State-changing processes for ions in cold traps: LiH$^-$ molecules colliding with He as a buffer gas

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Abstract

We report in the present study a quantum analysis of the collisional dynamics involving a negative ion, LiH$^-$ in its $^2\Sigma^+$ ground electronic state, and He as a buffer gas in the environment of cold ion traps. The work focuses on the evaluation of the internal cooling collisional rates, treating both the anion’s rotational quantum numbers and the spin-changing processes. The calculations are carried out over a range of energies capable of yielding the corresponding rates for state-changing events over a rather broad interval of temperatures, thus covering those usually reached in the cold traps experiments and even beyond to lower temperatures.

Keywords: state-changing collision, quantum scattering calculations, rotational cooling in ion traps, ion–molecule inelastic scattering

(Some figures may appear in colour only in the online journal)

1. Introduction

The buffer-gas technique for cooling trapped molecular ions has been successfully established as a convenient method for producing internally cold molecular species, as well as for cooling their translational degrees of freedom. To be able to generate a broad variety of such cold species, which are then trapped for further processing, has provided new opportunities for a range of important applications: from precision measurements [1], to quantum information models [2], quantum-controlled chemistry [3] and the formation of such molecules in the interstellar medium (ISM) [4].

Although the above schemes are applicable to either cations or anions, the latter types of charged molecular species play a central role in a wide range of areas, from the chemistry of highly correlated systems [5] to various aspects of atmospheric science [6]. They also turn out to be relevant for a broad variety of molecular processes involving the ISM environments [7]. On the other hand, it is currently not as yet simple to experimentally investigate negative ions in a controlled manner at the cold and ultracold temperatures which are expected to be relevant for many of the processes mentioned above. Indeed, by using supersonic beam expansion methods or by trapping the particles and then acting on them, the use of electron cooling, buffer gas cooling or resistive cooling [8–11] have already achieved temperatures of a few kelvin, while the ability to cool molecular anions to subkelvin temperatures is still in the planning [12]. To achieve it would finally allow the investigation of their chemical and physical properties to be extended over a much enlarged range of possibilities.

We already know that most temperature measurements usually rely on high-resolution spectroscopy which can then
resolve the molecular Doppler profile in order to determine the kinetic temperature of the trapped ions [13], while the corresponding effective temperatures for their internal degrees of freedom have also been measured using rotationally-resolved spectroscopy for rotational temperatures [14] and sometimes also vibrational hot band analysis for the vibrational temperatures [15]. On the other hand, the recent work done in the Innsbruck’s group on trapped molecular anions clearly demonstrates that the near-threshold, bound-free photodetachment spectroscopy can act as a ‘thermometry scheme’ for specific molecular anions which are kept into a multipole radiofrequency ion trap [16–18]. In such a scheme the ions are further subjected to buffer-gas cooling using cold helium gas, and the temperature of the latter can be varied between a few kelvin and room temperature.

The above experiments indeed point at the real possibility of investigating a new class of chemical processes involving molecular anions where one would then be able to prepare the ionic partner in a specific initial, selected internal state. The latter can then be used to give us more specific information on the chemical paths along which the experiments could develop [18].

To complete the task as best as possible, however, one needs to collect additional data on the details of the collisional dynamics in the traps: How is the buffer gas effectively cooling the translational motions? How large would the internal rotational cooling rates be for a specific initial population and how efficiently are the internal states excited to higher levels by collisional excitations from the buffer gas, in clear competition with the collisional cooling paths?

To try to answer such questions for the case of the OH− anion trapped with either He [18] or Rb [19] atoms, we have already studied in detail the forces at play and further employed them to obtain quantum data on the dynamics of state-changing collisions in the trap environments [18–20]. Any extension of such studies to other possible molecular anions, as those discussed in [12], would therefore require all of the above steps and the modelling of the ensuing collisional state-changing efficiency via realistic quantum calculations.

In the supplementary material of [12], one of the light anionic molecules which was suggested to be suitable for internal states cooling down to the ground rovibrational levels, under the conditions of cold ion traps, was the LiH (2Σ+) system which has been known for a while as an interesting and stable anion. It has also been studied by us by smoothly connecting the actual interaction was further extended to the long-range (LR) region by looking at the dynamics of its internal rotational quenching at the microkelvin regimes under the collisional action of 4He and 3He projectiles [21].

