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Vibrational relaxation and dissociative recombination of $H_2{}^+$ induced by slow electrons

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We present calculations of cross sections and rate coefficients for the dissociative recombination of $H_2{}^+$ ions initially in $v=0-6$ vibrational levels, together with rate coefficients for the competing electron-induced vibrational deexcitation. We used the multichannel quantum defect theory with a second-order treatment of the K matrix, and show that electronic interactions dominate not only the dissociative recombination but also the vibrational relaxation induced by slow electrons. Most of our rate coefficients for dissociative recombination are in good agreement with the measurements at the TSR storage ring [S. Krohn *et al.*, Phys. Rev. A **62**, 032713 (2000)]. On the contrary, our rates for vibrational deexcitation, close to former results obtained by *R*-matrix calculations [B. K. Sarpal and J. Tennyson, Mon. Not. R. Astron. Soc. **263**, 909 (1993)], are smaller by up to one order of magnitude than the experimental values which are deduced from the time evolution of the vibrational populations, measured by the Coulomb explosion imaging method.

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I. INTRODUCTION

Controlling the rotational and vibrational populations of molecular ions is a long-standing problem in various types of ion sources or ion-containing environments such as merged beams, ion storage rings, or fusion devices. On the other hand, knowing rates for dissociative recombination and rovibrational excitation or deexcitation of molecular ions in cold plasmas (in particular, interstellar plasmas), due to collisions with surrounding electrons, is crucial for our understanding of the ongoing chemistry and the local temperature. It is especially so for homonuclear ions which are not subject to fast radiative decay, since they have no permanent dipole moment.

A recent experiment has been performed at the TSR storage ring [1] in which rate coefficients for vibrational deexcitation of $H_2{}^+$ ions by slow electrons could be deduced from the time evolution of vibrational populations. We have made a theoretical study of this process [also called ‘‘superelastic collisions’’ (SEC)],

$$e^-(\varepsilon)+H_2{}^+(v)\rightarrow e^-(\varepsilon')+H_2{}^+(v'),\quad v'<v, \qquad (1)$$

where v and v' stand for the initial and final ion vibrational levels, and ε and ε' for the initial and final energy of the free electron, respectively. Vibrational excitation [$v'>v$ in Eq. (1)] could also be studied in the same set of calculations, but these endothermic reactions are not possible for the low energy range of the incident electron considered here.

We simultaneously obtain the rate coefficients for the competitive reaction of dissociative recombination (DR), usually seen as the dominant reaction path for slow electrons colliding with molecular ions:

$$e^-(\varepsilon)+H_2{}^+(v)\rightarrow H+H^*(\epsilon), \qquad (2)$$

where ϵ is the relative kinetic-energy release of the dissociating atoms. While the DR of HD^+ in a given vibrational level (especially the lowest one, $v=0$) has been extensively studied experimentally [3], and used as a test case for storage ring measurements, it has not been so for the homonuclear ion $H_2{}^+$ which does not decay radiatively to the ground level. Only recently relative values for the DR rate coefficients of the $v=0\rightarrow 6$ vibrational levels have been measured at the TSR storage ring [2,4], and absolute values were deduced from the measurement of the $v=0$ absolute DR cross section.

Although rotational transitions surely take place simultaneously with vibrational ones, we concentrate here, as in the experimental analysis, on vibrational effects. We mainly show that the vibrational transitions involved in SEC [Eq. (12)] are in fact dominated, in the $H_2{}^+$ case, by strong indirect electronic couplings. The rotational effects, already incorporated in dissociative recombination calculations [5–7], will be discussed for superelastic collisions in a later paper.

Sarpal and Tennyson [8] have calculated vibrational excitation and deexcitation rate coefficients for the low vibrational levels of $H_2{}^+$ in collisions with slow electrons by using the *R*-matrix method. They found rate coefficients of 8.5×10^{-8} cm^3 s^{-1} for the $v=1\rightarrow 0$ transition and 2.0×10^{-7} cm^3 s^{-1} for the $v=2\rightarrow 1$ transition for thermal electrons at a temperature of 100 K. Using the multichannel quantum defect theory (MQDT) with a first-order perturbative treatment of the electronic coupling, Nakashima *et al.* [10] also studied DR and SEC of the molecular hydrogen ion. The SEC rate coefficients which may be roughly de-

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duced from their cross-section values are in the same range as those of Sarpal and Tennyson, or smaller. Regarding other molecular ions, to our knowledge, SEC have been only studied for N_2^+, by Guberman [11] who used a second-order MQDT approach similar to the method used in the present paper.

