

# Quenching vibrations by collisions in cold traps: A quantum study for $\text{MgH}^+(\text{X}^1\Sigma^+)$ with $^4\text{He}(^1\text{S})$ <sup>#</sup>

DOMENICO CARUSO<sup>a</sup>, MARIO TACCONI<sup>a</sup>, FRANCO A GIANTURCO<sup>a,\*</sup> and ERSIN YURTSEVER<sup>b</sup>

<sup>a</sup>Department of Chemistry, The University of Rome ‘Sapienza’ and P.le Aldo Moro 5, 00185 Rome, Italy

<sup>b</sup>Department of Chemistry, Koc University, Rumelifeneriyalu and Sariyer, 34450 Istanbul, Turkey

e-mail: fa.gianturco@caspur.it

**Abstract.** Quantum dynamics of superelastic collisions involving vibrational levels of  $\text{MgH}^+(\text{X}^1\Sigma^+)$  ions in cold traps, interacting with  $^4\text{He}(^1\text{S})$  as a buffer gas at relative temperatures down to millikelvins, is discussed using an *ab initio* computed potential energy surface. The relative efficiency of collisional cooling with respect to collisional quenching of the internal vibrations is examined from the results of the relative sizes of the relevant cross sections in relation to predicting actual behaviour in cold traps. The present study indicates the feasibility of cooling vibrationally ‘hot’, trapped ions with the buffer gas.

**Keywords.** Scattering theory; ion-molecule collisions vibrational quenching.

## 1. Introduction

The ability to trap and cool dilute atomic gases has certainly revolutionized physics over the last twenty years. Hence, considerable attention has now turned to study and create trapped cold and ultracold molecular gases.<sup>1–3</sup> Although molecules are more complex than atoms and thus more difficult to cool below mK temperatures, they offer the possibility of investigating new effects associated with their specific properties like their internal state populations, their ability to orient themselves in traps using electromagnetic fields and their ability to undergo reactions, the latter being now studied in dilute gases and at temperatures below 1 K, thus holding promises to access chemical process dominated by quantum effects.

Dissipative cooling scheme needs to be applied after the molecules are slowed and trapped,<sup>4,5</sup> to produce molecular species down to 1 mK, without significant loss of the relevant molecules, because of the existence of the competition between translational energy and the internal energy of each molecule.

An important number of such cooling schemes have become available for cooling molecules: they include stochastic, cavity, evaporative and sympathetic cooling.<sup>6</sup> In the case of sympathetic cooling, the molecular

gas to be cooled is co-trapped within a colder gas at higher concentration and therefore heat flows from the hotter to the colder gas. This method has been experimentally demonstrated using collisions with cold helium to cool and trap molecules in the 100 mK range.<sup>6</sup> Of critical importance to successful sympathetic cooling is the dominance of elastic over inelastic processes across a broad range of collisional energies.<sup>7</sup> Inelastic losses that are due to state-changing collisions to untrappable states and reactions are particularly worrying since such processes lead to leakage from the trap and prevent thermalization.<sup>8,9</sup>

In the case of ionic molecules, they are usually stored in multipolar traps<sup>10</sup> and the need to bring and maintain them to a particular, trappable, quantum state is no longer a concern as long as the particles charge state is conserved. Nevertheless, multipolar traps can have somewhat strict requirements on the trajectories of the ionic particles within the trap. Only a limited portion of the phase-space accessible to the ions in the trap corresponds to stable trajectories, i.e., those that prevent the escaping of the ions from the trapping potential. Furthermore, the mixture of helium with  $\text{MgH}^+$  is basically a non-reactive system, so charge exchange processes and subsequent neutralization of  $\text{MgH}^+$  is to be considered completely suppressed. What we should try to understand, therefore, is if the collisions between the ions and the buffer gas atoms could disturb the trajectories of the trapped ions in such a way that they become unstable within the trap.

<sup>#</sup>Dedicated to Prof. N Sathyamurthy on his 60th birthday

\*For correspondence

If the ions to be trapped are initially formed by photoassociation or by chemical reactions,<sup>11</sup> then the possibility exists that they need to be brought down from some excited vibrational level via sympathetic collisions with the buffer gas. In the present study we therefore analyse such set of processes for an ionic polar molecule,  $\text{MgH}^+(\text{X}^1\Sigma^+)$  which is initially taken to be formed in some excited vibrational level, albeit translationally cold down to the mK range, interacting with  $^4\text{He}(^1\text{S})$  as the denser buffer gas employed to bring the ionic partner down to its ground roto-vibrational level. Furthermore, in the present analysis we will focus chiefly on the vibrational quenching efficiency in comparison with the sympathetic cooling probabilities, all quantities being obtained from an accurate quantum treatment of both the interaction forces and the nanoscopic dynamics.

