Quantum state preparation of homonuclear molecular ions enabled via a cold buffer gas: An *ab initio* study for the H_2^+ and the D_2^+ case

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Precision vibrational spectroscopy of the molecular hydrogen ions is of significant interest for determining fundamental constants, for searching for new forces, and for testing quantum electrodynamics calculations. Future experiments can profit from the ability of preparing molecular hydrogen ions at ultralow kinetic energy and in preselected internal states, with respect to vibration, rotation, and spin degrees of freedom. For the homonuclear ions (H_2^+, D_2^+), direct laser cooling of the rotational degree of freedom is not feasible. We show by quantum calculations that rotational cooling by cold He buffer gas is an effective approach. For this purpose we have computed the energy-dependent cross sections for rotationally elastic and inelastic collisions, $h_2^+(v = 0, N) + \mathrm{He} \rightarrow h_2^+(v = 0, N') + \mathrm{He}$ (where h = H, D), using *ab initio* coupled-channel calculations. We find that rotational cooling to the lowest rotational state is possible within tens of seconds under experimentally realistic conditions. We furthermore describe possible protocols for the preparation of a single quantum state, where also the spin state is well defined.

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I. INTRODUCTION

One of the outstanding challenges in the fields of few-body quantum physics and metrology is the achievement of ultrahigh-precision laser vibrational spectroscopy of the molecular hydrogen ion (MHI) H_2^+, a member of the family of one-electron molecules. These *ab initio* calculable systems at the intersection of atomic and molecular physics have enormous potential for ultraprecise spectroscopy at the 10^{-17} fractional inaccuracy level [1,2]. So far, experiments have reached the 10^{-9} level [3–5]. If a number of appropriately chosen rovibrational transitions of at least two of the three ions H_2^+, HD^+, D_2^+ are determined, it is possible to test the accuracy of the *ab initio* calculations and to determine the values of the constants m_e/m_p, m_p/m_d, charge radii of proton and deuteron, and the Rydberg energy [6]. Such determinations would be complementary to those performed on other systems and thus would provide an important consistency check, and could possibly lead to higher accuracy of the constants, and improved tests of their time independence.

The spectroscopy of H_2^+ and D_2^+ has been performed in several studies [7–12]. However, the techniques used so far do not promise to achieve fractional inaccuracies even at the level of present-day *ab initio* theoretical inaccuracies [13]. The challenge faced by methods of ultraprecise spectroscopy is the lack of accessible bound excited states in MHIs and that the homonuclear H_2^+ and D_2^+ lack electric-dipole-allowed rovibrational transitions. Therefore, a new suite of properly adapted manipulation techniques must be developed.

The charged nature of MHI enables their robust confinement in an ion trap and sympathetic laser cooling of their kinetic energy [14]. The preparation of MHIs in a single quantum state, the most suitable initial condition for ultrahigh-precision spectroscopy, is one of the necessary steps. For the heteronuclear HD^+ molecule rotational laser cooling [15] and optical pumping [4], both on rovibrational transitions, can be used for this purpose. This is not possible for the homonuclear H_2^+ and D_2^+, because of absence of spontaneous decay from rovibrational levels in the ground electronic state.

Suitable initial levels for future rovibrational precision spectroscopy [1,16] are, in particular, the two lowest-energy rovibrational states of H_2^+ [$(v = 0, N = 0)$ and $(v = 0, N = 1)$], see Fig. 1. Here v denotes the vibrational quantum number and N is the rotational angular momentum quantum number. It has been proposed [17] to use state-selective photoionization of the neutral H_2 [18], resulting in production of H_2^+ predominantly in $v = 0$, $N = 0$, 1, or 2, depending on the chosen laser excitation wavelength. This approach requires the use of a pulsed UV laser and appropriate experimental conditions (high density of neutral molecules).

In this paper we analyze an alternative approach to quantum state preparation, which is applicable to MHIs produced by standard electron-impact ionization. Here the ions are initially generated in a large number of rovibrational levels [17]. We propose to apply buffer gas cooling with cryogenic helium gas in order to relax the initial variety of internal states to the lowest-energy one. However, in homonuclear molecular ions having nuclear spin, the preparation in a *single* rotational state by cold buffer gas collisions is not possible in a straightforward way. We also propose approaches to resolve this limitation.

This paper is structured as follows: in Sec. II we recall key work done on cold He buffer gas cooling and give an overview

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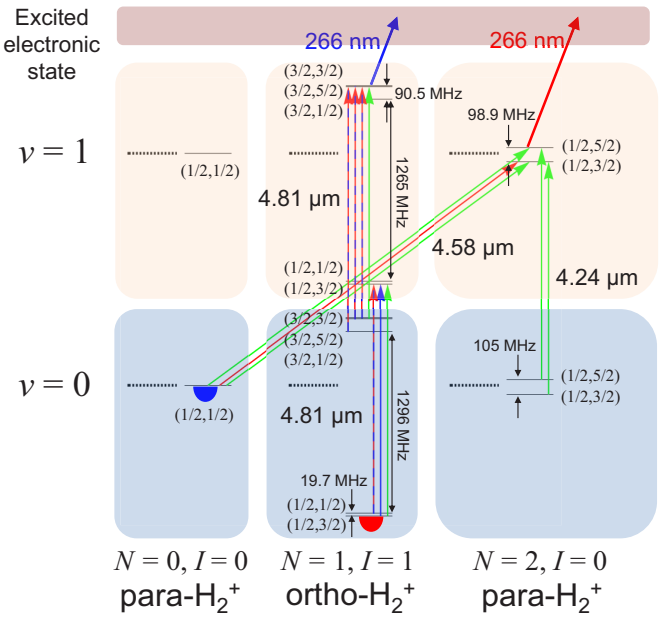