On the experimental side, superelastic collisions were first demonstrated to be efficient for the vibrational cooling of H_2^+ ions in the TARN-II storage ring [12]. But values for the SEC rate coefficients could only be deduced in a later experiment on the Heidelberg storage ring TSR, where the vibrational populations could be monitored in time by the Coulomb explosion imaging method. Through a simple kinetic model for the evolution of the vibrational population, assuming that transitions with $\Delta v < -1$ can be neglected, Krohn *et al.* [1] have deduced SEC rate coefficients which are higher by about one order of magnitude than the available theoretical values.

In the following sections, we will first sketch the theoretical approach used in the present calculations, and then compare our results with the available experimental and theoretical ones, with a discussion of the SEC mechanism and its influence on the vibrational cooling of H_2^+ ions.

II. THEORY

A. The MQDT formalism

The so-called two-step MQDT as applied to dissociative recombination [13] and electronic autoionization [14] rests on a quasidiabatic description of molecular states [15], where two classes of electronic states (monoexcited and diexcited, respectively) are defined. The short-range electronic interactions between states of different subspaces are then sorted out as an electronic coupling operator **V**, which couples the ionization channels (attached to the ground-state ion core), open and closed, to dissociative ones in the case of DR, or to core-excited ionization channels (or Rydberg series) in the case of electronic autoionization. From the operator **V**, a short-range reaction matrix (K matrix), solution of a Lippmann-Schwinger integro-differential equation [17] is built:

$$\mathbf{K}=\mathbf{V}+\mathbf{V}\frac{\mathbf{1}}{\mathbf{E}-\mathbf{H}_0}\mathbf{K}, \tag{3}$$

where $\mathbf{H}_0$ is the Hamiltonian operator excluding the electronic interaction **V**. In the case of weak coupling a perturbative solution of Eq. (3) can be obtained [13,16]. The energy dependence of the coupling can often be neglected since the electronic coupling is mainly built at short distance, where the external electron is strongly accelerated by the Coulomb attraction and thus insensitive to small differences in kinetic energy. We have recently shown analytically that in this case, the perturbative series of Eq. (3) converge at second order [18]. To be cast into the MQDT framework, the resulting K matrix is diagonalized:

$$\sum_j \pi K_{ij}U_{j\alpha}=-\tan\eta_\alpha U_{i\alpha}, \quad \alpha=1,2,\dots,N, \tag{4}$$

with eigenvalues $-\pi^{-1}\tan\eta_\alpha$ and unitary eigenvectors $U_{i\alpha}$. In the preceding equation, i and j are indices labeling the reaction channels, and N is the number of channels involved in the calculation. The eigenvalues η_α and the eigenvector elements $U_{j\alpha}$ are used in a frame transformation to build the channel coupling coefficients for the MQDT treatment of DR and SEC, i.e.,

$$\mathcal{C}_{v\alpha}=\sum_{v'} U_{v'\alpha}\langle v|\cos[\pi\mu(R)+\eta_\alpha]|v'\rangle_R, \tag{5}$$

$$\mathcal{C}_{d\alpha}=U_{d\alpha}\cos\eta_\alpha, \tag{6}$$

$$\mathcal{S}_{v\alpha}=\sum_{v'} U_{v'\alpha}\langle v|\sin[\pi\mu(R)+\eta_\alpha]|v'\rangle_R, \tag{7}$$

$$\mathcal{S}_{d\alpha}=U_{d\alpha}\sin\eta_\alpha, \tag{8}$$

where v and v' designate the vibrational states of the molecular ion, d the dissociative channel, and the integration $\langle\cdots\rangle_R$ is over the internuclear distance. Note that the nonadiabatic radial coupling between two ionization channels, v and v', is introduced here through the R dependence of the quantum defect μ. Indeed, a constant quantum defect would cancel all nondiagonal $v\neq v'$ terms from Eqs. (5) and (7), and thus decouple the ionization channels.

The last step of the MQDT treatment is the construction of the asymptotic scattering matrix and the calculation of the cross sections. We follow the method of Seaton [19] as first applied by Nakashima *et al.* [10] to the treatment of DR and related processes. The matrices $\mathcal{C}$ and $\mathcal{S}$ are used to build the "generalized" scattering matrix **X** which involves the whole set of channels, open or closed, for ionization or dissociation:

$$\mathbf{X}=\frac{\mathcal{C}+i\mathcal{S}}{\mathcal{C}-i\mathcal{S}}. \tag{9}$$

Then, the usual scattering matrix **S** is calculated by elimination of the closed channels:

$$\mathbf{S}=\mathbf{X}_{\mathrm{oo}}-\mathbf{X}_{\mathrm{oc}}\frac{1}{\mathbf{X}_{\mathrm{cc}}-e^{-2i\pi\nu}}\mathbf{X}_{\mathrm{co}}. \tag{10}$$

The index o (c) means open (closed) channel blocks. The parameters $\nu_v=1/\sqrt{2(E_v-E)}$, analogous to the effective quantum number of a Rydberg level, are defined for each closed channel with threshold energy E_v higher than the total energy E.