## 2. The potential energy surface

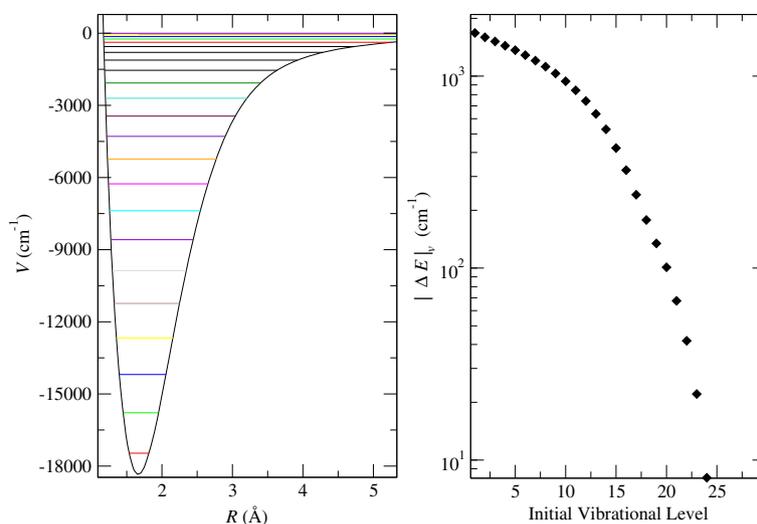
The calculations of the full potential energy surface (PES) were carried out using the  $(R, r, \theta)$  Jacobi coordinates, where  $R$  defines the He atom distance from the molecular center-of-mass,  $r$  is the intramolecular coordinate and  $\theta$  is the angle defined by  $\arccos(\hat{\mathbf{R}} \cdot \hat{\mathbf{r}})$ . The quantum chemistry model used the Coupled-Cluster Single and Double excitations<sup>12</sup> with non-iterative correction for the Triple excitations<sup>12</sup> (CCSD(T)) ansatz coupled with a Complete Basis Set limit (CBS) approach extrapolated from the aug-cc-pVnZ ( $n = T, Q, 5$ ) basis set series.<sup>12</sup> The geometry grid spans a total of

9464 geometries of the molecular complex, with  $\theta$  from  $0^\circ$  to  $180^\circ$  in  $10^\circ$  intervals, while the range of  $R$  values varied with the angle and ranged from 1.6 to 16.0 Å. The internal coordinate of  $\text{MgH}^+$ ,  $r$ , varied over a range of nine points from 1.3 to 3.0 Å. It extended over a span of about 20 vibrational levels of the molecular target, which had a well depth of  $17020 \text{ cm}^{-1}$  at  $r_{\text{eq}} = 1.5 \text{ Å}$ .<sup>13</sup>

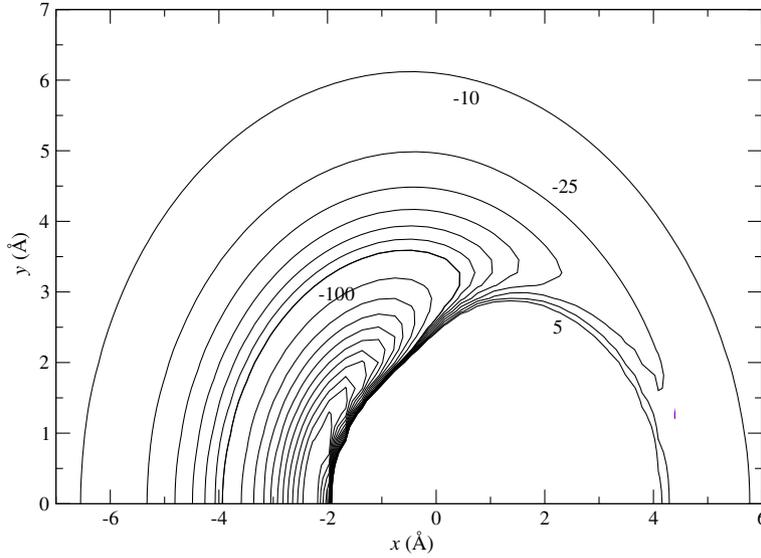
The data in figure 1 shows the vibrational level distribution of the  $\text{MgH}^+$  potential energy curve, which was numerically fitted and extended, for graphical purpose here, beyond the computed range in order to reach the asymptotic limit of  $E_{\text{MgH}^+} - E_{\text{Mg}^+} - E_{\text{H}}$ . The new fit has been used to solve the radial Schrodinger equation that generates the vibrational wavefunctions and energies (for  $J = 0$ ). The two plots in figure 1 show the distribution of the bound levels up to dissociation, although we shall be using the first 22 vibrational levels which fall within the range of the radial values covered by the raw points of our calculations.

