near-zero relative energy $E$, the average center-of-mass collision energies being given by the electron temperature $kT_\perp$. It may be important to point out that a big advantage of the merged beam configuration in a storage ring is the excellent velocity matching between electrons and ions, even in a case of small initial mismatches. The friction force exerted by the electrons on the ions rapidly drags the ion beam to a velocity that matches the electron velocity so that the energy of average relative motion between the two beams becomes zero. After injection, the angular spread of the ion beam is relatively large (however, below ± 7 mrad) and then reduces over a time of a few seconds if the cooling electron beam is present. Yet, the contribution to the electron-ion collision energies from the initial ion velocity spread and the initial space-charge effect across the electron beam has a maximum size of only $\approx kT_\perp$, which ensures that the collision energies always remain below $\sim$ 25 meV.

B. Coulomb explosion imaging of H$_2^+$

1. Experimental principle

The CEI technique was used to provide information about the vibrational distribution of the ion beam as a function of the storage time. Using a slow extraction scheme, a small part of the stored beam was steered toward a beam line where the CEI experiment took place (see Fig. 2). Detailed information about the CEI method, the setup itself and the measuring scheme have been published elsewhere [21,22], and only a short description will be given here.

In a CEI measurement, fast molecular ions collide with a thin foil (< 100 Å thick) where all binding electrons are stripped. The time scale of the stripping process ($\sim$ 10$^{-17}$ s) and the dwell time in the foil ($\sim$ 10$^{-16}$ s) are short compared to the vibrational and rotational times which are about 10$^{-14}$ and 10$^{-12}$ s, respectively. After leaving the foil, the charged fragments (two protons in the present case) repel each other due to the strong Coulomb force and their internuclear distance grows from a microscopic (about 1 Å) to a macroscopic scale (a few centimeters) after ~ 2 m of free flight.

The asymptotic kinetic energy $E_k$ released in the center-of-mass reference frame after the foil-induced Coulomb explosion can be determined using a three-dimensional imaging technique that measures the distance between the two fragments on the surface of a detector located downstream from the target. Details about the detector can be found in a previous publication [22]. In the present experiment, we used a Formvar target of 70 Å thickness and the distance between the target and the detector was 2965 mm. The geometry of the beam extracted to the Coulomb explosion target was determined by collimation and therefore independent of the size of the stored beam, which varied depending on the electron cooling time after injection. The target applied in the present experiment was the same one as that used for previous measurements [12,13] of vibrational populations in a stored HD$^+$ beam.
2. Determination of vibrational populations

The information about the vibrational distribution is contained in the measured kinetic-energy release. Due to the Coulomb repulsion between the two protons exiting the foil, the internuclear distance distribution of the molecule $P^{R}_{v}(R)$ is transformed into an asymptotic kinetic-energy distribution $P^{E_{k}}_{v}(E_{k})$ in the center-of-mass frame of reference. In a classical description of the Coulomb explosion process and adopting the quantum-mechanical probability density according to the nuclear wave function $\Psi_{v}$ for the initial internuclear distance distribution, this transformation can be written as

$$P^{E_{k}}_{v}(E_{k})dE_{k}=P^{R}_{v}(R)dR=\Psi^{2}_{v}(R)dR. \quad (3)$$

For a single event, the kinetic energy release $E_{k}$ of the two proton fragments in the center-of-mass frame of reference is given by the Coulomb law

$$E_{k}(R)=e^{2}/R, \quad (4)$$

where $e$ is the electron charge. Since each vibrational state has its specific wave function $\Psi_{v}(R)$, which can be transformed to a well-defined kinetic-energy distribution $P^{E_{k}}_{v}$, the measured spectra consist of a superposition of such kinetic-energy distributions weighted by the relative populations of the vibrational levels. Thus, by fitting a linear combination of normalized vibrational-state specific kinetic-energy distributions to the normalized experimental kinetic-energy spectrum, the relative population $p_{v}(t)$ of the vibrational states can be extracted:

$$P^{E_{k}}(E_{k}:t)=\sum_{v}p_{v}(t)P^{E_{k}}_{v}(E_{k}). \quad (5)$$

As shown in Ref. [13], this description is oversimplified, and three additional effects have to be taken into account. These are (i) the interaction of the fast molecules with the foil atoms leading to multiple scattering and charge exchange, (ii) the finite resolution of the imaging detector, and (iii) the influence of the initial momenta of the fragmenting states. These three processes were considered in detail in Ref. [13] regarding the CEI of HD$^+$, and we refer the reader to this paper for more information. For the present case of H$_2$$^+$, the vibrational wave functions were calculated by solving the Schrödinger equation for the electronic ground state of H$_2$$^+$ [23]. A Monte Carlo simulation of the Coulomb explosion process [24] was used to take into account the broadening of the distribution due to the interaction between the incident molecular ion and the target atoms [25] as well as the initial fragment momenta [13] and the time resolution of the detector. The parameters entering the simulation, mainly the target thickness, were taken over from the previous measurements [13] on HD$^+$ ions, where they could be fine tuned in order to reproduce with high accuracy the kinetic-energy spectrum of an ion beam completely relaxed to the vibrational ground state.