Finally, for the initial ion level v and for a multiplicity ratio r between the ion and dissociative states, the cross sections are given by

$$\sigma_{dv}=\frac{\pi}{2\varepsilon}\frac{r}{2}|S_{dv}|^2 \tag{11}$$

for dissociative recombination, and by

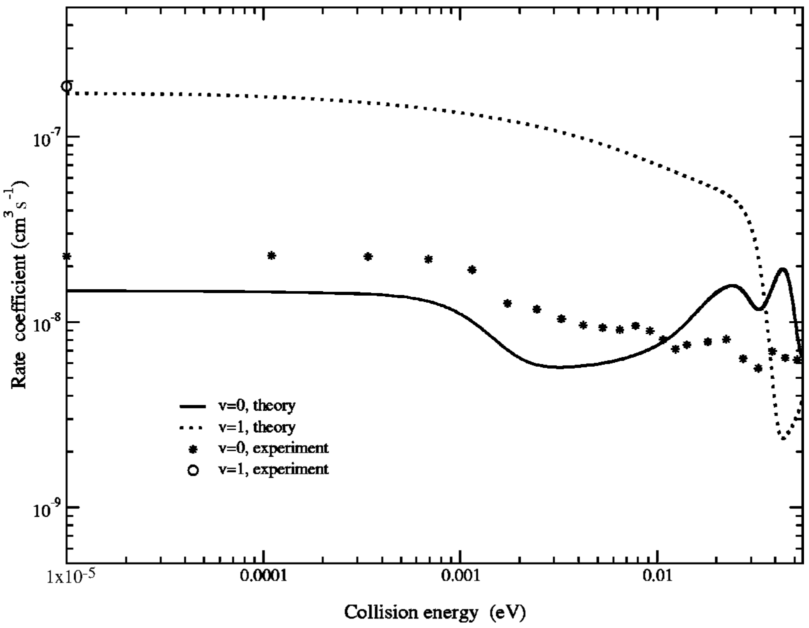

FIG. 1. Dissociative recombination rate coefficients for $H_2{}^+$ in $v=0$ and $v=1$ initial levels, compared with the TSR experimental results.

$$\sigma_{v'v}=\frac{\pi}{2\varepsilon}\,\frac{r}{2}|S_{v'v}|^2 \tag{12}$$

for superelastic collisions $(v'<v)$.

In order to compare our results with experiment, the theoretical cross sections are convoluted with an instrumental function to simulate the experimental conditions. In the case of storage ring experiments, the convoluted rate coefficient α can be obtained by averaging over an anisotropic Maxwellian distribution of electron velocities:

$$\alpha=\langle\mathbf{v}\sigma\rangle=\int\int\int\sigma(\mathbf{v})\mathbf{v}f(\mathbf{v}_d,\mathbf{v})d\mathbf{v}, \tag{13}$$

where $\sigma(\mathbf{v})$ is the calculated cross section as a function of the center-of-mass velocity $\mathbf{v}$ and $\mathbf{v}_d$ is the detuning velocity at the center of the velocity distribution. The function $f(\mathbf{v}_d,\mathbf{v})$ is the product of two Maxwellian functions given in Ref. [20].

$$f(\mathbf{v}_d,\mathbf{v})=\frac{m}{2\pi kT_{e\perp}}\exp\left(-\frac{m\mathbf{v}_\perp^2}{2kT_{e\perp}}\right)\sqrt{\frac{m}{2\pi kT_{e\parallel}}}\times\exp\left(-\frac{m(\mathbf{v}_\parallel-\mathbf{v}_d)^2}{2kT_{e\parallel}}\right), \tag{14}$$

where m is the electron mass, k is the Boltzmann constant, and $\mathbf{v}_\perp(\mathbf{v}_\parallel)$ the electron transverse (longitudinal) velocity. In our calculations, these temperatures are those given by Krohn *et al.* [1] in the TSR storage ring, namely, $kT_{e\perp}=12$ meV and $kT_{e\parallel}=0.1$ meV.

B. Molecular data

The MQDT treatment of DR and SEC processes requires data for potential curves of the ion ground state and the relevant doubly excited states of the neutral molecule, as well as for the R-dependent quantum defects and electronic couplings. We use here the same data as for the study of HD^+ dissociative recombination by Schneider *et al.* [6]. Most of these data were extracted from *ab initio* molecular structure calculations [21–26], completed by R-matrix [9,27–32] and linear algebraic method [31,32] results. More recent calculations by Tennyson [33] and by Sanchez and Martin [34] provide data for many excited states of H_2, but the internuclear range of these calculations is too short to be used in DR calculations.