In the present study we want to extend the analysis of [21] to more realistically higher temperatures which could then model and match the actual environment that was observed in the work on the OH− anion in [18]. We therefore intend to provide realistic data for the internal cooling of rotations in the case of LiH− anion trapped at a few kelvin of translational temperature and interacting with 3He as the buffer gas uploaded into the trap. Hence, we shall span a more extended energy range with respect to our earlier study of [21] and provide new data on the efficiency of the production of LiH− ions in their ground rovibrational state under the same experimental conditions as those reported by [18].

It is also interesting to note that a very recent computational study [22] on the dynamics of LiH− formation suggested that the processes of electron transfer and electron detachment were not expected to be very efficient, thus indicating that several paths to LiH− formation in its (2Σ+) electronic states could be used experimentally to successfully stabilize the anion.

The next section 2 will briefly review the feature of the relevant potential energy surface for the LiH− as a rigid rotor and the 3He projectile in its ground electronic state. The computational quantum dynamics will be summarized in section 3 and our results will be given by section 4. The final conclusions will be in section 5.

2. The anisotropic interaction potential

The original calculations of the interaction potential between the LiH (2Σ+) anion and 4He(3S) neutral atom have been described in detail in our earlier publication [21]. We therefore report here only a brief outline of its anisotropic features. The actual ab initio calculations were carried out using the MOLPRO’s suite of codes [23] and all the details over the basis set expansion choice, the number of points of the 2D potential energy surface, defined as $V(R, \theta_{eq})$, where the bond distance of the target anion was kept fixed at 1.697 Å, are all given in [21]. Here $R$ and $\theta$ indicate, using Jacobi coordinates, the distance between the 4He atom and the molecular centre-of-mass, while $\theta$ is the angle formed between that distance and the molecular bond: the $\theta = 0^\circ$ corresponds to the Li–H–He configuration.

The system, as expected, turned out to be very anisotropic and with only a very shallow attractive well of about $-15$ cm$^{-1}$, located around $\theta = 40^\circ$. The corresponding interaction was further extended to the long-range (LR) region by smoothly connecting the actual $ab$ initio points with the expression:

$$V_{LR}(R, \theta_{eq}) = \frac{C_4 f_4(\beta R)}{R^4} + \frac{C_6 f_6(\beta R)}{R^5} \cos \theta,$$

where the $f_n(\beta R)$ are the Tan–Toennies damping functions, discussed in detail in our earlier work [24]. The $C_4$, $C_6$, coefficients correspond to the dipole polarizability term and to the dipole-induced dipolar term, respectively [21].

To provide an overview of the interaction forces, we present in figure 1 the shape of the corresponding multipolar coefficients for the full rigid-rotor (RR) potential:

$$V_{RR}(R, \theta) = \sum_{\lambda=0}^{6} V_\lambda(R) P_\lambda(\cos \theta),$$

where
R α runs over all the included asymptotic states of the \((α, J)\) s \((α', J')\) U \((D)\) explicit inclusion of spin-rotation contributions, The time-independent scattering eigenstates, as yet without 3. An outline of the quantum scattering equations shall describe below.

\[ \Psi^{(α, J)+}(R, x) = \sum_{(α', J')} G_{(α, J)→(α', J')}(R) X_{(α', J')}(x), \]  

where \(α\) is the collective index of the molecular initial state while \(α'\) runs over all the included asymptotic states of the diatomic target, \(L\) is the relative angular momentum between the atom and the target. The \(X_{(α', J')}(x)\) terms are the asymptotic eigenstates of the whole system (the channel eigenstates). The \(G\) terms are the channel components of the scattering wave function, which must be determined by solving the Schrödinger equation, subject to the boundary conditions which we have extensively discussed in our earlier work. The scattering algorithm we are using in the present study is described in [25].