FIG. 1. The lowest rovibrational levels of H_2^+ and their hyperfine structure, together with laser-induced electric quadrupole transitions considered for quantum state preparation and spectroscopy, after cooling by a buffer gas has occurred. Only the spin structure (spin-rotation and spin-spin) splittings [19] are to scale. Red arrows and blue-red dashed arrows: Transitions to be driven for preparation of a single ortho-H_2^+ quantum state (red semicircle); blue arrows and blue-red dashed arrows: transitions to be driven for preparation of a single para-H_2^+ quantum state (blue semicircle). Green arrows: Selected transitions with particularly small systematic effects, suitable for frequency metrology. Numbers in parentheses denote (F, J) (see text). Dashed lines: Level positions in absence of spin structure.

of the interactions that occur between MHIs and a He gas. In Sec. III we describe the method and results of our scattering calculations. In Sec. IV we apply the results for predicting the efficiency of rotational cooling. Section V is dedicated to a discussion of the feasibility of quantum state preparation. Section VI summarizes the findings.

II. GENERAL CONSIDERATIONS

In the field of molecular ion spectroscopy, cold He buffer gas cooling in conjunction with ion trapping has been used successfully by several groups for many years [20–22], following initial studies with cold argon gas [23]. The rotational and vibrational cooling of molecules leads to a significantly reduced complexity of laser-induced rovibrational and electronic spectra, especially for polyatomic ions, enabling a deeper understanding of their structure and dynamical processes. The method was also applied to anions, OH^- [24] being a recent example.

Buffer gas cooling of H_2^+, however, has received only little experimental attention [25], and has not been used so far in connection with laser spectroscopy. A sophisticated variant of buffer gas cooling of molecular ions has been recently demonstrated, where the molecular ions are simultaneously translationally cooled by laser-cooled atomic ions (sympathetic cooling). MgH^+ ions, sympathetically cooled by laser-cooled Ca^+ ions, were additionally rotationally cooled by He gas at 4 K, in a cryogenic trap. A rotational temperature of 7.5 K was reached in approximately 1 s of buffer gas interaction time [26], at a He gas density of 10^{10} cm^{-3}.

In analogy to this work, we shall consider here trapping MHIs in an ion trap of the linear quadrupole type, where the molecular ions are sympathetically cooled by co-trapped laser-cooled beryllium ions [14]. In contrast to the system of Ref. [26], in this case some of the trapped ions are *lighter* than or of equal mass as the buffer gas molecules (H_2^+, D_2^+ vs He). No experimental results on the effect of the buffer gas on the translational degrees of freedom of such trapped ions are known to us. Simulations of the interaction of trapped ions with buffer gas have been performed, albeit without including sympathetic cooling via ion-ion interactions [27–30]. These simulations do indicate that collisions with a buffer gas, in the presence of trap micromotion, can lead to ion translational heating, with steady-state ion temperature even above the gas temperature. The effect is reduced if the buffer gas has the same mass as the ion (e.g., D_2^+ and ^{4}He) or a smaller mass. The use of the light helium isotope ^{3}He instead of ^{4}He would lead to reduced heating for D_2^+ and H_2^+, but would be a costly approach. However, based also on our own experimental study of collisional translational heating [31], and modeling of sympathetic cooling rates [32], we believe that the continuous sympathetic cooling of the MHIs by the laser-cooled atomic ions will, due to its strength, counteract any translational heating that the buffer gas may exert on the lighter trapped ions, at the low buffer gas densities, and hence low He atom-ion collision rates considered here.

In connection with rotational cooling, the issues of vibrational cooling and of competing reactions have to be considered first.

A. Vibrational cooling

At 300 K thermal equilibrium, H_2^+ is completely in the vibrational ground state $v = 0$. However, upon electron impact ionization, H_2^+ is produced in a range of vibrational levels v. Levels $v \leqslant 7$ occur with relative probabilities >3%, with approximately 40% of all ions being in $v < 3$ [33,34]. No data or calculations on the rotational level distributions upon ionization are known to us. Theard and Huntress [25] observed that vibrational deactivation is possible by collisions with He at thermal energies. They found the reaction rates between 0.1 and 0.5×10^{-9} cm^3/s, depending on v. At a He density $n_{\mathrm{He}} \simeq 7 \times 10^8$ cm^{-3} this leads to vibrational cooling times on the order of 10 s, an experimentally convenient time scale.

B. Competing reactions

A first competing reaction is $H_2^+ + H_2 \rightarrow H_3^+ + H$. It occurs initially, during the ion generation step. The rate for this reaction is close to the Langevin rate $\simeq 4.6 \times 10^{-10}$ cm^3/s [28,35]. The reaction will lead to a loss of H_2^+ ions and to an accumulation of H_3^+ ions in the ion trap [32]. The loss can be compensated by starting with a sufficiently large number of neutral H_2 molecules and by keeping their density small during ion generation, of order $n_{H_2} \simeq 10^8$ cm^{-3}. In addition, in a cryogenic environment (necessary for cold He buffer gas cooling), the H_2 gas is quickly removed by the pumping action

of the cryogenic surfaces of the apparatus, thereby bringing the reactions to a halt. The H_3^+ ions accumulated in the trap can be ejected from it by an appropriate secular motion excitation technique.

A second competing reaction is the exothermic recombination channel $H_2^+ + He \rightarrow HeH_2^+$, forming a triatomic complex which supports several bound states. This reaction releases up to 0.35 eV. This could be a more serious issue, since it directly competes with the rotational cooling collisions. The reaction can occur via two different processes: (i) radiative association (where a photon is emitted). This has been found to have a negligible rate [36]. (ii) Ternary (nonradiative) association, where an additional collision partner satisfies overall momentum and energy conservation. The corresponding reaction rate is then proportional to $(n_{He})^2$. If the He gas density is kept sufficiently small, the rate of this reaction can also be kept small compared with the nonreactive (rotational/vibrational cooling) rates of interest here. Such ternary association reactions have recently been used to perform action spectroscopy of a rotational transition of CD^+ [37] [ternary reaction rate of order 10^{-30} cm^6 s$^{-1}(n_{He})^2$]. The applicability of this technique to H_2^+ and D_2^+ is an interesting question deserving a separate study.