Similarly, right-hand plot in figure 1 shows the energy separation between levels up to  $\nu = 24$  although the values beyond  $\nu = 22$  are reported only for graphical completeness and will not be used here. It is to be noted that the largest energy gap in figure 2 corresponds to the computed spatial features of the interaction potential for the case where  $r = r_{\text{eq}}$ , i.e., a two-dimensional map in  $(x, y)$  with  $x = R \cos \theta$  and  $y = R \sin \theta$ : the H atom is located on the positive range of the  $x$  values.

One clearly sees from the behaviour of the interaction that the system exhibits a deep attractive well on the  $\text{Mg}^+$  side, with an absolute minimum very close to the linear configuration. The vibrational coupling



**Figure 1.** Computed locations of the vibrational levels of  $\text{MgH}^+(\text{X}^1\Sigma^+)$  (rotationless system) up to dissociation (left plot). Right plot:  $\Delta\nu = 1$  energy spacing between bound levels up to  $\nu = 24$  (see main text for details).



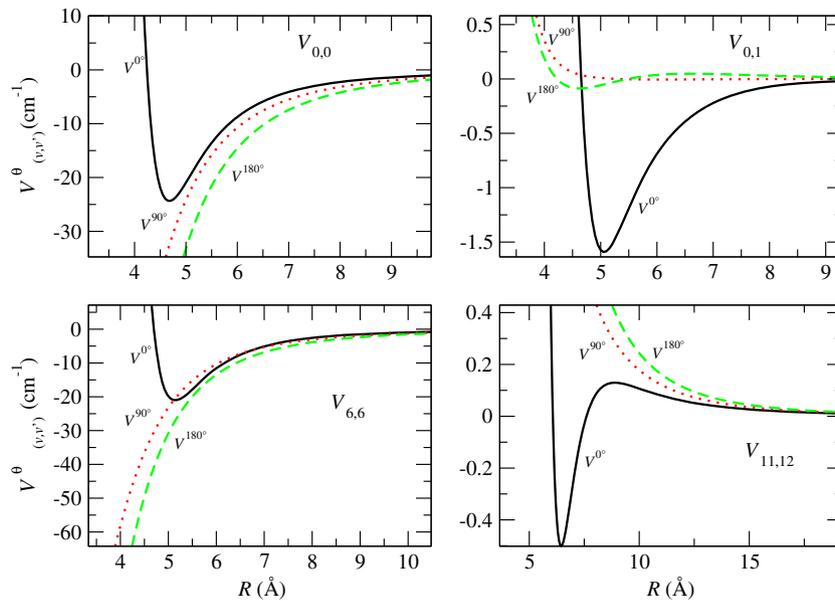
**Figure 2.** Isolines of the energy features for the PES at  $r = r_{\text{eq}}$  with  $x = R \cos \theta$  and  $y = R \sin \theta$ . The strongly attractive well is located on the  $\text{Mg}^+$  side of the target. Distances in  $\text{\AA}$  and energies in  $\text{cm}^{-1}$ .

induced by the present interaction involves the convolution of the PES over the target isolated vibrational states computed from the potential of figure 1:

$$V^{\nu,\nu'}(R, \theta) = \int \phi_{\nu'}(r) V(r, R, \theta) \phi_{\nu}(r) dr \quad (1)$$

and therefore describes the distortions of the vibrational states of the target ion due to the interaction with the impinging He atom.

The spatial orientational features of such terms, which we have computed for 22 vibrational states of  $\text{MgH}^+$ , are shown in figure 3 for a sampling of  $\nu$  values, both diagonal and off-diagonal, for different orientations and over the relevant range of radial distances. One sees from the data in that figure that the strongest vibrational coupling involves, as expected, the approach on the H-atom side where the lighter part of the ion is more easily affected by the perturbing He atom. One



**Figure 3.** Computed matrix elements from equation 1 as a function of  $R$  and for three values of the angle  $\theta$ . The two plots on the left show diagonal terms while these on the right report off-diagonal coupling terms.

further sees that the off-diagonal coupling acts over a broad range on  $R$  values, since the long-range polarization term remains active out to fairly large radial distances. The low energy range examined in the quantum dynamics discussed in the next section shows that the radial integration of the coupled equation was extended out to 500 Å, using the  $1/R^4$  asymptotic behaviour of the charge-polarization term.