Once the dynamics is cast in the conventional, time-independent formulation (e.g. see [26]), then the coupled equations in the space-fixed (SF) reference frame of the multichannel scattering problem for \(M\) channels can be expressed in atomic units as

\[ \left\{ \begin{aligned} &L^2(R) \frac{d^2}{dR^2} + \frac{L^2(R)}{R^2} + K^2 - V(R) \\ &G(R) = 0 \end{aligned} \right\} \]  

where \([L^2]_{ij} = δ_{ij} L_i(L_i + 1)\) is the matrix of the square of the orbital angular momentum operator, \([K^2]_{ij} = 2μ(E - ε_i)\) is the diagonal matrix of the asymptotic (squared) wavevectors, and \(G\) a column vector for the radial \(G\)'s channel components of the scattering wave function. The parameter \(V, V = 2μU, \) represents the potential coupling matrix. In the case of atom-RR diatomic scattering is given by

\[ 2μ \sum_{\lambda} V_{\lambda}(R) f_3(α, L, α', L', J), \]  

where \(α\) denotes the diatom initial states, \(V_{\lambda}(R)\) the multipolar coefficients already shown in equation (3) and by figure 1. The \(f_3\) terms represent the integrals over the angular coordinates of the coupling potential in the relevantly required basis set. The special case where spin-rotation coupling appears was discussed by the earlier work of Corey and McCourt [27] and will be further discussed in more detail in the subsection below.

The scattering equations of (5) were solved by employing out-in-house scattering code ASPIN, [28]. Numerical convergence of the final \(S\)-matrix elements, and hence of the final state-to-state inelastic cross section was achieved within more than 1%. Some of the specific parameters employed will be further discussed in the following section.

In the present case we further need to take into account the doublet electronic state for the target molecule. Hence, we have to consider two levels for each total angular momentum since the rotational levels are now split by spin-rotation coupling contributions.

In the pure Hund’s case (b) the electronic spin momentum \(S\) couples with the nuclear rotational angular momentum \(N (N = R \text{ for a } Σ \text{ state})\) to form the total angular momentum \(J\) given by

\[ J = N + S. \]
interaction. In this representation each state has a de
cm B where

\[ F \]

(\[ N \]

quantum number along the

J

and

parity with respect to the inversion of the SF axis

is split in two sublevels

and

1

1

2

3

4

5

6

7

Here each level (with \( N \geq 1 \)) is split in two sublevels

\( F_1 \) and

\( F_2 \), and the corresponding rotational wave functions are

\[
|F_1Jm⟩ = \begin{cases} 
J = N + \frac{1}{2}, & S J m \\
J = N - \frac{1}{2}, & S J m
\end{cases}
\]

\[
|F_2Jm⟩ = \begin{cases} 
J = N + \frac{1}{2}, & S J m \\
J = N - \frac{1}{2}, & S J m
\end{cases}
\]

where \( m \) is the projection of the \( J \) quantum number along the

SF \( z \) axis.

For a given \( N \) value, the energies of the two levels in

equations (8) are [29]

\[
E_{J=N+\frac{1}{2}} = BN (N + 1) + \frac{1}{2} \gamma N,
\]

\[
E_{J=N-\frac{1}{2}} = BN (N + 1) - \frac{1}{2} \gamma (N + 1),
\]

where

\( B \)

is the rotational constant and
\( \gamma \)

is the spin-rotation

interaction. In this representation each state has a definite
parity with respect to the inversion of the SF axis [27]. The
energies of some of the fine-structure levels are given in
Table 1, where the columns are labelled by the quantities
defined via equations (8). The actual values of the target
parameters were

\( B = 6.657 \text{ cm}^{-1} \)

and

\( \gamma = 6.124 \times 10^{-4} \text{ cm}^{-1} \).

The error bars for each parameter involve the third
significant figure. The spin-parity \( \epsilon \) is defined as ‘even’ or
‘odd’ for the two spin states of \( |+1/2⟩ \) and \( |-1/2⟩ \) indicated in
equation (9).

We checked the importance of centrifugal distortion on the rotational energy of LiH by extracting them from the computed potential energy curve of the molecular anion. We used a complete active space self consistent field wave function, an aug-cc-pV5Z basis set for the H atom and a cc-
pV5Z basis set for the Li atom. The CAS used in the calculation has been of 3 active electrons within 5 active orbitals.