For the homonuclear molecule H$_2$$^+$, the detection efficiency for fully reconstructed three-dimensional CEI events was reduced in comparison to HD$^+$ (where the H$^+$ and D$^+$ fragments hit separate regions of the CEI detector) because of the lower accuracy of the hit time measurement used to determine the longitudinal fragment coordinates [22]. While valid distributions of the total kinetic-energy release $E_{k}$ could be obtained only from subsets of the data, distributions of the transverse (two-dimensional) energy release could be used with the full statistics. To determine the vibrational populations, we have therefore applied both three-dimensional data (when available with sufficient statistics) and two-dimensional energy distributions. The data were fitted with either the three-dimensional fragment energy distribution of Eq. (5) or, in the two-dimensional case, with an appropriate projection of the spherically symmetric fragment coordinate distribution, derived from Eq. (5), onto the transverse plane. The results from both procedures were found to be consistent with each other.

III. RESULTS

A. Vibrational population distribution

In order to measure the vibrational state population of the H$_2$$^+$ beam, and its change due to the DR and SEC processes, the beam was stored in the ring and merged with the electron cooler beam at near-zero relative energy ($E=0$) for a time $t$. After this time, the electron beam was turned off, and a small fraction of the ion beam was continuously extracted toward the CEI setup, until the stored beam intensity became too weak and the extracted ion rate too small. The remainder of the stored beam was then kicked out of the ring, and a new injection took place. The kinetic-energy release spectra obtained with the CEI detector were measured after various times of storage and electron interaction. As pointed out in Sec. II B 2, these distributions directly represent superpositions of the initial nuclear probability distributions for the various vibrational states of H$_2$$^+$ according to their populations. Vibrational deexcitation of the molecular ions will hence show up as a narrowing of the measured energy-release distributions.

In order to prove that the change in the vibrational-state population is only due to the interaction with the electron beam, a first measurement was taken over 12 s of storage without merging the molecular ions with the electron beam. The acquired events were divided into three time slices, 0–4 s, 4–8 s, and 8–12 s, respectively. The spectrum shown in Fig. 3(a) is the three-dimensional CEI kinetic-energy release measured during the first 4 s of storage. No changes in the shape of this distribution were observed during the whole storage period. The normalized kinetic-energy release spectra were fitted by the functions $P^{E_{k}}(E_{k}:t)$, Eq. (5), allowing for $v=0, \ldots, 11$; results for the vibrational populations up to $v=5$ for each of the time slices are shown in Fig. 3(b). It is seen that neither the collision-induced dissociation from the residual gas in the ring nor the motional electric fields of about 20 kV/cm present in the dipole magnets of the ring cause significant changes of the initial vibrational-state distribution, in good agreement with the results obtained at CRYRING [15].
The vibrational populations derived from the CEI kinetic-energy release spectrum averaged over all storage times in absence of the electron beam are shown in Fig. 4. These results were obtained from fits to the two-dimensional kinetic-energy spectra with full statistics (cf. Sec. II B 2) and agree within the statistical errors with the results of Fig. 3 obtained from three-dimensional spectra. We compare our results for $H_2^+$ with earlier results obtained from a photodissociation experiment carried out by Von Busch and Dunn [26] on the same ion, and with predicted populations calculated under the assumption that $H_2^+$ is formed in the ion source by ionization of ground state $H_2$ obeying the Franck-Condon principle. The populations of the first two vibrational states measured in the present experiment are between 5% and 8% higher than the Franck-Condon populations. Similar deviations for the lowest vibrational states were also seen in the CEI measurement of HD$^+$ carried out earlier with our setup and in fact, already in the photodissociation experiment on $H_2^+$ by von Busch and Dunn [26] see Fig. 4. Possible reasons for the deviations were discussed in Ref. [13].