### 3. Results and discussion

The calculations were carried out using the quantum Coupled-Channel (CC) method for solving the scattering equations. The in-house code which we have employed has been described in great detail before<sup>14–16</sup> and therefore we will not be repeating here its description. Suffice to say that the expansion over the asymptotic roto-vibrational states of the target always included 22 vibrational levels and up to 18 rotational levels per vibrational state. The number of closed channels needed for convergence turned out to be at least two, although many more were kept for the processes considered. The inelastic cross sections that we are interested in correspond to the cumulative quenching cross sections for target ions in an initially excited vibrational state  $\nu'$ , with  $1 \leq \nu' \leq 5$ . They are defined as:

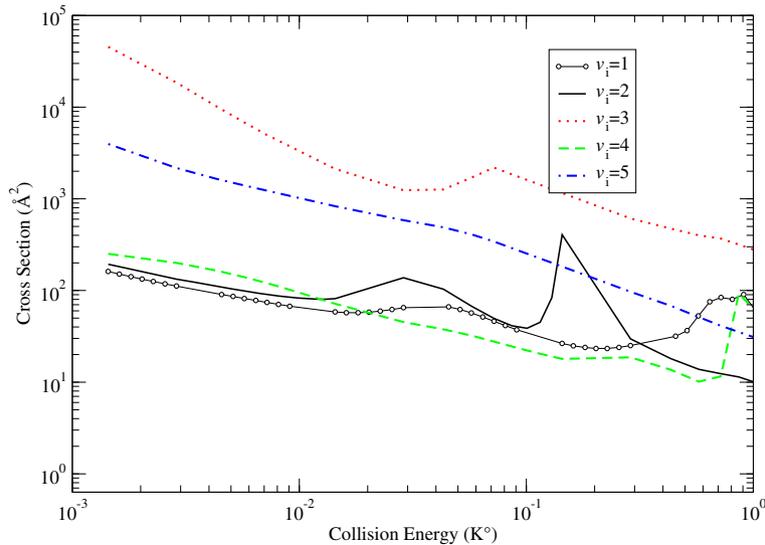
$$\sigma_{\nu'}^{sum}(E) = \sum_{\nu} \sigma_{\nu' \rightarrow \nu}(E) \quad \text{with } \nu < \nu'. \quad (2)$$

The energy range employed in the calculations, where we have also computed the elastic, cooling cross sections for each of the initial states examined for the quenching of vibrational internal energy of the ion, has been typical of those employed experimentally in the

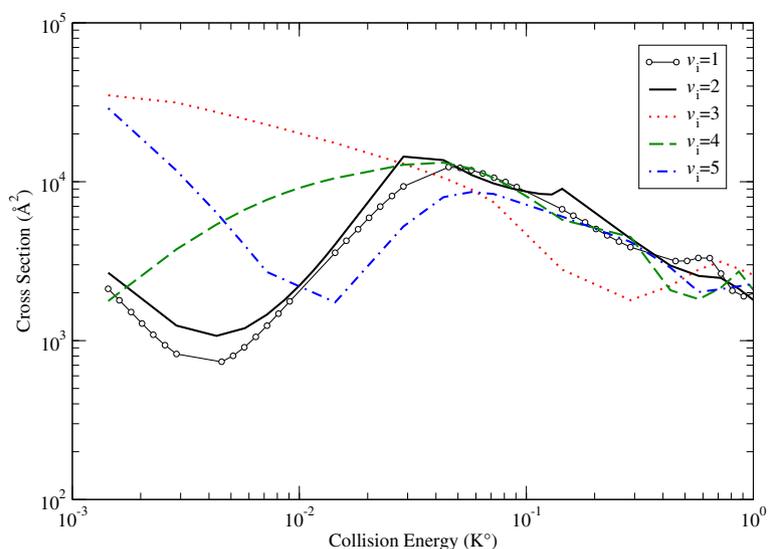
traps: between 1K and 1mK of temperature. The calculations reported in figure 4 show the energy behaviour, down to the mK regime, of the cumulative quenching cross sections in the case of  $\text{MgH}^+$  ions initially formed in one of the lowest five vibrational levels. Below about  $10^{-2}$  Kelvin one sees that all these quenching cross sections exhibit similar behaviour, in the sense that they increase in size as the temperature decreases and do so in a nearly linear fashion on a LogLog scale. This means that they are getting closer to reaching the Wigner's regime,<sup>17</sup> whereby the dominance of  $s$ -wave scattering causes a linear divergence of cumulative quenching cross sections on that scale.<sup>18</sup> One further sees that the quenching of vibrations is associated with fairly large cross sections that depend on the initial level of the trapped ion but do so not uniformly: the quenching of the ion in its  $\nu = 3$  level turns out to be more efficient than all other processes from neighbouring levels, an effect that we shall not further discuss here for reason of brevity. Suffice to note, that quenching efficiencies from the lowest two excited vibrational states of  $\text{MgH}^+$  ( $\nu = 1$  and 2) reach, around the mK temperature of a typical trap,<sup>10</sup> values of the order of  $10^2 \text{Å}^2$ .