We found a slight change in the value of \( B \), found to be

6.659 cm\(^{-1}\), and a distortion correction \( D = -8.36 \times 10^{-4} \text{ cm}^{-1} \).

The smallness of the latter, we did not include the centrifugal distortion and employed instead the simpler formula (9), as already discussed in [21].

As mentioned before, we give in Table 1 some of the numerical values associated with the fine-structure level splitting of equation (8) and the corresponding \( (N, J) \) values associated to them. We further summarize in Figure 2 a pictorial view of the levels, where the smallness of the energy splitting due to the fine-structure effects is also clearly displayed.

From the energy spacings of both the table and the figure we see that the \( \Delta N \neq 0 \) transitions are obviously much larger than the spin-rotation splitting values which correspond to spin-reorientation processes within each term of the \( N \) manifold. If one further recognizes that the present interaction potential is basically describing electrostatic interactions without direct magnetic terms, we already see that spin-reorientation can only come in via the angular momentum coupling anisotropy, where the spin term acts essentially as a spectator. This feature has been discussed many times before in the relevant literature (e.g. see [30]) and will be further discussed below when analysing our present findings.

4. Results from calculations

4.1. Computed inelastic cross sections

It is important to note at this point, as already discussed in the relevant literature, that the present coupling situation includes an additional degree of freedom which does not exist for the simpler case of a \(^1S^+\) atom and a \(^1Σ^+\) molecule [27, 30, 31], namely the parity index of the initial and final states described by equation (8). These collisions can be inelastic in \( S \) and elastic in \( J \) and vice versa. They can also be inelastic in both \( S \) and \( J \). We know, in fact, that in the present case \( N \) and \( S \) are coupled (see equation (7)) to form \( J \), the total angular momentum. Thus neither \( N \) nor \( S \) are fixed in their directions: both precess around \( J \).

Since for \( S = -1/2 \) \( J < N \), it follows that \( S \) and \( N \) form an acute angle: \( N \cdot S < 0 \). The opposite occurs for \( S = +1/2 \). Hence, since there are no spin-dependent terms in the interaction potential, the collisions in the traps cannot directly affect either the magnitude or the orientation of \( S \). On the other hand, the collisions can cause such changes for the \( N \) vector and therefore, after the collision, a recoupling of the new \( N' \) with \( S \) to form \( J \) can result in changes of both \( |J⟩ \) and the spin parity from \( |±1/2⟩ \) to \( ±1/2⟩ \).

We therefore see that the anisotropy of the interaction potential (fully electrostatic) can modify the collisional torque and therefore cause ‘spin-flip’ effects through the angular momenta recoupling process after the collision has occurred.

The above analysis was clearly presented years ago by Alexander et al [30, 32], who considered the recoupling formalism that establishes the cross section for a particular \( NJ \rightarrow N'J' \) transition as a sum of irreducible tensorial
components of order $K$,

$$\sigma_{N J \rightarrow N' J'} = \frac{\pi}{k^2} (2J' + 1) \sum_k \left\{ \frac{N}{J'} \frac{N'}{J} \frac{K}{S} \right\}^2 p^k(N', N),$$

where \{\ldots\} is a 6j symbol.

In the last expression, $K$ represents a momentum transfer index which can be classically interpreted as the degree of reorientation of the nuclear rotational angular momentum during the collisions. Thus, equation (10) can be regarded as a weighted sum of probabilities associated with increasingly large degrees of angular momentum transfers.

The low order tensor opacities, and therefore the small collisional transfers of angular momentum, correlate with small nuclear rotational angular momentum reorientation angles as mentioned earlier. The contribution of each term decreases as $K$ increases, which is in fact a manifestation of the propensity toward the conservation of the orientation of $N$ during collisions. Various aspects of the above analysis will be brought to light by our calculations of the present study.

Three specific examples of their behaviour are reported by the inelastic cross sections shown by figures 3–5, where three different types of processes are shown starting from three different initial $N$ values, $N = 1$ through $N = 3$ from figure 3 through 5. All the initial states are associated with the even spin parity of the $S = +1/2$ orientation.