Finally, the reaction $H_2^+(v) + He \rightarrow HeH^+ + H$ can occur. However, it is an endothermic reaction if $v = 0, 1, 2$, e.g., by 0.77 eV if $v = 0$. Thus, at the low collision energies of interest here, this reaction does not affect H_2^+ in the ground vibrational level $v = 0$. The reaction is exothermic for vibrationally excited $H_2^+(v \geqslant 3$, where $v = 3$ requires additional rotational and/or translational energy) [25,38,39], with reaction rates (averaged over rotational states) in the range 0.09 to 0.34×10^{-9} cm^3/s [25]. This implies that the vibrationally ($v \geqslant 3$) excited MHIs produced during electron impact ionization will be destroyed if this is performed in the presence of He gas. This is acceptable and even desirable for the present purpose. The product HeH^+ ions can subsequently be expelled from the ion trap. We point out that this reaction might also be of interest as a means of detecting a laser-induced vibrational excitation from the vibrational ground state (action spectroscopy). The excitation could, e.g., be a second (or higher) overtone electric quadrupole transition. The very small normalized excitation rate for such transitions rate would likely require a high-power laser source in order to achieve effective excitation.

Summarizing, if rotationally and vibrationally excited H_2^+ molecules interact with He gas, vibrational deactivation and molecule loss occur, with similar time constants. However, in a cryogenic environment, the loss of H_2^+ in the vibrational *ground* state is suppressed. This is expected to allow capturing and storing a sufficient number of $H_2^+(v = 0)$ molecules in the trap. Therefore, the important questions are whether this vibrational deactivation can be followed by rotational deactivation *within* the vibrational ground state and what the characteristic cooling times are.

III. SCATTERING CALCULATIONS

The simplicity of MHIs notwithstanding, the particular problem of scattering theory $He + MHI(v, N) \rightarrow He + MHI(v', N')$ has, to the best of our knowledge, not been treated before exactly. Scattering of He by other diatomic ions has been discussed before, e.g., Li_2^+ [40] and MgH^+ [41,42]. The quantum analysis for MHIs is complicated by the presence of nonzero electron spin, but the solution has been obtained using the time-independent coupled-channel approach, including dynamical recoupling of angular momenta [43–45].

A. Symmetry considerations

H_2^+ molecules contain protons, which are fermions with nuclear spin $I_p = 1$. The molecules can have total nuclear spin $I = 0$ (denoted by para-H_2^+) or $I = 1$ (ortho-H_2^+). (The same distinction is well known for neutral H_2.) The para molecules have a spin wave function antisymmetric under proton exchange and therefore can only exist in rotational levels with even N (for which the rotational wave function is symmetric); ortho-H_2^+ molecules require odd N values.

The deuteron, a boson, has nuclear spin $I_d = 1$, hence the total nuclear spin of D_2^+ can have the values $I = 0, 1, 2$. The total spin values $I = 0, 2$ are associated with spin wave functions that are symmetric under exchange of the two identical nuclei. Hence, this case is called ortho-D_2^+. Because the deuterons are bosons, the total molecular wave function must be *symmetric* under nucleus exchange and this requires that the rotational state be of *even* N. (Note that for H_2^+, the $N = 0$ level instead occurs for para-H_2^+, because protons are fermions.) D_2^+ with $I = 1$ is denoted by para-D_2^+ (antisymmetic spin wave function) and is associated with odd-N rotational states (antisymmetric rotational wave function). (The same distinction holds for neutral D_2.)

In collisions with nonmagnetic particles such as He, the total nuclear spin I is conserved and para and ortho molecules do not interconvert. Therefore, in collisions, only rotational quantum number changes $\Delta N = N - N' = 0, \pm 2, \pm 4, \ldots$ are allowed.

B. Methods

The *ab initio* calculation requires as input the *ab initio* potential energy surface (PES) for the $He + MHI(v, N)$ system. Recent high-level *ab initio* calculations, using a state-of-the-art multireference configuration interaction approach that included all single and double excitations, computed the PES [39]. Specifically, for the interaction potential of the He-h-h$^+$complex (where h denotes H or D) we used the $M = 8$ fitting choice using FCI/cc-pVQZ level for the basis set expansion [39]. From the potential in chemical coordinates $V_{M8}(R_1, R_2, R_3)$, we generated the subreactive potential of the initial collision state $He + h_2^+(v, N)$ in Jacobi coordinates $V_{M8}(r|R, \theta)$. R is the distance of the He atom from the center of mass of the MHI, θ is the angle between He atom position vector and the MHI axis, and r is the distance between the H or D atoms. Here we limit ourselves to MHIs in the ground vibrational level $v = 0$. The detailed features of the potential are analyzed elsewhere [46]. Multipolar coefficients up to $\lambda = 20$ were included. They were obtained from the full three-dimensional PES by averaging over the ground-state vibrational wavefunction of the molecule.

1. *The* H_2^+ *case*

We solved the coupled-channel equations using a quantum scattering computer code developed by one of the present authors [47] and computed the elastic $(0, N) \rightarrow (0, N' = N)$ and state-changing $(0, N) \rightarrow (0, N' \neq N)$ cross sections as a function of collision energy up to 4000 cm^{-1}. The number of rotational states (N values) included in the asymptotic expansion of target states was checked for convergence by having all the open channels included plus at least two closed channels above each energy threshold as part of the full expansion of the coupled-channel wave function. The partial integral cross sections, depending on the total angular momentum of the system, have been carefully checked for convergence against the basis set size and propagator parameters and found to be well within 1%. In particular, we have propagated the solution from $R = 0.1$ nm to $R = 5$ nm with 500 steps of the Variable-Phase propagator [47]. The convergence of the sums on the partial cross sections to obtain the corresponding state-to-state integral cross sections was also controlled by extending the J values up to at least $J_{max} = 80$. The reliability index for our computed cross sections is around 1%–2%.

