LiH\(^{(X^2\Sigma^+)}\)+\(^3\)He rotational quenching at ultralow energies: spin-flip and isotopic effects from quantum dynamics on an ionic system

D. Lópe-Durán, M. Tacconi, and F.A. Gianturco

Department of Chemistry and CNISM, University of Rome “Sapienza”, Piazzale A. Moro 5, 00185 Rome, Italy

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Abstract. We study in this work the quantum scattering between a helium atom and a LiH\(^-\) molecule at low and ultralow energies. For the noble gas we have considered the two natural isotopes \(^3\)He, \(^4\)He, plus a “mock” \(^{3.5}\)He. Our aim is to clarify the role played by the isotopic changes of the mass in the buffer gas (in this case, helium) during collision events where the interaction is described through a newly computed ab initio rigid rotor potential between He and LiH\(^-\). The main conclusion of the present study is that this anionic species could be a good candidate for He-driven sympathetic cooling in traps since its elastic cross sections are always found to be larger than the inelastic ones in a relevant range of nearly vanishing energies. The \(^3\)He isotope is found to be more efficient than the other examples, yielding larger quenching rates in comparison with its heavier counterparts. Spin-flip inelastic channels are also analysed and discussed in terms of their dependence on the present, weak, interaction potential between partners and found to provide a further, interesting feature of the present mixture. The new results are also compared with those found by us in earlier, similar, quantum calculations on different systems.

PACS. 34.35.+a Interactions of atoms and molecules with surfaces – 34.50.-s Scattering of atoms and molecules – 34.50.Cx Elastic; ultracold collisions – 34.50.Ez Rotational and vibrational energy transfer

1 Introduction

The area of cold and ultracold molecular processes has witnessed a spectacular growth in the last few years, both from the theoretical and the experimental points of view [1–5]: many processes can indeed occur at very low collision energy, the most striking of them being the Bose-Einstein condensation, a feat first experimentally achieved in 1995 [6–8]. The typical temperatures reached in this kind of experiments are of the order of nK to mK. At these very low temperatures the de Broglie wavelength of the partners becomes large compared with the molecular dimensions; a completely quantum mechanical description is thus required and many fascinating effects are unveiled: control of chemical reactions [9,10], production of bosonic [11–14] and fermionic [15–18] quantum gases, formation of triatomic [19] and tetra-atomic molecules [20], testing of fundamental symmetries [21], such as the electric dipole moment of the electron [22–24], and quantum computation [25–27] are all examples of possible applications of the cold and ultracold molecular dynamical studies. Broadly speaking, there are two methods to produce cold, usually diatomic, molecules: direct and indirect ones. The former are based on the cooling of pre-existing molecules; the buffer gas cooling (BGC) [28] and the Stark deceleration are placed among them [29–32]. The most general, and fairly successful method is the BGC and many works have been devoted to it; this technique allows one to trap and cool down the molecule by transferring its excess energy to a buffer gas, usually helium. Next, an electromagnetic set-up prevents the species from escaping the trap [33,34].

Adding or removing a charge from the diatomic partner has dramatic consequences (for an illustrative comparison among the anionic, neutral, and cationic molecules of OH see Refs. [35–37]). The attractive well of the potential energy surface (PES) of the charged species is normally deeper than for the neutral: this influences the features of its bound states and so its behavior in the collisional processes. The scattering of cold, charged species with BGC gases has found a novel application in the study of the Coulomb crystals (CC): they are “solid state” plasmas that contain only particles with charges of the same sign and have been widely studied, theoretically and experimentally, during the last 10 years using laser cooled ions in traps [38–43]. A CC represents a very promising candidate system for quantum information processing, as inspired by the work of Cirac and Zoller [44]. Small “crystallized” ensembles of ions held in traps can be used to demonstrate quantum gates, simple algorithms [45–52], and to generate multiparticle entanglement [53].
Another interesting effect in ultralow collision processes is the change of the BGC mass: when comparing the collision behaviour of Li\(^+\)+H\(_2\) and Li\(^+\)+D\(_2\), for instance, we found that the individual inelastic cross sections are smaller in the case of the deuterated partner, for which Ramsauer-Townsend minima also appear in the elastic cross sections [54]. Another important feature of the molecular target that enrich the collisional dynamics and, hence, has to be taken into account is the electronic spin of the molecule and the consequent splitting of the rotational levels produced by the spin-rotation interaction. The collisional quantum dynamics of \(2\Sigma\)-molecules interacting with \(^3\)He and \(^4\)He have already attracted the interest of the computational community as in Balakrishnan et al. [55] where the CaH\((\Sigma^+\Sigma^-)\)-He system was analysed in details or in a more recent work of Guillon et al. [56] in which the N\(_2\)\((\Sigma^+\Sigma^-)\)-He has been studied. In general, however, it is not obvious how to anticipate the results of the collision or to identify some specific trend when changing the mass of the noble gas [57], hence the interest in analysing such effects in the present study. In conclusion, we find that the selection of an anionic species that is expected to exhibit a fairly weak, nearly van-der-Waals in nature, interaction with the buffer gas of choice here (i.e. He) can provide novel information on the general behaviour of collisional cooling at ultralow temperatures:

- give indication on the relative importance of the translational cooling channels vis à vis the rotational quenching channels;
- provide information on the feasibility of selecting a simple, light molecular anion as a partner for buffer gas cooling with He;
- see if the presence of spin-rotation coupling effects plays the role this effect has played in previous work;
- provide quantitative evidence for the possible differences in the size of final cross sections which can be had by using either \(^3\)He or \(^4\)He isotopes.

The paper is organized as follows: in Section 2 we describe the interaction potential and the quantum dynamics of this system, while in Section 3 the computational results are reported in detail. Finally, Section 4 summarizes the present conclusions and compares our findings with those of earlier works [55].

### 2 Interaction and dynamics

#### 2.1 Potential energy surface

##### 2.1.1 Isolated LiH\(^-\)

The initial calculations have been performed on the isolated fragment, LiH\(^-(\Sigma^+\Sigma^-)\), using the CCSD(T) method as implemented in the MOLPRO [58] suite of codes. We have employed the following basis sets: the aug-cc-pV5Z for the hydrogen atom and the cc-pV5Z for the Li atom. In an additional set of calculations we have also added bond functions (BF) at the centre of the molecule. In either set of calculations we have computed the molecular interaction energy always using the counterpoise implementation of the BSSE correction [59]. We have therefore obtained two potential energy curves (PEC) (with or without BF) that were fitted to an analytical Morse function and which have produced the results that are summarized in Table 1, where we also report the results from previous theoretical calculations [60,61] and the available experimental data [62] (for a recent and thorough review of the available theoretical data on the LiH\(^-\) molecular anion see Ref. [63]). The smaller value we obtained for the dissociation energy \(D_0\) with respect to previous computations is mainly due to the smaller basis sets we employ here compared to the previous works.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>5Z</th>
<th>5Z+BF</th>
<th>GNB</th>
<th>GL</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r_{eq}/\text{Å})</td>
<td>1.697</td>
<td>1.698</td>
<td>1.66</td>
<td>1.67</td>
<td>1.724</td>
</tr>
<tr>
<td>(\omega_e/\text{cm}^{-1})</td>
<td>1131.25</td>
<td>1131.72</td>
<td>1213.84</td>
<td>1167.5</td>
<td>920 ± 80</td>
</tr>
<tr>
<td>(\mu/D)</td>
<td>3.99</td>
<td>5.06</td>
<td>4.69</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(D_0/mE_h)</td>
<td>74.08</td>
<td>74.19</td>
<td>76.92</td>
<td>76.25</td>
<td>–</td>
</tr>
<tr>
<td>(D_0/mE_h)</td>
<td>71.5</td>
<td>71.61</td>
<td>74.16</td>
<td>–</td>
<td>74.12 ± 0.8</td>
</tr>
</tbody>
</table>

\(^a\) See reference [60], \(^b\) See reference [61], \(^c\) See reference [62].

Table 1. Computed properties of the ground state of LiH\(^-\) obtained at the CCSD(T) level and at the optimized geometry, using different basis set expansions. \(r_{eq}\) is the equilibrium distance; \(\omega_e = \hbar \omega\) where \(\omega\) is the angular frequency in the harmonic approximation of the vibrational motion, \(\mu\) the electric dipole. The pole in respect to the dipole is calculated is the centre of minimum of the potential well and the vibrational ground state, respectively. Finally, \(T_e\) is the total electronic energy.

Another test therefore tells us of the realistic quality of our chosen basis set for LiH\(^-\).