Cooling and quenching of ^{24}MgH$^+$($X\,^1\Sigma^+$) by ^{4}He(^1S) in a Coulomb trap: A quantum study of the dynamics

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The quantum dynamics of the rotational quenching of the ^{24}MgH$^+$($X\,^1\Sigma^+$) molecular cation interacting with ^{4}He(^1S) as a buffer gas, at relative temperatures ranging from 1 K down to millikelvins, is described by accurate close coupling scattering calculations on an *ab initio* potential energy surface. The efficiency of the process is quantitatively analyzed by employing the *ab initio* quenching rates and cross sections and effective decay rate values are obtained from simple unimolecular kinetics over a broad range of trap conditions.

I. INTRODUCTION

The core technology behind the currently used ion traps is a well-established one, since radio-frequency (RF) quadrupole traps [1–3] or even the relatively more recent RF many-pole 22-pole traps [4–6] have their roots in the seminal work of the Nobel prize awarded to W. Paul, who showed over the years how a specifically crafted spatial disposition of an array of electrodes driven by a RF potential could generate an effective trapping electric potential that can, in turn, confine charged particles in a restricted volume of their phase space. As a consequence, multipolar RF ion traps have become incredibly useful tools for tackling real cutting-edge physical and chemical scientific research.

For example, a multipolar trap can be easily added to a laser system that may thus further allow the Doppler cooling of the trapped ions. Whenever the translational temperature drops below a critical value which depends on the operational parameters of the trap and the properties of the trapped ions (basically their mass-over-charge ratio), a transition toward an ordered spatial structure of the ions within the trap is observed and what is now called Coulomb crystal (CC) is said to be formed.

In a typical experimental setup, the ions within the CC can be continuously monitored by collecting the fluorescence which originates from the electronic excitations promoted by the cooling lasers. In this way, the kinetics of a chemical reaction between the ion and a surrounding neutral atomic or molecular species can be studied and its low-temperature reaction rate estimated [7,8]. In other words, it has become evident that a CC is an ideal environment to study the low-temperature chemical behavior of ionic species.

Molecular ions can be prepared *in situ* and incorporated into a CC structure exploiting the fact that the direct cooling effect which the lasers have on the atomic ions can be transferred to the molecular ions by the Coulomb interaction between the ions (sympathetic cooling). For example, the ^{24}MgH$^+$ ion can be produced from a CC of ^{24}Mg$^+$ by the reaction with an effusive flux of H$_2$ gas. Once formed, the ^{24}MgH$^+$ is sympathetically cooled by the laser-cooled ^{24}Mg$^+$ until a ^{24}Mg$^+$/^{24}MgH$^+$ bicrystal arises [9]. While the translational degrees of freedom of a molecular ion can be readily controlled by using the sympathetic cooling, evidence has been gathered by the scientific community that in the typical experimental setup the rotational degrees of freedom are usually out of control and that a realistic estimate of the rotational temperature of a molecular ion incorporated into a CC structure is expected to be often no lower than 300 K [10]. In an effort to gain total control over the degrees of freedom of the trapped ions, a series of optical pumping techniques dealing with the rotational temperatures of the trapped molecular ion have been proposed and their effectiveness demonstrated [11,12]. Another possibility to quench the rotational energy of a "Coulomb-crystallized" charged molecule may be given by the use of the helium buffer gas (HBG) technique [13]. In the present paper we therefore intend to computationally investigate the effectiveness of the HBG as a rotational cooler of the MgH$^+$ ion in a collision energy range which is compatible with the CC environment (temperature of 10^{-3}–10^1 K). In order to do so, we have evaluated the MgH$^+$($X\,^1\Sigma^+$)-^{4}He interaction potential [14] and calculated the rotational quenching cross sections by using fully *ab initio* quantum methods. The rate constants for the quenching processes have thus been obtained and then used to estimate the typical lifetime of an excited rotational state of MgH$^+$ into the HBG.

Section II is devoted to a brief description of the methods we have employed to compute the interaction potential and the quantum quenching dynamics. In Sec. III we present our results, while Sec. IV contains our conclusions.