The quantities reported in all three figures represent the possible options during inelastic collisions that were outlined in the previous qualitative discussion:

(i) ‘pure spin-flip’ processes indicate that the transitions involved correspond to $|N, +1/2\rangle$ as initial state that goes into $|N', N, -1/2\rangle$ as a final state. In other

Figure 2. Pictorial representation of the fine-structure level splitting value (left panel) and of the first six rotational level energy separations (right panel).

Figure 3. Computed inelastic cross sections over a broad range of collision energies. The meaning of the processes labelled: ‘pure spin-flip’, ‘rotational cooling’ and ‘rotational heating’ is explained in the main text. The initial state of the LiH target is given a $|N = 1, S = +1/2\rangle$, rotational level energy separations (right panel).
words, through the recoupling terms of equation (10) the \( J \)-orientation process controls the spin-parity change while the orientation of \( N \) is conserved and the \( P^k \) contribution increases since the momentum transfer to total-reorientation vanishes;

(ii) the processes labelled as ‘rotational cooling’ describe rotational state-changing collisions where both \( N \) and \( S \) change to all available values of the final \( N' \) level. Hence, all transitions from the selected initial \( N \) go down to all \( N' < N \) levels available and to all its \( S \)-controlled levels. For the data of figure 2, only \( N' = 0 \) is obviously available for the \( N = 1 \) initial state;

(iii) the processes labelled as ‘rotational heating’ describe the opposite collisional events whereby transitions occur, from an initially selected state, to all accessible upper final states (without the pure elastic channels) and involve also the spin-parity changes.

The overall behaviour of the above three types of inelastic processes is fairly similar in the three figures and can be described by the following general features:

(1) in the low-collision energy regimes (e.g. from \( 10^{-3} \) cm\(^{-1} \) to about \( 40 \) cm\(^{-1} \)) the parity-reorientation process seems to dominate the collisions since it corresponds to the recoupling situation whereby no angular momentum transfer occurs and the electronic spin changes because now the anisotropy of the interaction acts at reorienting the rotational angular momentum \( N \);

(2) as the collision energy increases into the region of realistic trap conditions, the collisional cooling of molecular rotations involves changes in both \( N \) and \( S \) through the reorientation of \( J \) and therefore their sum overcomes the pure ‘spin-flip’ processes since it also include cases where spin-parity changes form \( S = +1/2 \) to \( S = -1/2 \). Such contributions increase at higher collision energies since the corresponding cross sections extend their range of opacity contributions (contributing relative angular momentum \( L \) values) as a larger number of their values contribute to the \( P^k \)'s probabilities of equation (10). In the lower energy range, in fact, fewer \( L \) values contribute and therefore the sum in equation (10) has fewer terms with \( K = 0 \), while the latter terms dominate over spin-parity change processes [30, 32] as the collision energy increases.

(3) Another interesting point to note is the large values of ‘rotational heating’ cross sections that we obtain beyond about \( 100 \) cm\(^{-1} \) of collision energy. We see from the levels’ positions given by figure 2 that the accessible excitation processes become more numerous and the variety of transitions involving both rotational-state changes and spin-parity changes increase thereby contributing to the dominance of the excitation channels over the cooling channels that are instead larger at lower energies.

One should also keep in mind that the present study treats the molecular target as a RR in its ground state vibrational level. The weakness of the interaction with He atoms, and the energy range considered, would not make vibrational excitations to be significant for the present study. The RR approximation further implies that the level of anharmonicity for the ground-state vibrational wavefunction is very small. We have tested this assumption and found it to be verified for the target anion. We therefore can consider the present treatment to realistically handle the collisional energy transfer processes in the title system.

4.2. Investigating the resonant features

The data from the present calculations reported and discussed in figures 3 through 5 indicate the presence in the computed cross sections of several marked structures which could be attributed to resonant behaviour and that may be worth
In order to gain further insight into the quantum dynamics of the light system at hand, the most prominent of them appears on all types of cross sections and is located down to the low collision energies around $3 \times 10^{-3} \text{ cm}^{-1}$. As is well known, resonant structures could originate either from closed-channel effects, as in Feschbach resonances, or from dynamical trapping beyond centrifugal barriers as in the case of shape resonances due to open-channel effects. To briefly investigate the options, we have repeated the calculations around that range of collision energies and have excluded all the closed-channels which we had included in the previous calculations: the data in figures 3 through 5 included at least four closed $J$ states to reach convergence at all energies.