To extract the influence of the DR and SEC processes on the vibrational-state population, the kinetic-energy release spectra were measured after four different storage times ($t=1, 3, 5, \text{ and } 8 \text{ s}$) during which the beam was continuously interacting with the electrons (Fig. 5). As the electron beam was turned off before starting the CEI measurement, it can be assumed (according to Fig. 3) that the recorded spectra correspond to the “frozen” vibrational distribution reached after the respective electron interaction times. Significant changes in the vibrational distribution are evident as the width is getting narrower—a strong sign of deexcitation. A shift of the peak position also occurs and is due to the anharmonicity of the potential well of $H_2^+$, a molecule in a high vibrational state having on the average larger internuclear distances that lead to smaller kinetic-energy releases in the Coulomb explosion process [see Eq. (4)]. The measurement time for the spectra shown in Fig. 5 was about 6 h for the run with $t=1 \text{ s}$ and 10 h for $t=8 \text{ s}$.
The full-statistics two-dimensional kinetic energy distributions corresponding to the time slices of the spectra shown in Fig. 5 were again fitted using the theoretical distributions derived from Eq. (5) and the vibrational population distributions as a function of the storage time were extracted. Figure 6 shows the time evolution of the populations for the first six vibrational states. A simple extrapolation of the present \( v = 0 \) data leads to the conclusion that the hydrogen molecular ions will be mainly in the ground vibrational state after a storage time of about 20–30 s. In order to relate our results to the measurements carried out at CRYRING [15] and TARN II [16] one has to consider the quantity \((L/C)n_e\) and the transversal temperature \(kT_\perp\), where \(L\) is the interaction length with the electrons, \(C\) the ring circumference, and \(n_e\) is the electron density \((L/C = 0.027\) and \(n_e = 6.1 \times 10^6 \text{ cm}^{-3}\) in the present experiment). The CRYRING measurements \((n_e = 10^7 \text{ cm}^{-3}, L/C = 0.015,\) and \(kT_\perp = 10 \text{ meV}\)) [15] were carried out under experimental conditions similar to those of this experiment and showed significant variations of the DR energy spectra and of the DR rate at \(E = 0\) on a time scale of \(\sim 20\) s, similar to our results for the time needed to reach strong vibrational relaxation. The measurement at TARN II [16] shows an increase of the derived \(v = 0\) population to \(\sim 80\%\) within \(\sim 10\) s. The product \((L/C)n_e\) had about the same size as in our case, but the lower transversal temperature \((kT_\perp = 1 \text{ meV})\) is expected to lead to cooling about three times faster. This is approximately confirmed by comparing our extrapolated time for strong vibrational relaxation (20–30 s) to the TARN result \((\sim 10\) s). It should be pointed out, however, that in the TARN II experiment, the vibrational population was not directly measured, and the changes in the population were inferred only from the theoretical DR rates, using a Franck-Condon distribution as the initial population; nevertheless, qualitatively, the time behavior of the derived \(v = 0\) population is comparable to the one measured here. In the following, we will analyze our measured vibrational population evolution considering the influence of both the DR and the SEC processes.

**B. Superelastic processes**

Both DR and SEC affect the vibrational population distribution of \(H_2^+\), but in different ways. While the DR process preferentially removes molecular ions in those vibrational states that have larger DR rate coefficients than other states, SEC transfers population from high to low vibrational states. The difference between the effects of both processes can be illustrated by assuming a situation in which the initial vibrational populations are equal for all the vibrational levels and it is not the ground state but an upper vibrationally excited state that has the smallest DR rate coefficient. In such a case, assuming DR to be the dominant interaction with the \(H_3^+\) ions, the vibrational population will be concentrated, after some time, in this excited vibrational state. On the other hand, such inverted distribution cannot occur (for electron energies below the excitation energy of the first vibrational level in \(H_2^+\) if SEC dominates, as only population transfer from high vibrational states to lower ones is possible. In the following, we present a model that describes the time dependence of the vibrational populations of \(H_2^+\) due to both DR and SEC.

**1. Model for the time-dependent vibrational population of \(H_2^+\)**

Since no significant changes of the vibrational population are taking place in the absence of the electron beam, it seems appropriate to use a simple model where only DR and SEC are affecting the vibrational population of the \(H_2^+\) ions interacting with electrons at near-zero relative energies. This also implies that radiative transitions between the vibrational states are much slower than the slowest rate due to DR and SEC, an assumption holding for \(H_2^+\) and the electron density used.