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II. METHODS

The MgH$^+$-He potential energy surface (PES) has been accurately evaluated within the *ab initio* approach to the electronic structure calculation. The details of this calculation and the main characteristic of the PES have already been reported by us in previous work [14]. Such calculations were carried out using the (R, r, θ) Jacobi coordinates, where R defines the distance of He from the molecular center of mass, r is the intramolecular nuclear distance, and θ is the angle defined by $\arccos(\widehat{\mathbf{R}} \cdot \widehat{\mathbf{r}})$. The quantum chemistry model we have employed was the coupled-cluster single and double excitations with noniterative correction for the triple excitations [CCSD(T)] ansatz, coupled with a complete basis set (CBS) limit approach extrapolated from the augmented coupled-cluster polarized valence multiple ζ (aug-cc-pVnZ) (where $n = 3, 4, 5$) basis set series as implemented in the software package GAUSSIAN08 [15] and can be considered reliable and very accurate. Because we are interested in the rotational quenching dynamics, the r dependence of the PES has been averaged over the ground-state vibrational wave function of MgH$^+$:

$$V^{00}(R, \theta) = \int \phi_0^*(r) V(r, R, \theta) \phi_0 dr, \tag{1}$$

where $V(r, R, \theta)$ is *ab initio* PES, $\phi_0(r)$ is the vibrational ground-state wave function of the MgH$^+$($X\,^1\Sigma^+$), and $V^{00}(R, \theta)$ is the r-averaged interaction potential that will be used in the quantum calculations of the rotational quenching dynamics. In order to do so, the $V^{00}(R, \theta)$ function has to be further expanded in terms of Legendre polynomial, $P_\lambda(\cos \theta)$:

$$V^{00}(R, \theta) = \sum_\lambda V_\lambda^{oo}(R) P_\lambda(\cos \theta). \tag{2}$$

Figure 1 reports the first few $V_\lambda^{00}(R)$ coefficients as defined by Eq. (2). The fairly large coefficients with $\lambda > 0$ reflect the anisotropy of the original interaction potential and are responsible for the strength of the coupling between the rotational levels of the MgH$^+$ with the He projectile.

To solve the problem of the rotational quenching dynamics corresponds to solving the nuclear time-independent Schrödinger equation (TISE) for the nuclei that move on the potential defined by Eqs. (1) and (2), enforcing the usual
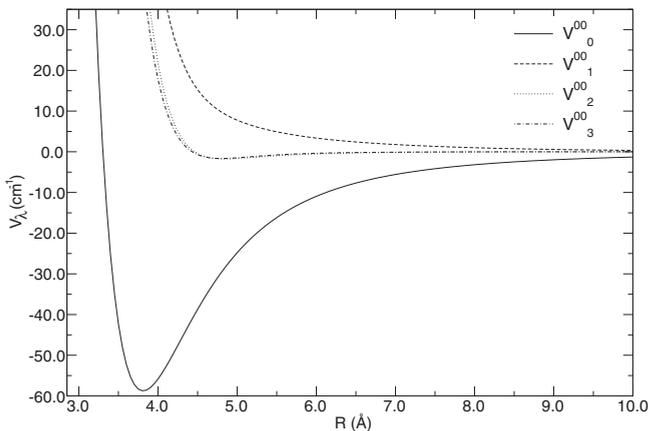
scattering boundary conditions [16]. Our numerical strategy to the solution of the TISE is the coupled channel approach as implemented in our in-house developed scattering code ASPIN [17]. Details of the method have been given many times before [17,18] and therefore they will not be reported in the present paper.

The physical observables that we obtain from ASPIN are the state-to-state partial cross sections $\sigma^J(a' \leftarrow a, E)$, that is, partial cross sections for the transition processes between rotovibrational states of the target molecule (a and a' are the collective quantum numbers which identify the rotovibrational states) for a given value of the total angular momentum, J, and at a total system energy, E. As we want to describe the rotational quenching process, we are principally interested in the deexcitation transition cross sections, $\sigma^J(j_f \leftarrow j_i, E)$, between different rotational states of the same vibrational level: $(v_0, j = j_f) \leftarrow (v_0, j = j_i)$ for $j_i > j_f$ and with v_0 indicating the vibrational ground state of the MgH$^+$. For the sake of notation clarity, in the following formulas we assume implicitly that the the system is always in its vibrational ground state, v_0. It is also important to obtain the corresponding elastic partial cross sections, $\sigma_{el}^J(j_i, E)$, which can measure the efficiency of the linear momentum-transfer process for the rotational state j_i. The rotationally summed (cumulative) quenching partial cross sections, $\sigma^J(j_i, E)$, are defined as