Besides the first $(2p\sigma_u)^2\ {}^1\Sigma_g^+$ doubly excited dissociative state [9,22–29], the lowest Rydberg states of six different series with excited $2p\pi_u$ ion core (${}^1\Sigma_u^+$ [32], ${}^1\Pi_{g,u}$ [31,32], ${}^3\Sigma_u^+$ [32], ${}^3\Pi_{g,u}$ [32]) are involved in the calculations. Also included are the second Rydberg states of these series [30,32].

These dissociative states should converge *diabatically* at large internuclear separations to unstable excited H^- and H^+ states. However, in our *quasidiabatic* representation, they converge either to $H(n=1)+H(n=2)$ (the lowest states of ${}^1\Sigma_g^+$, ${}^{1,3}\Sigma_u$, ${}^{1,3}\Pi_g$ symmetry), or (the lowest states of ${}^{1,3}\Pi_u$ symmetries and the second Rydberg states of the other symmetries) to the limit $H(n=1)+H(n=3)$ which lies just below the $v=5$ vibrational level of the $H_2{}^+$ ion ground state.

The ${}^1\Sigma_g^+$ states couple with "$d\sigma$" and "$s\sigma$" partial waves of the incident electron. The couplings are much larger for the d partial wave, but the s wave plays an important role in the resonance interference pattern due to the indirect DR process [6]. The other dissociative states were assumed to couple to a single partial wave of the incident electron. All the electronic couplings strongly depend on the nuclear distance R but are considered to be constant with respect to the electron energy. We thus performed a second-order calculation [16] of the K matrix that is exact in this case [18]. All the cross sections and rate coefficients reported below have been calculated for incident electron energies ranging from 10^{-5} eV to 100 meV with a step size of 10^{-5} eV.

TABLE I. Rate coefficients for dissociative recombination of H_2^+ with electrons of near-zero kinetic energy.

v	Theory (this work) 10^{-8} cm^3 s^{-1}	Theory [10] 10^{-8} cm^3 s^{-1}	Experiment [4] 10^{-8} cm^3 s^{-1}
0	1.47	2.31	1.87±0.15
1	17.16	18.1	18.7±11.2
2	5.16	1.34	15.3±9.5
3	9.61	1.98	18.0±11.5
4	9.17	3.26	9.9±6.3
5	37.10		84±57
6	65.65		118±80

III. RESULTS AND DISCUSSION

A. Rate coefficients for dissociative recombination

The DR rate coefficients obtained by convolution over an anisotropic Maxwellian velocity distribution [Eqs. (13) and (14)] are shown in Fig. 1 for the ground and the first excited vibrational levels ($v=0$ and $v=1$) of the H_2^+ ion. Also shown are DR rate coefficients for the same levels, recently measured at the TSR storage ring [2,4]. For $v=1$ (as for higher vibrational levels) no absolute value was measured, but relative rate coefficients were derived using Coulomb explosion imaging measurements at near-zero collision energy. Most of the experimental and theoretical absolute values are in good agreement at very low electron kinetic energy, and for $v=0$ this holds until about 10^{-2} eV. Rydberg resonances appear at a higher energy and the differences observed there might be due to the lack of rotational structure in the calculation.

In Table I we present our calculated and the TSR measured DR rate coefficients for the seven lowest vibrational levels ($v=0$–6) at $\varepsilon=10^{-5}$ eV. Also shown are the rate coefficients calculated by Nakashima *et al.* [10] (convoluted with an isotropic Maxwell-Boltzmann distribution at 100 K electron temperature). All results are then normalized with respect to the rate for the $v=1$ state and the relative rate coefficients obtained from this normalization are compared with the experimental values in Fig. 2. The errors on the experimental absolute values for $v>0$ in Table I (last column) are much larger than for the relative values of Fig. 2. This is due to the large error bar on the measurement of $v=0$ rate relative to $v=1$ (Fig. 2), since the absolute values for $v>0$ are all deduced from that for the $v=0$ initial ion level [2].

In all results presented in Table I, the rate coefficients are much larger for the initial level $v=1$ than for $v=0$. This behavior which is clearly displayed in Fig. 2 is due to a better overlap of the excited vibrational wave function ($v=1$) with the dissociative one. We also notice a sharp increase in our calculated DR rate coefficient and the measured one at $v=5$. This is attributed to the opening of new dissociative states converging to the H ($n=3$) asymptotic limit and is absent from the pioneering results of Nakashima *et al.* [10] where only the lowest ${}^1\Sigma_g^+$ dissociative state was included.