If we now turn to the data shown in figure 5, we clearly see that the corresponding cooling cross sections for targets in the same vibrational levels ( $\nu = 1$  and  $\nu = 2$ ) are more than one order of magnitude larger under the same temperature conditions of 1 mK.

These results, therefore indicate that in ionic traps with  $\text{MgH}^+$ , when the latter is being produced in one of its lower vibrational states, the efficiency of its sympathetic cooling by He as a buffer gas is in general higher than the probability of adding extra translational energy to the trap's partners by collisional quenching of



**Figure 4.** Computed inelastic integral cross sections for different initial vibrational levels of the target ion.



**Figure 5.** Computed elastic integral cross sections as a function of the initial vibrational levels of  $\text{MgH}^+$ .

the cation's vibrational levels. The consequence of this findings from our present calculations is that it could become feasible to keep the molecular ion in the trap by He buffer cooling even when the initial molecule were to be formed in one of its excited levels.

In conclusion, by using an accurate calculation of the ionic forces, and their effects on the interaction between partners in the trap, and by further employing the *ab initio* PES within a time-independent quantum treatment of the quenching and cooling collisions, we have shown that it is indeed possible to assess beforehand the likelihood of such a mixture to survive after the trapping process without excessive trap losses of the molecular species.

### Acknowledgements

We thank the computational support of the CASPUR and CINECA consortia and the financial support of the Research Committee of the University of Rome 'Sapienza'.

### References

1. Doyle J M, Friederich B, Krems R V and Masnou-Seeuws 2004 *Eur. Phys. J D* **31** 149
2. Kohler T, Goral K and Julienne P 2006 *Rev. Mod. Phys.* **78** 1311
3. Bethlem H L, Berdem G and Meijer G 1999 *Phys. Rev. Lett.* **83** 1558
4. Bethlem H L, van Roij A, Jongma R T and Meijer G 2002 *Phys. Rev. Lett.* **88** 133003
5. Balakrishnan N and Dalgarno A 2001 *Chem. Phys. Lett.* **341** 652
6. Doyle J M and Friederich B 1999 *Nature* **401** 749
7. De Mille D 2002 *Phys. Rev. Lett.* **88** 067901
8. Julienne P S 2003 *Nature* **424** 24
9. Bodo E and Gianturco F A 2006 *Int. Rev. Phys. Chem.* **25** 313
10. Drewsen M, Mortensen A, Martinussen R, Staunum P and Sorensen J L 2004 *Phys. Rev. Lett.* **93** 243201
11. Drewsen M, Jensen I S, Lindballe J, Nissen N, Martinussen R, Mortensen A, Staunum P and Voigt D 2003 *Int. J. Mass. Spectr.* **229** 83
12. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Rob M A, Cheeseman J R, Montgomery Jr. J A, Vreven T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C, Pople J A 2003 Gaussian 03 (Wallingford: Gaussian, Inc.)
13. Jorgensena S, Drewsen M and Kosloff R 2005 *J. Chem. Phys.* **123** 094302
14. Martinazzo R, Bodo E and Gianturco F A 2003 *Comp. Phys. Commun.* **151** 187
15. Bovino S, Bodo E, Yurtsever E and Gianturco F A 2008 *J. Chem. Phys.* **128** 224312
16. Bodo E, Scifoni E, Sebastianelli F and Gianturco F A 2002 *Phys. Rev. Lett.* **89** 283201
17. Wigner E P 1948 *Phys. Rev.* **73** 1002
18. Balakrishnan N, Karchenko V, Faerey R and Dalgarno A 1999 *Chem. Phys. Lett.* **280** 5