$$\sigma^J(j_i, E) = \sum_{j_f} \sigma^J(j_f \leftarrow j_i, E), \tag{3}$$

where $\sigma^{J,E}(j_f \leftarrow j_i)$ are the partial cross sections for the transition process $j_f \leftarrow j_i$, with $0 < j_f < j_i$ at the collision energy E. The integral cumulative quenching cross sections, $\sigma(j_i, E)$, can be obtained by further summing over the total angular momenta, J, of the rotationally summed cross sections $\sigma^J(j_i, E)$. In a similar manner, we define the integral elastic cross section, $\sigma_{el}(j_i, E) = \sum_J \sigma_{el}^J(j_i, E)$. Once the $\sigma(j_i, E)$ are known, the rotational quenching rate constants, $\Gamma_{j_i}(T)$ can be evaluated as the convolution of the $\sigma(j_i, E)$ over a standard Boltzmann distribution:

$$\Gamma_{j_i}(E) = \int \sigma(j_i, E) \sqrt{\frac{4E}{\pi (k_B T)^3}} \exp(-E/k_B T) dE.$$

III. RESULTS AND DISCUSSION

It is worth noting at the outset that for the present system (a $^1\Sigma$ diatom interacting with a ^1S atom) all the angular momentum couplings are fully accounted by our description of the nuclear dynamics and hence the calculations of the rotational quenching process given by our computational model can be considered as basically exact. The numerical convergence of the $\sigma^J(j_i, E)$ cross sections has also been carefully checked against the basis set size and propagator parameters and it is well within 1%. In particular, we have propagated the solution from $R = 0.8$ Å to $R = 50.0$ Å with 12 500 steps of the LogDer propagator [19]. From $R = 50.0$ Å to the numerical asymptotic region $R = 1000$ Å the solution matrix is then propagated by using our implementation of the VarPh (variable phase) propagator [18]. The molecular basis set consists of 1 vibrational state and 30 rotational functions. In
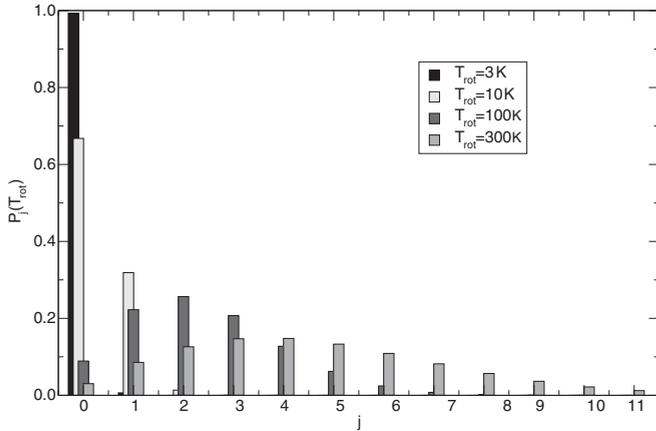

FIG. 1. Evaluated $V_\lambda^{00}(R)$ for $\lambda = 0, 1, 2, 3$, as defined by Eq. (2).

FIG. 2. Calculated rotational Boltzmann distribution over the rotational states of the ^{24}MgH$^+$ at temperatures of 3, 10, 100, and 300 K. For the calculation we have used the rotational constant of ^{24}MgH$^+$, $B_e = 6.3870$ cm^{-1} reported by the NIST database [20].