B. Rate coefficients for superelastic collisions

Superelastic collisions and dissociative recombination being competitive processes, their cross sections are obtained in the same calculation and expressed in terms of matrix elements of the same scattering matrix (12). The competition between the two processes shows up in the shape of the resonances due to temporary capture into bound Rydberg states, as shown, for example, in Fig. 3 for the case of $v=1$ initial ion level. These resonances, which appear as deep windows in the DR cross section due to a strong $v=1$ direct process, appear mostly as peaks in the SEC cross section.

We also note that the two processes have the same order of magnitude, which could be an indication that SEC, although being a transition between vibrational states, is mainly driven (like DR), by electronic interactions which

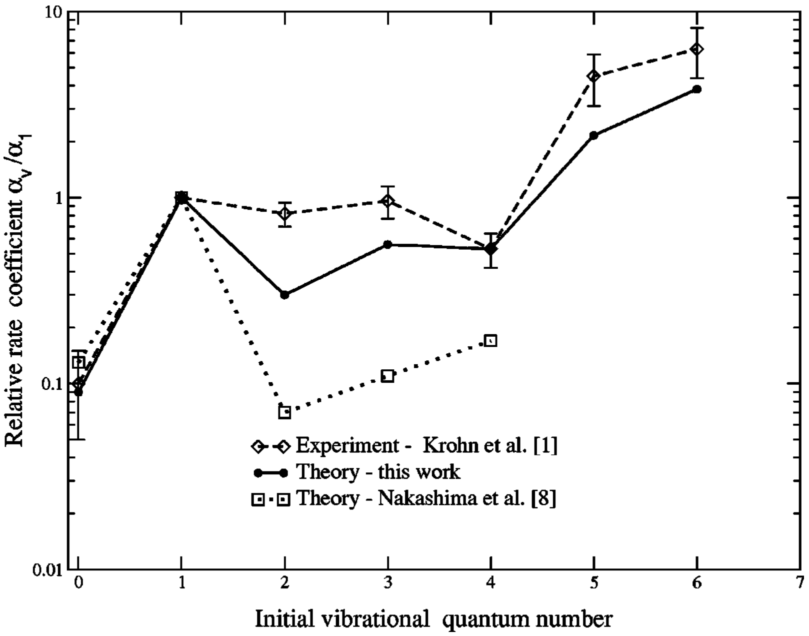

FIG. 2. Relative rate coefficients of dissociative recombination for different vibrational levels (normalized to $v=1$). Experimental values correspond to near-zero kinetic-energy electrons, while our rates are calculated for 10^{-5} eV.

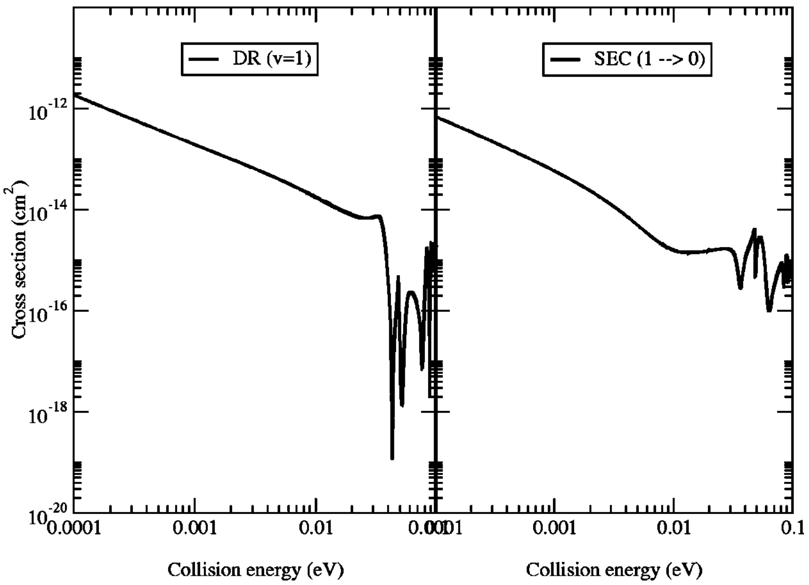

FIG. 3. Cross sections of DR and SEC for H_2^+, $v=1$.

indirectly couple the vibrational states via the doubly excited states. To check this interpretation, we have computed SEC cross sections after artificially removing the radial vibrational couplings, by neglecting the *R* dependence of the quantum defects in the calculation of the channel coupling coefficients [Eqs. (5)–(8)]. The resonance energies and shapes are changed but the order of magnitude of the cross sections remains the same as in the actual calculations with all the interactions taken into account (Fig. 4). Moreover, although generally smaller for $|\Delta v|>1$ transitions, the cross sections do not follow the $|\Delta v|=1$ propensity rule which holds for purely vibrational transitions.