The results are compared in the two panels of figure 6, where we provide as an example the case of one of the initial molecular states discussed in the previous figures, i.e. consider the transitions from the $|N = 3, S = +1/2\rangle$ initial state to all the lower ones.

Figure 6. Computed inelastic cross sections in the low-energy range of the large resonance feature of figures 3 through 5. The upper panel reports the data where rotational quantum number and the spin-parity change from each state, while the lower panel reports the cases where the spin-parity is not modified when changing the total rotational quantum number $N$. The unmarked curves include closed channels in the calculations, while the marked curves have no closed channels included.

The following information could be gathered by looking at the modified behaviour of the cross sections indicated in both panels of figure 6:

(i) as expected, the spin quantum number plays the role of a simple spectator: the parity changes or the parity-conservation processes do no affect the coupled channel dynamics and all cross section curves shown in the present work are essentially the same in both panels of that figure;

(ii) since we are considering in the example the ‘rotational cooling’ processes, we see that when $-\Delta N$ increases along each series of cross sections their corresponding values decrease quite markedly. Around the resonance peak, in fact, the cross section values change by more than three orders of magnitude when going from $-\Delta N = 0$ through $-\Delta N = 3$. Furthermore, the possible role of closed-channels dynamics becomes more marked as $-\Delta N$ increases;

(iii) additionally, spin-conserving cross sections are uniformly larger than those where both $N$ and $S$ change: in the former cases the larger momentum transfer terms in equation (10) play a greater role than in the latter situation where spin-parity changes can result in fewer $K$ values contributions to the probabilities of equation (10). Thus result is similar to what we have previously discussed in figures 3 through 5;

(iv) a remarkable finding is also given by the fact that essentially no size changes are seen in the $N = 0$ and $-1$ cross sections when the closed-channels are excluded in the computed dynamics. The resonances in these channels are therefore largely due to open-channel effects of barrier trappings of the complex of light atoms behind the few angular momenta contributing at such low energies (shape resonances). As $-\Delta N$ increases, however, we see that the changes in the cross sections increase, suggesting that greater effects from closed channel dynamics could occur for the transitions with $-\Delta N > 1$.
The opacity function was also computed at the energy for which another resonant structure appears in the ‘rotational cooling processes reported earlier by figure 3. The opacity data as a function of the total relative angular momentum \( L \) (classically speaking, the collisional impact parameter) are reported by figure 7.

In the present case only the \( -\Delta N = 1 \) transition was possible and we see once more, in fact, that no visible changes in the cross sections occur when all the closed channels are excluded during the dynamics.

Furthermore, we also see that the dominant relative angular momentum values appear to cover a broad range of opacity values and uniformly increase their contributions as \( L \) increases. The largest contributions are clustered around the \( L = 25 \) value. Such values indicate that mainly one type of shape resonance contributes to the resonant cross section, while those at the lower \( L \) values undergo tunnelling more rapidly, thereby giving rise less efficiently to the formation of trapped complex. In other words, the resonant features appear to be linked to centrifugal trapping dynamics between weakly interacting light particles rather than to virtual excitations into closed rotational states of \( \text{LiH} \), these being the signature features of a Feshbach resonance.

Another example of the above behaviour could be had by analysing yet another of the cross-section features, i.e. the one appearing in figure 4 around 60 \( \text{cm}^{-1} \) for the cross sections associated to the ‘spin-flip’ changes due to the recoupling dynamics. The behaviour of the relevant cross sections is reported by figure 8.