order to obtain the quenching integral cross sections, $\sigma(j_i, E)$, and the elastic integral cross sections, $\sigma_{el}(j_i, E)$, converged within 1% on the whole collision energy range considered here, up to 18 partial waves ($J = 0, \ldots, 17$) have been used in the calculations. In this study we have considered the deexcitation process starting from different rotational initial states with the rotational state $j = 11$ being the most excited. In fact, as shown by the calculated Boltzmann distribution reported by Fig. 2, even at $T = 300$ K the 98.8% of the MgH$^+$ are distributed over the 12 rotational states considered in the present calculations. It is hence safe to say that our calculations fully account for all the possible rotational distributions that can characterize the molecular ions within the CC environment. Figures 3 and 4 report the results of our scattering calculations: elastic cross sections and cumulative rotation quenching cross sections, respectively, as a function of the collision energy (given in kelvin).
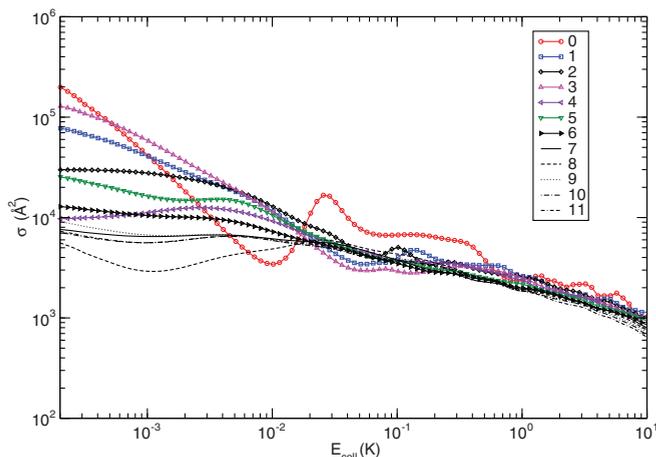

FIG. 3. (Color online) Computed integral elastic cross sections, $\sigma_{el}(j_i, E)$, as function of the temperature of the relative motion, E_{coll}, (E_{coll} is given in kelvin). The numbers reported by the legend are the rotational quantum number, j_i, of the initial rotational state.
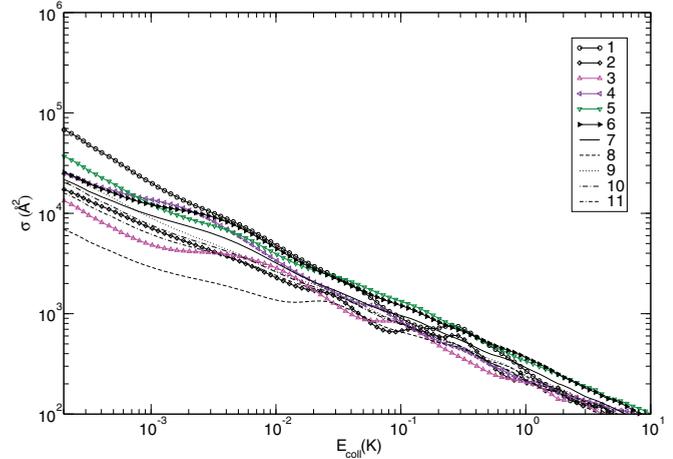

FIG. 4. (Color online) Computed rotation quenching, cumulative cross sections, $\sigma(j_i, E)$, as function of the temperature of the relative motion, E_{coll}, (E_{coll} is given in kelvin). The numbers reported by the legend are the rotational quantum number, j_i, of the initial rotational state.

By looking at Fig. 3, it is immediately apparent that even at the lowest end of the energy range considered here, the so-called Wigner regime of the elastic cross sections (constant behavior of the elastic cross section on a log-log scale) is still far from having been reached. Furthermore, the $\sigma_{el}(j_i)$ values span about two orders of magnitude starting from 5.0×10^3 Å^2 ($j_i = 8$) to 2.0×10^5 Å^2 ($j_i = 0$). In the intermediate and higher energy range (0.01–1 K), (with the notable exception of the initial state $j_i = 0$ which shows a marked resonance around 0.03 K), all the cross sections behave almost uniformly without any relevant resonance structure. In the high energy range ($T > 1.0$ K) even the elastic cross section of the $j_i = 0$ state comes closer to the other ones and no particularly distinctive behavior between the different initial states can be noted. The quenching cross sections reported by Fig. 4 show a somewhat similar behavior: At the lowest collision energy their values span less than one order of magnitude: from 7.0×10^3 Å^2 ($j_i = 8$) to 3.0×10^4 Å^2 ($j_i = 2$), while, as the collision energy increases, they show a very similar value for nearly all the cross sections.