The rate coefficients for superelastic collisions were then obtained, as for DR, by convoluting the SEC cross sections with an anisotropic Maxwellian velocity distribution [Eqs. (13) and (14)]. These rate coefficients, given in the second column of Table II, are in reasonable agreement with former theoretical results (third column) obtained with the *R*-matrix method [8]. Also shown (fourth and fifth columns) are the rate coefficients extracted by Krohn and co-workers [1,4] from the measured time evolution of the vibrational populations. The results presented in the fourth column were obtained using the DR rates of Nakashima *et al.* [10] (third column of Table I) for the kinetics (see the following section), while those of the fifth column are obtained using recent DR rates measured by Krohn [4] (fourth column of Table I). They are both larger than the theoretical values by up to one order of magnitude. For the most recent and reliable experimental values (last column of Table II), the ratio to our calculated rates for $\Delta v=-1$ SEC varies between 2 and 12. To help analyzing this discrepancy, we will simulate the time evolution of vibrational populations for these various sets of rates, since the experimental values were deduced from such simulations.

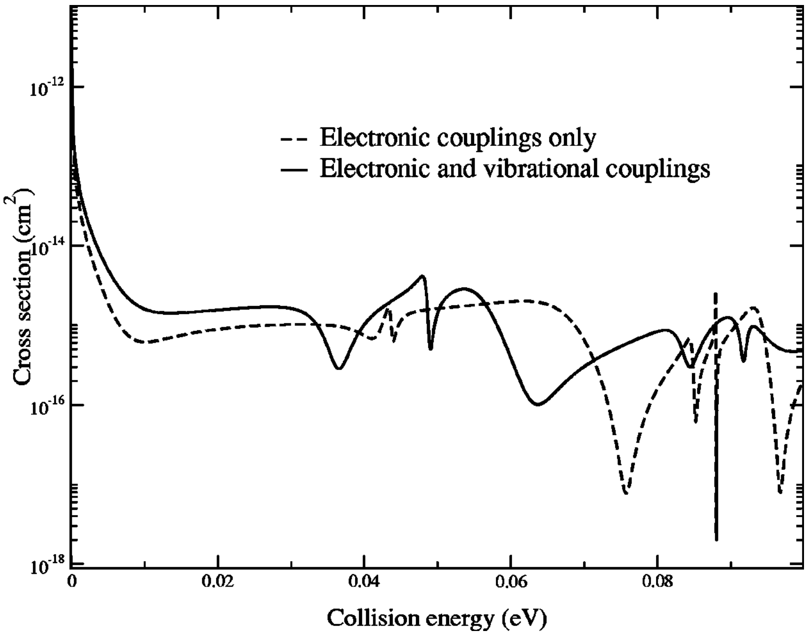

FIG. 4. Superelastic collision cross section for H_2^+, $v=1$ calculated with (full line) and without (dashed line) vibrational coupling.

TABLE II. Rate coefficients for superelastic collisions of H_2^+ with electrons of near-zero kinetic energy.

$v \to v'$	Theory (this work) 10^{-8} cm^3 s^{-1}	Theory [8] 10^{-8} cm^3 s^{-1}	Experiment [1] 10^{-8} cm^3 s^{-1}	Experiment [4]
$1\to 0$	4.47	8.5	60	39 ± 8
$2\to 1$	16.95	20.0	120	76 ± 16
$2\to 0$	3.15			
$3\to 2$	9.61		220	121 ± 26
$3\to 1$	6.73			
$3\to 0$	1.70			
$4\to 3$	27.20		240	146 ± 30
$4\to 2$	2.605			
$4\to 1$	3.78			
$4\to 0$	1.07			
$5\to 4$	103.21		440	210 ± 42
$5\to 3$	16.36			
$5\to 2$	1.85			
$5\to 1$	2.58			
$5\to 0$	0.91			
$6\to 5$	79.91		-	-
$6\to 4$	31.35			
$6\to 3$	6.27			
$6\to 2$	1.12			
$6\to 1$	1.81			