For para-H_2^+ we performed exact scattering calculations, including the electron-spin-rotation coupling $\mathbf{s_e} \cdot \mathbf{N}$. We repeated them by treating the molecule as a pseudo-$^1\Sigma$ system (i.e., ignoring electron spin and therefore ignoring the spin-rotation coupling). We compared the cross sections for both cases (summed over the spin states in the exact treatment) and found that they agree within 20%, mostly within 10% [46]. Thus, the spin dependence of the cross sections can be neglected for the present purpose.

For the more complicated case of ortho-H_2^+ (where electron-spin–nuclear-spin coupling is present in addition), we have also performed exact calculations. We found an even better agreement between the summed exact and the spinless cross sections. Therefore, in the following we use the latter. Details will be reported elsewhere [46].

2. *The* D_2^+ *case*

The PES does not depend on the mass of the hydrogen isotope, therefore the calculations for D_2^+ are performed using the same PES as for H_2^+. We have not taken into account the spins, since the H_2^+ case indicates that their effect is small.

C. Rate coefficients of inelastic collisions

Rate coefficients $k(T)$ are computed, for a given collisional temperature T, from the cross sections by an integration over the collision energy, with a temperature-dependent kernel. The collisional temperature is related to, but not identical to, the temperature of the He buffer gas. In the absence of micromotion of the ions, consideration of the center-of-mass motion of the collision partners leads to

$$T = \frac{m_{He} T_{ion} + m_{ion} T_{He}}{m_{He} + m_{ion}}. \quad (1)$$

Figure 2 shows a subset of the H_2^+ inelastic scattering coefficients for the rotational levels relevant to this study (for additional coefficients, see: [48]). Rotational excitation processes $N \rightarrow N' > N$ are seen to be energetically suppressed at low temperature, since the kinetic collision energy is insufficient for providing the difference in rotational energy between final and initial level, amounting to 42 K $\times$ $[N'(N'+1) - N(N+1)]$. The deexcitation rates for $N \rightarrow N - 2$ are larger than the rates for $N \rightarrow N - 4$ [46]. For excitation, the difference is a factor 10 or more.

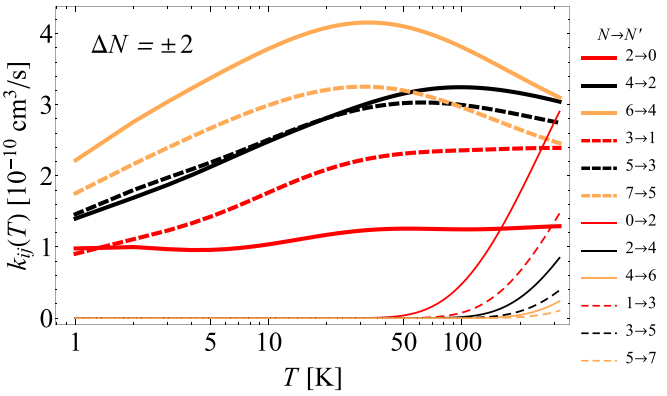

FIG. 2. Rate coefficients $k_{i,j}(T)$ for rotational deexcitation $N \rightarrow N - 2$ and rotational excitation $N \rightarrow N + 2$. Full lines: para-H_2^+, dashed lines: ortho-H_2^+. $\Delta N = N - N'$.

Figure 3 shows some rate coefficients for D_2^+.

D. Rate coefficients of elastic collisions

For H_2^+ we show in Fig. 4 the rates for elastic collisions $N \rightarrow N' = N$. At, e.g., $T = 10$ K, the elastic rates for $N = 0 \rightarrow 0$ and $N = 1 \rightarrow 1$ are approximately 10 and 6 times larger than the deexcitation rates $N = 2 \rightarrow 0$ and $N = 3 \rightarrow 1$. For D_2^+ the elastic rates are presented in Fig. 5.

IV. COOLING DYNAMICS

A. Method

The rate coefficients allow computing the cooling dynamics using simple rate equations. They read $d\mathbf{p}(t)/dt = n_{He}\, \mathbf{K}(T) \cdot \mathbf{p}(t)$, with the fractional rotational populations

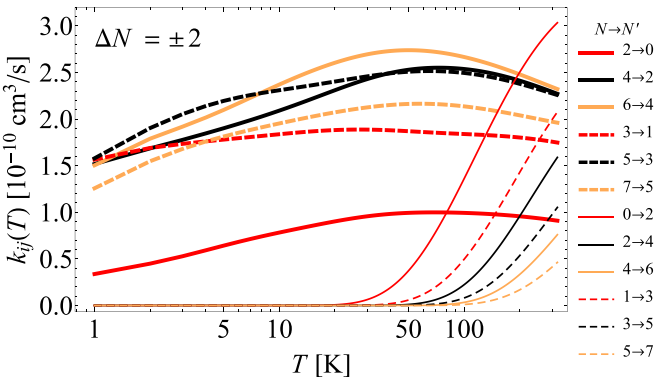

FIG. 3. D_2^+ rate coefficients $k_{i,j}(T)$ for rotational deexcitation $N \rightarrow N - 2$ and rotational excitation $N \rightarrow N + 2$. Full lines: ortho-D_2^+, dashed lines: para-D_2^+. $\Delta N = N - N'$.