Assume an ensemble with \(N_v(t)\) molecules in the different vibrational states \(v\) and initial \((t = 0)\) occupation numbers \(N_v^0\). Furthermore assuming there are \(n\) vibrational states \((v = 0 \text{ up to } v = n - 1)\), the numbers \(N_v(t)\) are given by a set of coupled differential equations:

\[
\frac{dN_v(t)}{dt} = - (\alpha_{\text{SEC}}^{(v)} + \alpha_{\text{DR}}^{(v)}) N_v(t) + \alpha_{\text{SEC}}^{(v+1)} N_{v+1}(t),
\]

where \(\alpha_{\text{SEC}}^{(v)}\) and \(\alpha_{\text{DR}}^{(v)}\) denote the SEC and DR rate coefficients, respectively, for a given vibrational level \(v\), with \(\alpha_{\text{SEC}}^{(0)} = 0\) and (neglecting feeding from higher states \(v \geq n)\)

\(\alpha_{\text{SEC}}^{(n)} = 0\). The SEC processes were assumed to be dominated by \(\Delta v = 1\). This set of equations can be written in matrix form as

\[
\frac{d\mathbf{N}(t)}{dt} = \mathbf{A} \mathbf{N}(t),
\]

where \(\mathbf{A}\) is the rate matrix.
with \( N^T(t) = (N_{v-1}(t), \ldots ,N_0(t)) \) and a matrix \( \mathcal{A} \) composed of the rate coefficients. The equations can be uncoupled by determining the eigenvectors and the eigenvalues of \( \mathcal{A} \). The general solution for \( N(t) \) is given by
\[
N(t) = S \exp(\mathbf{L} \cdot t) S^{-1} N^0,
\]
where \( S \) is the matrix of the eigenvectors and \( \mathbf{L} \) is a vector with the eigenvalues \( L_v \) of \( \mathcal{A} \). The vector \( N^0 \) is defined by the initial populations. The expression \( \exp(\mathbf{L} \cdot t) \) is a diagonal matrix where each element is given by \( \exp(L_v \cdot t) \), provided all eigenvalues are different. Normalizing \( N_v(t) \) to the total number of molecules,
\[
p_v(t) = \frac{N_v(t)}{\sum_v N_v(t)},
\]
the time evolution of the relative population of a vibrational state \( v \) is obtained.

2. Comparison: Model and experiment

Although in principle it is possible to fit the data shown in Fig. 6 using the rate coefficients \( \alpha_{\text{DR}} \) and \( \alpha_{\text{SEC}} \) as free parameters, this does not work out in practice because of the small number of data points that could be obtained in a total running time of several days. Instead, we will assume values for the DR and SEC rate coefficients, and directly compare the results of the model with the data.

For the DR rate coefficients \( \alpha_{\text{DR}}^{(v)} \), we have used the values calculated by Nakashima et al. [3] for the first five vibrational states (corrected for the present electron-velocity distribution with beam temperatures according to Sec. II A). For the SEC rate coefficients, theoretical calculations have been performed only for the vibrational states \( v = 1, 2 \) [20], yielding \( \alpha_{\text{SEC}}^{(1)} = 8.5 \times 10^{-8} \text{cm}^3 \text{s}^{-1} \) and \( \alpha_{\text{SEC}}^{(2)} = 2.0 \times 10^{-7} \text{cm}^3 \text{s}^{-1} \). In order to evaluate the time dependence of the vibrational population for \( v = 0 - 5 \) on the basis of these results, we have arbitrarily assumed the SEC rate coefficients for the levels \( v = 3, 4, 5, \) and 6 to be equal to the one calculated by Sarpal and Tennyson [20] for the \( v = 2 \) level. For the DR rate coefficients, only the values for the \( v = 5 \) and 6 levels are missing, and they were assumed to be close to the rate coefficient for the \( v = 4 \) level, as calculated by Nakashima et al. [3]. It will be shown later that these assumptions do not change the main conclusion when the time evolution obtained from the model is compared to the experimental data. The initial population \( N^0_v \) in Eq. (7) is set to the measured values as shown in Fig. 4; the level \( v = 6 \) was included to describe feeding of \( v = 5 \), and feeding from \( v > 6 \) was neglected.