C. Time evolution of vibrational populations

Following the numerical approach of Krohn *et al.* [1], we used our rate coefficients from Tables I and II to simulate the time evolution of the population of the first six vibrational states of H_2^+ in collision with slow electrons. There was no restriction to a particular type of vibrational transition in our computation, except for the absence of vibrational excitation since the collision energies considered are always less than one vibrational quantum ($\hbar\omega \simeq 0.27$ eV in H_2^+). The populations of the six vibrational states are solutions of a system of coupled differential equations:

$$\frac{dN_v(t)}{dt} = -\left(\alpha_{DR}^{v} + \sum_{v'<v} \alpha_{SEC}^{v\to v'}\right) n_e \eta N_v(t) + \sum_{v'>v} \alpha_{SEC}^{v'\to v} n_e \eta N_{v'}(t), \qquad (15)$$

where $n_e = 6.1\times 10^{6}$ cm^{-3} denotes the electron density (which is constant during the measurements, owing to the injection conditions), $\eta = 0.027$ the ratio between the electron cooler length and the ring circumference, α_{DR}^{v} is the absolute dissociative recombination rate coefficient for initial vibrational level v, and $\alpha_{SEC}^{v\to v'}$ is the superelastic collision rate coefficient from v to v' $(v'<v)$. $N_v(t)$ is the number of molecules in the vibrational state v at time *t*, with initial value $N_v(0)$ taken from experiment [1]. The numerical solutions of this differential system are then normalized to the total number of molecules in all the vibrational states, to yield the evolution of the relative populations $P_v(t)$ of the vibrational states:

$$P_v(t) = \frac{N_v(t)}{\sum_{v'} N_{v'}(t)}. \qquad (16)$$

Figure 5 shows the time evolution for three different simulations, together with the experimental measurements (dots). The full lines are obtained using our theoretical rate coefficients (second columns of Tables I and II) and the dashed lines are obtained, as in Ref. [1], using the larger SEC rate coefficients fitted by Krohn *et al.*, and the smaller (for $v \geqslant 2$) DR rate coefficients of Nakashima *et al.* [10]. Clearly, our calculated rates for various processes lead to a much slower time evolution of the relative populations than measured in the TSR storage ring, especially for the decay of the $v=3$ and $v=4$ vibrational levels.

In order to check the effect of vibrational transitions with $|\Delta v| > 1$, for which we obtain substantial rates (see, e.g., $3\to 1$, $4\to 2$, $5\to 3$, $6\to 4$ in Table II), we have calculated the time evolution obtained with our rate coefficients for DR and for $\Delta v = -1$ transitions, but setting to zero all the rates for $|\Delta v| > 1$ superelastic collisions. The results, shown by the dotted lines in Fig. 5, are farther away from the experimental evolution than the full lines, but the effect is small. The relaxation of H_2^+ ions is thus dominated by the $\Delta v = -1$

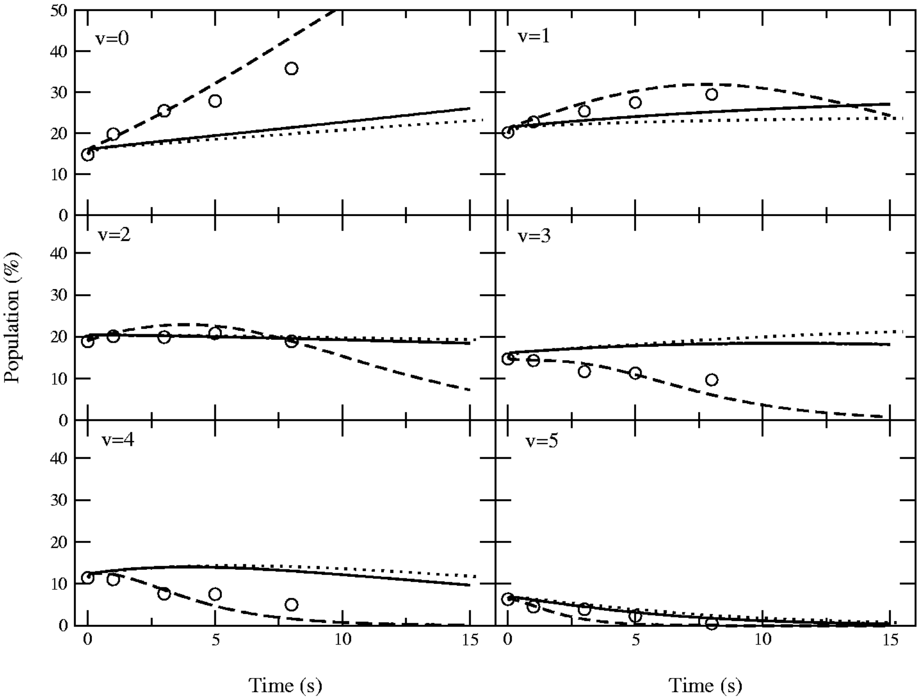

FIG. 5. Measured (circles) and fitted (dashed line) [1] time evolution of the vibrational populations in H_2^+ using the $\Delta v = -1$ model compared with the present calculations including $|\Delta v| > 1$ SEC (full line) and neglecting them (dotted line).

vibrational transitions, for which the calculated rates are too small to reproduce the fast decay observed in the storage rings.