This fairly featureless behavior of the quenching cross sections reflects on the calculated quenching rate constants (reported by Fig. 5). In fact, the calculated quenching rates show little dependence on the initial quantum state and on the temperature: They take values from 1.8×10^{-10} cm^3 s^{-1} to 5.8×10^{-10} cm^3 s^{-1} around $T = 0.001$ K and from 2.0×10^{-10} to 5.0×10^{-10} cm^3 s^{-1} at temperatures in the range 0.01–1.0 K. Once the quenching rate constants are known, it then becomes possible to estimate the mean lifetime of the rotational excited state of the MgH$^+$ in the HBG environment. In order to do so, let us consider the simple, unimolecular kinetic equation,

$$\frac{d}{dt}N^{(\text{MgH}^+)^*}(t) = -\Gamma(T)N^{\text{He}}(t)N^{(\text{MgH}^+)^*}(t), \qquad (4)$$

where $N^{(\text{MgH}^+)^*}(t)$ is the number density of any of the excited rotational states of the molecular ion present at the time t, $N^{\text{He}}(t)$ is the number density of the He in the buffer gas, while
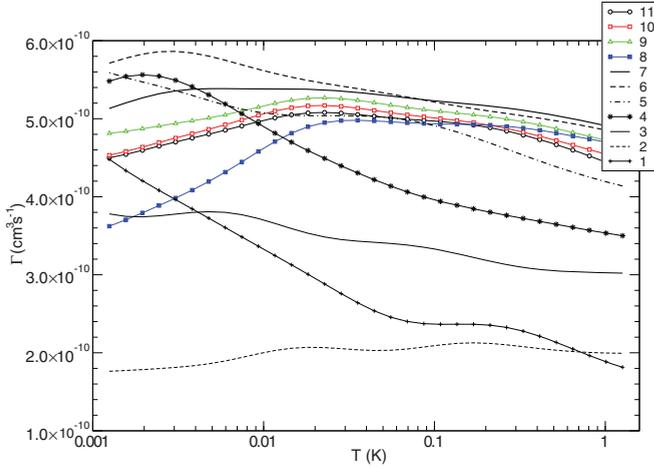
FIG. 5. (Color online) Computed rotational quenching rate constants, $\Gamma_{j_i}(T)$, as function of the temperature T (T is given in kelvin) of the macroscopic He/MgH$^+$ gas mixture.

$\Gamma(T)$ is some effective, temperature-dependent quenching rate. Such a simple model does not distinguish between the initial excited states of the ion: This assumption is here justified by the slow dependence upon the initial rotational state found by our calculated $\Gamma_{j_i}(T)$ and by the fact that we want at this stage to obtain a qualitative estimate of the typical quenching times which could be expected under trap conditions. Furthermore, we can safely assume that the number density of the He in the buffer gas is constant [$N^{He}(t) = N_0^{He} = $ const] given the loading procedure followed for the buffer gas into the trap [13]. We also assume its temperature to be taken as remaining costant in the trap. Incorporating these further assumptions in Eq. (4), we obtain