Figure 6 shows a comparison of the measured relative populations of the vibrational states \( v = 0 - 5 \) with time evolutions for \( p_v(t) \) as calculated for DR and SEC separately as well as for the combination of both processes, using the rate coefficients as calculated or assumed on the basis of available calculations as described above. Clearly, none of these models can explain the data, the predicted time development being too slow in all three cases. Although we have only estimated the SEC rate coefficients for \( v > 2 \) and the DR rate coefficient for \( v = 5 \), changes to their assumed values can somewhat improve agreement for the higher vibrational states, but do not dramatically influence the behavior of the model for the three lowest vibrational states (\( v \leq 2 \)) as more than 50\% of the population is already localized in these levels at \( t = 0 \) (see Fig. 4). As will be discussed below, considering the existing experimental data for the DR rate coefficients of \( \text{H}_2^+ \) and \( \text{HD}^+ \), it is possible to demonstrate that the disagreement between the model and the data is mainly due to the SEC rate coefficients and in particular their values for \( v = 1 \) and 2.

As shown by the measurement at CRYRING [15], the DR rate coefficients of \textit{vibrationally cold} \( \text{H}_2^+ \) and \( \text{HD}^+ \) are very close to each other (see Fig. 10 in Ref. [15]), the absolute value for the DR rate coefficient of \( \text{HD}^+ (v = 0) \) having been measured in three independent experiments [27] and being in good agreement with theoretical values [2]. Thus, the DR rate coefficient for the \( v = 0 \) state of \( \text{H}_2^+ \) cannot be changed by any considerable amount without contradicting previous experimental results. A modification of the DR rate coefficients for the next-higher vibrational states in order to fit the time dependences of Fig. 6 would require large increases of their values (by about an order of magnitude) that would seem rather artificial and in particular imply a much different trend for the low-lying vibrational levels of \( \text{H}_2^+ \) as opposed to the measured relative rate coefficients of excited vibrational states of \( \text{HD}^+ [12,13] \).

On the other hand, increased values for the much less studied SEC rate coefficients appear much more plausible. The simple fact that the vibrational population concentrates around the \( v = 0 \) state is consistent with the fact that SEC is the dominant cooling process. Although DR could also produce a similar effect, that would require the DR rate coefficient for \( v = 0 \) to be the smallest among all the vibrational states, which again would be different from the observed behavior of the rate coefficients for the vibrationally excited \( \text{HD}^+ [12,13] \). Moreover, a comparison between the dashed and the dashed-dotted lines in Fig. 6 indicates that the inclusion of DR tends to move the model results away from the data points in all cases (except \( v = 2 \) and 3). On the theoretical side, as pointed out above, the calculation by Sarpal and Tennyson [20] for the SEC rate coefficients did not consider the doubly excited resonant state of \( \text{H}_2^+ (1 \Sigma^+_g) \) (see Fig. 1), which through coupling to the vibrationally excited Rydberg states of \( \text{H}_2 \) could strongly increase the SEC rate.

In order to fit the data shown in Fig. 6, we have by trial and error increased the rate coefficients for the SEC process until a reasonable agreement was obtained with the data. The full lines in Fig. 6 represent the calculated time dependency for SEC rate coefficients \( \alpha_{\text{SEC}}^{(v)} \) set to the following values (in units of \( 1 \times 10^{-6} \text{cm}^3 \text{s}^{-1} \)); \( \alpha_{\text{SEC}}^{(1)} = 0.6, \alpha_{\text{SEC}}^{(2)} = 1.2, \alpha_{\text{SEC}}^{(3)} = 2.2, \alpha_{\text{SEC}}^{(4)} = 2.4, \alpha_{\text{SEC}}^{(5)} = 4.4 \). While the specific results for \( \alpha_{\text{SEC}}^{(v)} \) may not represent a unique fit result, the agreement between the data and the model obtained for this choice demonstrates the level of SEC rates consistent with our data and indicates that SEC are in fact the dominant cooling process. The SEC rate coefficients we have used here are about 6–7 times larger than the theoretical results of Sarpal and
Tennyson [20] and one to two orders of magnitude larger than the DR rate coefficients for the corresponding vibrational levels [3].

IV. CONCLUSIONS

By a direct measurement of the vibrational population in stored $\text{H}_2^+$ ions interacting with a beam of cold electrons, we have analyzed the development of this population as a function of the electron-ion interaction time. Based on the comparison of the data with a simple model including the rates of dissociative recombination and superelastic collision processes, we have demonstrated that the current theoretical understanding of the interaction of low-energy electrons with $\text{H}_2^+$ is not complete. Changes of the vibrational population in the molecular ions are in progress. An extended measurement of the vibrational relaxation using the Coulomb explosion method, in combination with state-specific cross sections for the beam loss by DR, will make it possible to obtain more precise experimental values for SEC rate coefficients in the future.

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[27] W.J. van der Zande (private communication).