The effect of dissociative recombination on the time evolution of vibrational populations has been assessed in two ways. First, comparing the fourth and fifth columns of Table II, which differ only by the values used for DR rates in the fit of the SEC rates, shows that the faster DR used for the $v \geqslant 2$ levels in the last column (experimental values of Table I, rather than those of Nakashima *et al.* [10]) allows to fit the time evolution with rates for $\Delta v = -1$ transitions lower by about a factor of 2, by accelerating the decay of $v \geqslant 2$ levels. For our own calculations, which used DR rates much closer to the experimental ones (see the second column of Table I), we have also performed a test calculation using exactly the experimental values for DR rates (fourth column of Table I). The effect on the population decay was very small (less than 10%) and unable to reconcile our time evolution with the measurements.

The present theoretical values for superelastic collision rates, although close (within a factor of 2) to previous theoretical calculations [8] when comparison is possible, and of the same order as DR rates ($\sim 10^{-7}$ cm^3 s^{-1}), are too small to reproduce the fast relaxation of H_2^+ vibrational populations observed in storage rings [1,12]. On the theoretical side, possible reasons for this discrepancy are the following.

(i) Inaccuracies of the molecular data for the high dissociative states, the Rydberg states with excited $2p\pi_u$ ion core: Indeed, the largest discrepancy between theoretical and experimental time evolutions in Fig. 5 (besides the $v=0$ ion level, which accumulates all the discrepancies of the other rates) are noted for $v=3$ and $v=4$ levels, for which the contribution of these high dissociative states is important. Cross sections and rates are very sensitive to small displacements of the dissociative curves (through nuclear wave function overlaps) as well as to the size of electronic interactions or to contribution of higher electronic partial waves, not yet included. This is even more true for superelastic collisions than for dissociative recombination. Indeed, in a first-order calculation with open channels only (“direct” processes), the DR cross section is roughly proportional to the square of the Rydberg-valence interaction integrated over the nuclear motion [13], while the SEC cross sections vary as the product of two such quantities, i.e., roughly as the fourth power of the Rydberg-valence interaction [10]. Although the indirect process involves a complex channel mixing with a less predictable dependence on molecular data, the SEC cross sections might change significantly with new data without a large effect on DR cross sections.

(ii) Higher orders of the *K* matrix: In the present calculations, the Rydberg-valence electronic couplings have been assumed to be energy independent, which is valid in the small energy range studied ($\varepsilon < 0.1$ eV). If some couplings vary substantially at larger energy, our second-order treatment of the short-range reaction matrix [Eq. (3)] would not be converged [18], and higher-order terms should be included even for low-energy calculations. We have checked however that the largest cross sections (namely, that for $\Delta v = -1$ transitions), are the less sensitive to such high-order effects, and thus the time evolution should not change notably.

(iii) Rotational effects: Including the rotational structure and couplings is certainly the next step in these calculations. Although rotational interactions are small, it has been shown [7] that for the lightest H_2 molecule they can affect substantially the DR cross sections, at least in the resonance region [5,6]. It might hold also for vibrational transitions, even though they are mainly driven by indirect electronic interactions.

IV. CONCLUSION

We have computed rate coefficients for dissociative recombination and competitive vibrational deexcitation for the $H_2{}^+$ molecular ion with slow electrons. The dissociative recombination rate coefficients obtained are in good agreement with the measurements at the TSR storage ring, in particular, the relative values of the rates for successive initial vibrational states.

The superelastic collision process is shown to be driven by indirect electronic interactions between vibrational states, via the doubly excited states. The rate coefficients obtained here are close to previous theoretical results of Sarpal and Tennyson [8], and are of the same order as the DR rate coefficients (and often larger). But they are smaller by up to one order of magnitude than the values extracted from a fit of the time evolution of the vibrational populations of $H_2{}^+$ measured at the TSR storage ring, within a model restricted to the $\Delta v = -1$ transitions. The present theoretical values do not allow to reproduce the fast time evolution of vibrational populations measured at the TSR storage ring, even when the transitions with $|\Delta v| > 1$ are taken into account and the DR rate coefficients obtained in the same set of calculations or in the experiment are used.

We plan to study the effect of all interactions not included in the present calculations, especially rotational couplings, which could lead to faster ion decay by electronic collisions. Improved molecular data—energy of the dissociative states and interaction strength with the ionization continuum—may also affect the rates for superelastic collisions with vibrationally excited ions. It is unfortunate that no direct comparison with experimental absolute values for these rates is possible.

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