$$\frac{d}{dt} N^{(MgH^+)^*}(t) = -\lambda N^{(MgH^+)^*}(t), \quad (5)$$

where $\lambda = \Gamma N_0^{He}$ describes a quantity which can be viewed as an effective unimolecular decay rate for the process. The mean lifetime of any of the MgH$^+$ excited states present in the trap is then given by $\tau = 1/\lambda = 1/(\Gamma N_0^{He})$. If we assume a number density of He in the HBG between 2.0×10^{16} cm^{-3} and 3.0×10^{16} cm^{-3} [21] and a range of Γ values at $T = 0.01$–0.1 K between 2.0×10^{-10} cm^3 s^{-1} and 5.0×10^{-10} cm^3 s^{-1} (see Fig. 5) we obtain that the mean lifetime of a typical MgH$^+$ rotationally excited state in the trap, τ, has a value in the HBG between 80 and 200 ns, a time interval which corresponds to an effective decay rate between 1.2×10^7 s^{-1} and 5.0×10^6 s^{-1}. It therefore indicates that the process of rotationally cooling of the molecular ion by the addition of the HBG is a very efficient one and one can expect a very fast reduction of the excited state population within a very short time interval, even at the upper end of the selected temperature range (e.g., 0.1 K). One should indeed be aware that several approximations have been taken when getting to the final Eq. (5) and that to estimate the ^{4}He number density may not be a simple task. However, the simulated data shown in Fig. 6 indicate that even by reducing the buffer-gas density by several orders of magnitude, the effective lifetimes of any of the excited rotational states never become larger than 0.1 s. This is certainly an indicator of good collisional
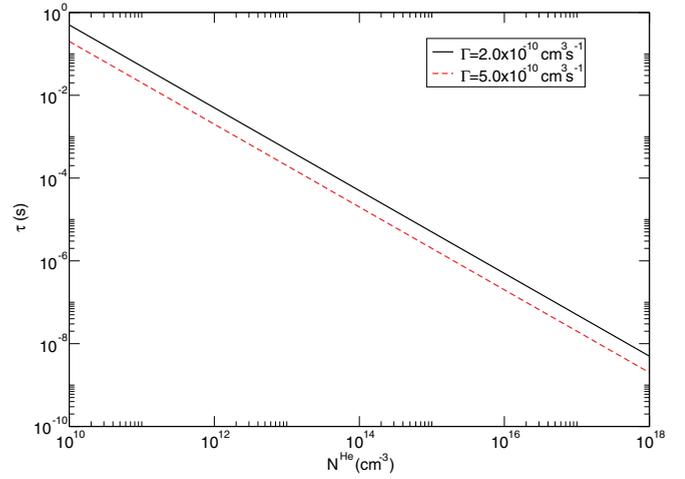

FIG. 6. (Color online) Computed effective lifetimes for any of the rotational excited states of the MgH$^+$ in a cold multipolar trap with temperatures between 0.01 and 0.1 K for different number densities, N^{He} of the HBG environment. See main text for details.

quenching efficiency for the system under consideration, even within the simplified picture of the evolution that we have taken in our present modeling of it.

IV. CONCLUSIONS

In the present work we have examined some computational aspects of the well-established technique of buffer-gas loading for the production of internally cold molecular ions which have already been translationally cooled to a CC structure [7,9]. Although the use of He as a buffer gas is considered fairly simple, it may prevent strong spatial localization due to frequent collision with the buffer-gas atoms [22] and usually limits the cooling to the kelvin range. However, in the present analysis we have considered the primary molecular ion (MgH$^+$) to be in its ground electronic state and to have already been trapped into a stable CC structure, while having rotational temperatures around 300 K or only slightly lower. Within this set of conditions, the ^{4}He buffer gas is treated as having variable number density and to cause collisional quenching of the internal rotational levels of MgH$^+$ chiefly via single collision events.

The quantum treatment of the collisionally quenching dynamics has been carried out using an essentially exact method which employed an accurate, *ab initio* computed potential energy surface describing their interaction. At the expected internal temperature of the molecular ions in the CC, the rotational levels of the $\nu = 0$ vibrational state that are deemed to be significantly populated go up to $j = 11$, which was therefore the highest excited level we have considered to be populated in the present calculations. Furthermore, we have also taken the molecular ion to be in its ground-state vibrational level, which is a reasonable assumption given the usual experimental conditions [23].

The calculations provided both elastic and superelastic (quenching) state-to-state cross sections over a broad range of trap temperatures going from 0.1 mK to about 1 K. We have usually obtained from them the corresponding cumulative quenching cross sections by summing over the total number

of each set of downward final states, although in each set the $\Delta j = 1$ cross sections were invariably found by our calculations to be the dominant ones in term of size. Thus, one may say that all cumulative quenching processes in the present system are really chiefly provided by the $\Delta j = 1$ corresponding cross sections. The range and size of the final quantities (shown by Figs. 3 and 4) indicate the following behavior:

(i) All cross sections turn out to be fairly large in size, for both the elastic and the inelastic channels;

(ii) in the range of temperatures between 0.1 and 1.0 K the elastic cross sections are larger than the quenching cross sections, thus possibly

(iii) indicating a substantial effect of the buffer gas on the spatial localization of the molecular ions;

(iv) both sets of cross sections, in that same temperature range but also further down to a few mK, turn out to depend very little on the initial state of the ionic rotor, thereby indicating that quenching processes are little affected by that variable;

(v) the cumulative quenching cross sections yield corresponding rates which we reported in Fig. 5 between about 1 mK and 1.0 K; they show, as expected, a rather weak dependence of the initial rotor state (j value), varying between about 2×10^{-10} and 5×10^{-10} cm^3 s^{-1} when starting from $j = 2$ or from $j = 11$.