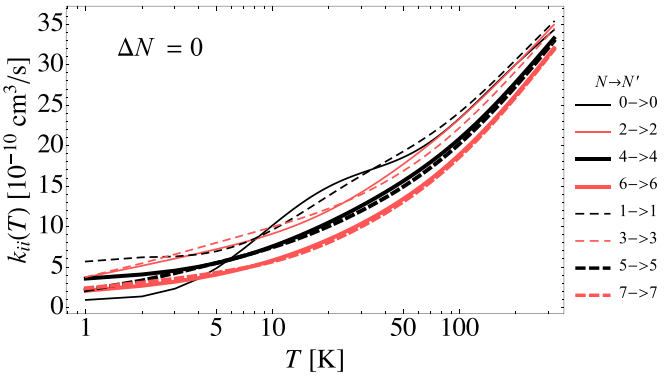

FIG. 4. H_2^+ rate coefficients for rotationally elastic collisions $N \to N$, as a function of collisional temperature. Full lines: para-H_2^+, dashed lines: ortho-H_2^+. $\Delta N = N - N'$.

$\mathbf{p}(t) = (p_1(t), p_2(t), \ldots, p_{n-1}(t), 1 - \sum_{i=1}^{n-1} p_i(t))$, and

$$\mathbf{K} = \begin{pmatrix} -\sum_{i=2}^{n} k_{1,i} & k_{2,1} & \cdots & k_{n,1} \\ k_{1,2} & -\sum_{i=1,\neq 2}^{n} k_{2,i} & & \vdots \\ \vdots & & & \\ k_{1,n} & \cdots & & -\sum_{i=1}^{n-1} k_{n,i} \end{pmatrix},$$

where i is an index corresponding to a particular rotational level N, and $k_{i,j} = k_{i,j}(T)$ are the inelastic rate coefficients from level i to level j. The cases of ortho- and para-H_2^+ are treated separately, since interconversion is absent over the considered time scales.

The initial conditions $p_i(t = 0)$ and the gas temperature T_{He} must be chosen according to experimental considerations. He gas temperature as low as 4 K can be reached by standard techniques in cryogenic ion traps. MHIs sympathetically cooled by laser-cooled beryllium ions exhibit residual kinetic energy which is mostly micromotion energy. Its magnitude can be of order $k_B \times (1\,\mathrm{K})$, if a large number of MHI is simultaneously trapped. If a single molecular ion is trapped and advanced laser cooling techniques are applied, the energy can be much less. The micromotion is not of thermal character. However, according to Eq. (1) we can neglect its effect if we assume a comparatively large collisional temperature,

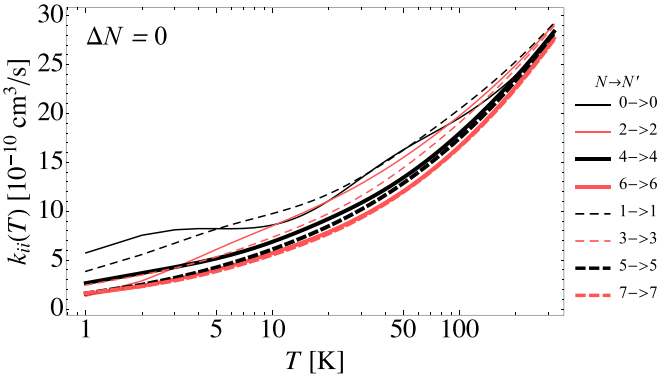

FIG. 5. D_2^+ rate coefficients for rotationally elastic collisions $N \to N$, as a function of collisional temperature. Full lines: ortho-D_2^+, dashed lines: para-D_2^+.

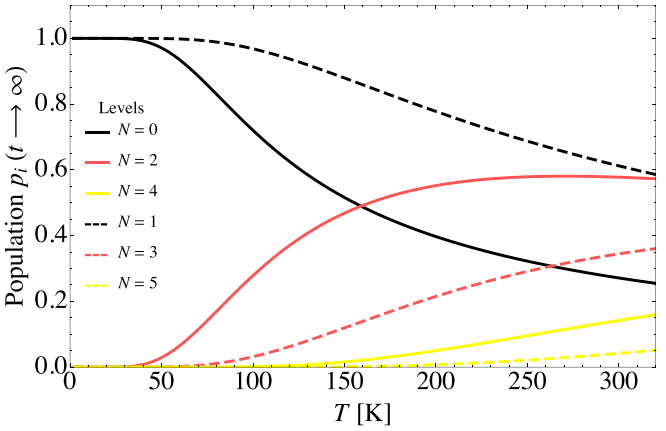

FIG. 6. Steady-state solution of the rate equations for rotational cooling of H_2^+, as a function of collisional temperature. Ortho and para subensembles are treated independently.

$T \geqslant 10$ K. The He gas temperature is $T_{\mathrm{He}} = 3$ T for H_2^+ (2 T for D_2^+), if the ion temperature can be neglected. In the calculations, T is kept constant in time since we assume that the He gas acts as a thermostat.

As mentioned above, H_2^+ ions produced by electron impact ionization occur in a large range of rotational and vibrational states. Ortho- and para-H_2^+ will both be present. Collisions with He (even at $T_{\mathrm{He}} = 300$ K) will relax the vibrationally excited levels to the vibrational ground state $v = 0$ and also reduce the rotational temperature. For the purpose of showing the feasibility of buffer gas cooling we nevertheless assume a high initial rotational temperature $T_{\mathrm{rot}} = 1000$ K and set the values $p_i(t = 0)$ according to the corresponding Boltzmann distribution. It is sufficient to consider $n = 6$ levels for both para-H_2^+ and ortho-H_2^+. We include processes with $|\Delta N| \leqslant 10$. For D_2^+, for simplicity, we restrict the number of initially populated rotational levels to the same as for the H_2^+ simulations. Therefore, in this case the calculations were done with the initial condition $T_{\mathrm{rot}} = 500$ K.

B. Results

1. Steady-state solution

The steady-state solution $p_i(t \to \infty)$ of the rate equations is found upon setting $d\mathbf{p}(t)/dt = 0$ and solving the resulting algebraic equations. Figure 6 shows the result for H_2^+ and for different values of T. We verified that these steady-state population fractions for each nuclear spin subsystem indeed correspond to a Boltzmann distribution with $T_{\mathrm{rot}} = T$. We find that the steady-state population fraction in the lowest rotational state for para-H_2^+ exceeds 95% if $T < 50$ K while for ortho-H_2^+ this occurs if $T < 100$ K. The result is independent of the helium density n_{He}, since $d\mathbf{p}/dt$ is proportional to it. From an experimental point of view, such collisional temperatures (and consequently, He gas temperatures) represent a modest requirement which can be easily met. This is owed to the large rotational constant of H_2^+, 29.1 cm^{-1} (41.9 K).

The result for D_2^+ is shown in Fig. 7. Note that the collisional temperature required for cooling 95% of the ortho-D_2^+ ions into $N = 0$ is 30 K, and 50 K for the para-D_2^+ ions into $N = 1$. These lower values compared to H_2^+ (but

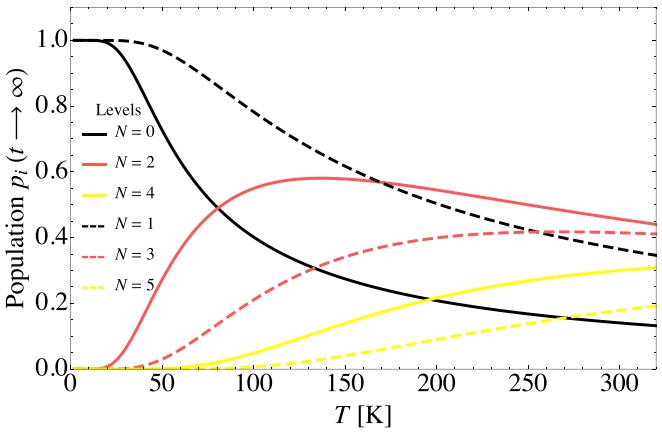

FIG. 7. Steady-state solution of the rate equations for rotational cooling of D_2^+, as a function of collisional temperature. Ortho and para subensembles are treated independently.

still easily reachable experimentally) are due to the two times smaller rotational constant of D_2^+.

2. Time dependence

Figure 8(a) shows an example of the time dependence of the cooling, for one particular value T and density n_{He}. Figure 8(b) shows the overall time evolution of the rotational energy content. We may define a characteristic time constant τ by $\langle E_{\mathrm{rot}}\rangle(\tau) - \langle E_{\mathrm{rot}}\rangle(t=\infty) = (\langle E_{\mathrm{rot}}\rangle(t=0) - \langle E_{\mathrm{rot}}\rangle(t=\infty))/e$, where $\langle E_{\mathrm{rot}}\rangle$ is the level-averaged rotational energy. Because $d\mathbf{p}/dt$ is proportional to n_{He}, at fixed temperature τ is inversely proportional to n_{He}. The product $\tau \times n_{\mathrm{He}}$ changes moderately with decreasing collisional temperature from 3×10^9 to 5×10^9 s/cm^3, see Fig. 8(c). We note that τ also depends weakly on the assumed initial rotational temperature, because the time evolution of $\langle E_{\mathrm{rot}}\rangle(t)$ is not a simple exponential but a superposition of different exponentials.

The rotational cooling process for D_2^+ is shown in Fig. 9. Because of the similarity of the rate coefficients of D_2^+ and H_2^+, also the characteristic time for D_2^+ is similar to that for the H_2^+ case.

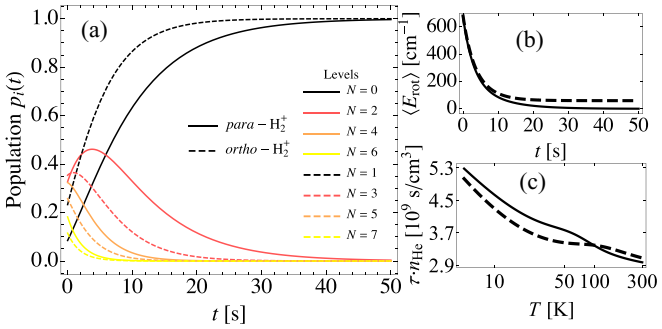

FIG. 8. (a) Time-dependent solution of the rate equations for rotational cooling of H_2^+ at a helium density $n_{\mathrm{He}} = 1 \times 10^9$ cm^{-3}, collisional temperature $T = 20$ K, and initial rotational temperature $T_{\mathrm{rot}} = 1000$ K. (b) The time dependence of the average rotational energy per H_2^+ molecule $\langle E_{\mathrm{rot}}\rangle(t)$. (c) The temperature dependence of $\tau \times n_{\mathrm{He}}$, where τ is the characteristic time of the rotational cooling.

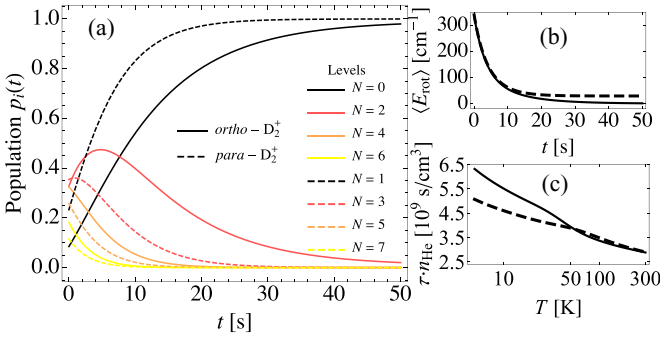

FIG. 9. (a) Time-dependent solution of the rate equations for rotational cooling of D_2^+ at a helium density $n_{\mathrm{He}} = 1 \times 10^9$ cm^{-3}, collisional temperature $T = 20$ K, and initial rotational temperature $T_{\mathrm{rot}} = 500$ K. (b) The time dependence of the average rotational energy per D_2^+ molecule $\langle E_{\mathrm{rot}}\rangle(t)$. (c) The temperature dependence of $\tau \times n_{\mathrm{He}}$, where τ is the characteristic time for cooling.