The weak dependence of the quenching rates on the initial rotational state of the ion, and their substantial size in the range of temperatures of possible experimental interest, suggested to us the use of a simple kinetic model to obtain some qualitative estimates of the decay (quenching) rates of the ionic species within the trap as caused by ^{4}He as the cooling buffer gas. The model, outlined in the previous section, suggests that the rotational population of the ion could be very quickly quenched by the buffer gas, indicating effective decay lifetimes that, as expected, depend very strongly on the number density of the ^{4}He buffer gas but which can vary from 0.1 s down to 10 ns over a broad range of density values (e.g., see Fig. 6).

In conclusion, the present calculations indicate a rather efficient quenching dynamics for MgH$^+$ CC arrangements upon buffer-gas loading with ^{4}He, although the size of the elastic cross sections also suggest the possible occurrence of a reduction of spatial localization and of internal coherence of the trap construct.

[1] W. Paul and H. Steinwedel, Z. Naturforsch. A **8**, 448 (1953).

[2] W. Paul, Angew. Chem., Int. Ed. Engl. **29**, 739 (1990).

[3] G. C. Stafford, P. E. Kelley, J. E. P. Syka, W. E. Reynolds, and J. F. J. Todd, Int. J. Mass Spectrom. Ion Processes **60**, 85 (1984).

[4] D. Gerlich and S. Horning, Chem. Rev. **92**, 1509 (1992).

[5] D. Gerlich, J. Chem. Soc., Faraday Trans. **89**, 2199 (1993).

[6] D. Gerlich, Phys. Scr., T **59**, 256 (1995).

[7] M. Drewsen, I. Jensen, J. Lindballe, N. Nissen, R. Martinussen, A. Mortensen, P. Staanum, and D. Voigt, Int. J. Mass Spectrom. Ion Processes **229**, 83 (2003).

[8] S. Willitsch, M. T. Bell, A. D. Gingell, S. R. Procter, and T. P. Softley, Phys. Rev. Lett. **100**, 043203 (2008).

[9] K. Molhave and M. Drewsen, Phys. Rev. A **62**, 011401 (2000).

[10] A. Bertelsen, S. Jorgensen, and M. Drewsen, J. Phys. B **39**, 83 (2006).

[11] P. F. Staanum, K. Hojbjerre, P. S. Skyt, A. K. Hansen, and M. Drewsen, Nat. Phys. **6**, 271 (2010).

[12] T. Schneider, B. Roth, H. Duncker, I. Ernsting, and S. Schiller, Nat. Phys. **6**, 275 (2010).

[13] J. D. Weinstein, R. de Carvalho, T. Guillet, B. Friedrich, and J. M. Doyle, Nature (London) **395**, 148 (1998).

[14] D. Caruso, M. Tacconi, E. Yurtsever, and F. A. Gianturco, Indian J. Chem, in press.

[15] M. J. Frisch *et al.*, GAUSSIAN08 (Gaussian, Inc., Wallingford, CT, 2003).

[16] J. R. Taylor, *Scattering Theory: The Quantum Theory of Nonrelativistic Collisions* (Dover, New York, 2006).

[17] D. Lopez-Duran, E. Bodo, and F. A. Gianturco, Comput. Phys. Commun. **179**, 821 (2008).

[18] R. Martinazzo, E. Bodo, and F. A. Gianturco, Comput. Phys. Commun. **151**, 187 (2003).

[19] D. E. Manolopoulos J. Chem. Phys. **85**, 6425 (1986).

[20] Y. Ralchenko, A. E. Kramida, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (version 4.0) [http://physics.nist.gov/asd], National Institute of Standards and Technology, Gaithersburg, MD, 2010.

[21] D. M. Egorov, Ph.D. thesis, Harvard University, 2004.

[22] D. Gerlich, Phys. Scr., T **59**, 256 (1995).

[23] I. S. Vogelius, L. B. Madsen, and H. Drewsen, Phys. Rev. A **70**, 053412 (2004).