3. Operating conditions

The rate coefficient k for the $N = 2 \rightarrow N' = 0$ and $N = 3 \rightarrow N' = 1$ deexcitations at $T = 10$ K are $(1, 1.6) \times 10^{-10}$ cm^3/s. At this collisional temperature, $\tau \times n_{\mathrm{He}} \approx 4.5 \times 10^9$ s/cm^3. Thus, over the time τ the probability for such an energy-relaxing collision to occur is $k_{N=2(3),N'=N-2}(10\,\mathrm{K})(\tau \times n_{\mathrm{He}})(10\,\mathrm{K}) \approx 0.5\,(0.7)$. This implies that the actual time scale for achieving cooling to the steady-state τ_c should conservatively be taken one order larger. This ensures that the rotational relaxation has fully occurred, i.e., $k_{N=2(3),N'=N-2}(10\,\mathrm{K})(\tau_c \times n_{\mathrm{He}})(10\,\mathrm{K}) \gg 1$.

In an experiment aimed for precision spectroscopy of H_2^+ it would be desirable to use density values n_{He} so low that the mean time between (elastic plus inelastic) collisions with He is larger than the spectroscopy cycle time t_{cycle}. Thus, $n_{\mathrm{He,upper}} = 1/[k_{\mathrm{tot}}(T)\, t_{\mathrm{cycle}}]$, where $k_{\mathrm{tot}}(T)$ is the total collision rate coefficient in the ground rotational state. Assuming the ideal gas behavior for He (i.e., thermal equilibrium with the cryostat cold enclosure), the corresponding upper limit for the pressure is $p_{\mathrm{He,upper}} = k_B T_{\mathrm{He}} n_{\mathrm{He,upper}}$. For $T = 10$ K, at the end of rotational cooling the elastic collisions by far dominate (compare Figs. 2 and 4), so that $k_{\mathrm{tot}}(T) = k_{N=0,N'=0}(T)$ or $k_{N=1,N'=1}(T)$ for para or ortho species, respectively. If $t_{\mathrm{cycle}} = 1$ s, we find for both H_2^+ and D_2^+ $n_{\mathrm{He,upper}} \simeq 1 \times 10^9$ cm^{-3} and therefore $p_{\mathrm{He,upper}} \simeq 4 \times 10^{-9}$ mbar.

Experimentally, a viable approach could be to first perform the buffer gas rotational cooling, and then to pump out the He gas, effectively reducing collision rates strongly. In absence of collisions, the MHIs will not heat up again by any obvious mechanism. We point out that black-body radiation as a driving force for rotational heating is here ruled out, because black-body radiation essentially does not interact with homonuclear molecules and is weak due to the cryogenic environment.

V. QUANTUM STATE PREPARATION

A. The H_2^+ case

An initial gaseous sample of neutral H_2 in thermal equilibrium at 300 K will be a mixture of 25% in $I = 0$ and

75% in $I = 1$, the values arising from nuclear spin statistics (1 vs 3 nuclear spin states, respectively). By electron-impact ionization followed by cold He buffer gas cooling, the sample will be turned into a mixture of 25% para-H_2^+ in $N = 0$ and 75% ortho-H_2^+ in $N = 1$, since the nuclear spin state is not affected by the ionization or the collisions with He. The H_2^+ molecules are then spread over six quantum states (ignoring Zeeman substructure), with 25% in the $N = 0$ single quantum state and 25% in the $N = 1$, $J = 5/2$ single quantum state.

For a deterministic preparation of a single quantum state, we suggest the following nonoptical approach: nowadays it is routinely possible to convert neutral H_2 into nearly 100% para-H_2 by a paramagnetic catalyst at 20 K. This gas can be used in the experiment. During subsequent electron-impact ionization the nuclear spin state is expected to be preserved, leading to nearly pure para-H_2^+, which is then rotationally cooled to close to 100% in $N = 0$, which is a single quantum state. This represents deterministic preparation of a single quantum state by nonoptical means.

It is also possible to prepare either pure ortho- or pure para-H_2^+ by destroying selectively the other species by a $1 + 1'$ resonance-enhanced multiphoton dissociation (REMPD) laser process, where the first photon is resonant with a suitable rovibrational (electric quadrupole or Raman) transition, and the second can be at the easily available wavelength 266 nm (Fig. 1). The proton fragment resulting from REMPD can be subsequently ejected from the trap. This "nuclear purification" can be extended such that only one desired hyperfine state remains in the trap. We now discuss two specific cases, deemed to be relevant to ultrahigh precision spectroscopy of H_2^+. In the following, F and J denote the total spin and total angular momentum quantum numbers, respectively, arising as follows: **F** is the sum of nuclear spin **I** and electron spin $\mathbf{s}_e$, and **J** is the sum of **F** and rotational angular momentum **N**.

(1) Preparation of para-H_2^+. After buffer gas cooling of a para-ortho mixture, para-H_2^+ is present in a single (disregarding Zeeman degeneracy) internal state $\psi_{0,0|0,1/2,1/2} = |v = 0, N = 0, I = 0, F = 1/2, J = 1/2\rangle$ (blue semicircle in Fig. 1). Undesired ortho-H_2^+ molecules are in the five hyperfine states $\psi_{0,1|1,1/2,J=(1/2,\,3/2)}$ and $\psi_{0,1|1,3/2,J=(1/2,\,3/2,\,5/2)}$. These molecules are removed by laser vibrational excitation of electric quadrupole transitions (selection rules $\Delta L = 0, \pm 2$, $\Delta J = 0, \pm 1, \pm 2$, $J + J' \geqslant 2$), e.g., to the states $\psi_{1,1|1,F'=F,J'=3/2}$ and $\psi_{1,1|1,F'=F,J'=5/2}$, respectively, followed by photodissociation at 266 nm. The frequencies of the necessary five vibrational transitions (blue and blue-red-dashed arrows in the figure) lie within 97 MHz, and can be excited sequentially by a single quantum cascade laser at 4.81 μm.

(2) Preparation of ortho-H_2^+. Similarly, the single state $\psi_{0,1|1,1/2,3/2}$ of ortho-H_2^+ (red semicircle) is obtained by (i) vibrationally exciting the undesired para-H_2^+ molecules by a quantum cascade laser at 4.58 μm on the transition $\psi_{0,0|0,1/2,1/2} \rightarrow \psi_{1,2|0,1/2,3/2}$ (red arrow), (ii) vibrationally exciting the other four undesired ortho-H_2^+ spin states, $\psi_{0,1,|1,3/2,J} \rightarrow \psi_{1,1|1,3/2,5/2}$ and $\psi_{0,0|1,1/2,1/2} \rightarrow \psi_{1,1|1,1/2,3/2}$, at 4.81 μm (blue-red-dashed arrows), all followed by UV-induced dissociation from the $v = 1$ levels. During these excitations, the desired state $\psi_{0,1|1,1/2,3/2}$ remains unaffected, because the laser frequency is detuned by -19.7 MHz or further, which significantly exceeds the Doppler half linewidth of the transition when the ions are sympathetically cooled, 1.6 MHz for a secular temperature 10 mK. Note that even if pure ortho-H_2 were employed as start gas, REMPD is still required for generating a single quantum state.

Three of the purification transitions mentioned above have also been proposed as transitions of metrological interest [1,16]. We see that two midinfrared lasers suffice for state preparation and spectroscopy. Purification of other spin states is in principle feasible in a similar way. Finally, if one wishes to produce para-H_2^+ in $N = 2$, one may perform buffer gas cooling at approximately $T = 90$ K, followed by $1 + 1'$ REMPD of those molecules that are in $N = 0$ and $N = 1$.

B. The D_2^+ case

In thermal equilibrium at 300 K, 1/3 of a D_2 ensemble is para ($I = 1$ with three nuclear Zeeman substates; odd N), and 2/3 is ortho ($I = 0, 2$ with six nuclear Zeeman substates; even N). This ratio is expected to be maintained after electron-impact ionization and after buffer gas cooling. While ortho-D_2^+ will be cooled into the $N = 0$ state by cold He, it still has two nuclear "species" $I = 0, 2$. Thus, preparation of ortho-D_2^+ in a single quantum state is more complicated than for the para-H_2^+ case, where there is only a single value $I = 0$. In fact, the $N = 0$ state of ortho-D_2^+ possesses three quantum states $\psi_{0,0|0,1/2,1/2}$, $\psi_{0,0|2,F=(3/2,\,5/2),J=F}$ (energetically split by the nuclear-spin–electron-spin interaction), compared to a single one in para-H_2^+.

Para-D_2^+ will eventually be cooled into the $N = 1$ state, which possesses five quantum states $\psi_{0,1|1,1/2,J=(1/2,\,3/2)}$, $\psi_{0,1|1,3/2,J=(1/2,\,3/2,\,5/2)}$.

Thus, starting from a thermal ensemble of D_2, after rotational cooling, the largest fractional population in a single quantum state is 1/3, in the ortho-state $\psi_{0,0|2,5/2,5/2}$. Preparation of a single quantum state should be possible using a REMPD-based purification similar to that described for H_2^+.

Today, it is technically well feasible to generate nearly pure ortho-D_2 and approximately 80%-enriched para-D_2 gas, similar to the H_2 case [49]. While their use in rotational cooling is favorable, the additional procedure of REMPD will nevertheless be necessary if the preparation of a single quantum state is required, both for the $N = 0$ and for the $N = 1$ target rotational level.

VI. PRESENT CONCLUSIONS

In the present work we have computed *ab initio* the rotationally and in part spin-state-resolved elastic and inelastic cross sections for two of the simplest nonreactive molecule-neutral-atom collisions, $H_2^+(v = 0, N) + \mathrm{He} \rightarrow H_2^+(v = 0, N') + \mathrm{He}$ and $D_2^+(v = 0, N) + \mathrm{He} \rightarrow D_2^+(v = 0, N') + \mathrm{He}$. We found the rotational cooling rate coefficients to be of similar size as those for vibrational cooling. In a complete picture, a sample of initially rotationally and vibrationally excited MHI made to interact with cold He buffer gas will undergo the concurrent processes of vibrationally excited ion destruction, vibrational cooling, and rotational cooling. We computed that for both H_2^+ and D_2^+ initially in $v = 0$, complete rotational cooling into the rotational ground state is possible already for a moderately low collisional temperature of 20 K ($T_{\mathrm{He}} = 60$

and 40 K for H_2^+ and D_2^+, respectively) within a time of approximately 40 s for a He density of 10^9 cm^{-3}. Here the rotational ground state is specific to the particular total nuclear spin I of the MHI. For molecules initially in $v = 1, 2$, more relaxation channels exist, but the cooling time is expected to be similar.

Two approaches were presented for achieving single-quantum state preparation of homonuclear MHIs: starting with catalytically produced pure para-H_2, or removing undesired hyperfine states by hyperfine-state-resolved, stepwise photodissociation. Such controlled laser dissociation is always required for D_2^+ single quantum state preparation, due to its richer spin structure.

Using an appropriate cryogenic trap apparatus, the cooling, photodissociation, and collision-free times can be made compatible with the duration of experimental spectroscopy protocols. On the whole, we find that because of its relative simplicity, cryogenic buffer gas cooling of homonuclear MHIs by helium appears as an attractive approach for enabling next-generation spectroscopy experiments on these fundamental quantum systems. We believe that the basic concepts of the present analysis are applicable also to other homonuclear molecular ion species.

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