The figure reports the opacity functions associated with processes that cause only spin-symmetry changes and no changes in the nuclear rotational angular momentum \( N \) of the initial \( \text{LiH} \) target. The coupled equation expansion involves a set of \( J \) angular momentum values which are energetically closed and increase up to \( 13/2 \) to get numerical convergence. When the number of closed channels is reduced up to \( J_{\text{max}} = 9/2 \), the spin-changing opacity changes very little, while it gets modified more markedly when the spin-changing transitions involve only the levels only up to \( J = 7/2 \). Here again the coupling is modified not by state-changing dynamics (here \( \Delta N = 0 \)) but rather by the extension of the recoupling terms in equation (10). When only two \( J \) values are possible the reorienation processes between \( N \) and \( J \) are artificially reduced and therefore the opacity functions change for that process. The ‘close’ channels are needed not to control the dynamics (as seen by the very similar dependence on \( L \) of all cross sections) but rather to correctly describe the recoupling between \( N \) and \( J \) when \( S \) changes parity.

**4.3. Calculations of state-changing rates**

The previous cross sections can now help us to identify the behaviour of the corresponding state-changing rates over a range of temperatures which can realistically describe that in a cold ion trap.

We have calculated the above rates from a few kelvins up to 50 K of trap temperature and employing cross section values up to 1000 \( \text{cm}^{-1} \). For the integration’s convergence we started with \( E \) values above threshold and employed for each state-to-state rate a unevenly-spaced number of energy values. Numerical convergence was thus checked to be better than \( 10^{-2} \).

The data we are presenting below involve both ‘rotational cooling’ and ‘rotational heating’ processes with and without spin-symmetry changes.

The following comments could help understanding the data reported by figure 9:

(i) as expected, the \( \Delta N = 0 \) rates are the largest ones and describe the reorientation of \( N \) around \( J \) after the spin-parity changes. As discussed before, the \( K \) value goes to zero and the recoupling effects in equation (10) are dominating the process;

(ii) the state-changing ‘rotational cooling’ rates are also fairly large and become comparable in size as the trap temperature reaches about 50 K. The largest differences are seen around 5–10 K when the dynamics involve
fewer contributing $L$ values during the reorientation of $N$ and $J$;

(iii) the ‘rotational heating’ processes are seen to be largest when $\Delta N = 1$ and $\Delta J$ and the spin-symmetry does not change \cite{30, 32}. On the other hand, they are slowly increasing with temperature and, around 50 K, still remain smaller by one or more orders of magnitude than the ‘rotational cooling’ process of the upper panel.

When we now examine the results reported by figures 10 and 11, the general trend remains essentially the same as that in figure 9, although more transitions are now possible since the initial states selected for LiH$^-$ target are now \( |N = 1, S = +1/2 \) in figure 10 and \( |N = 3, S = +1/2 \) in figure 11.

What we basically see, therefore, is that the state changing processes involving $\Delta N = -n$ transitions are largely dominated by the $\Delta N = -1$ process in both sets of data in the two figures. Furthermore, the corresponding $\Delta N = +1$ excitation processes remain largely less efficient than the cooling processes while dominating the ‘rotational heating’ events. As mentioned before, we also see that the $\Delta N = \Delta J$ processes remain the preferential ones.

5. Conclusions and outlook

In the present study we have analysed in some detail the quantum dynamics of state-changing collisions of a simple molecular anion, the $\Sigma^+$ LiH, at the relatively low temperatures of a cold trap when $^4$He($^1S$) participates as a buffer gas partner.

The special situation created by the presence of a doublet electronic configuration for the molecular partner has been taken into account to discuss the fine-structure effects in the possible dynamics, at least from the computational viewpoint.

The resonance features which appear in the various types of examined cross sections are briefly analysed and indicate that their occurrence is chiefly due to open-channel, relative angular momentum trapping of the colliding light partners, rather than to the presence of virtual excitations of the molecular anion’s states during the collisions. It therefore seems that the fairly weak interaction forces of the system
allow for very little participation of Feshbach resonant features in the cross sections. The behaviour of the rotational cooling rates indicate also general similarities between the present system and the one already analysed earlier experimentally: the OH (3Σ+7) plus 4He (5S) [18]. In the latter case, in fact, the ΔJ = −1 computed state-changing rates turned out to depend very little on the temperatures of the trap in the range between 10 and 50 K and to be of the order or about 5 × 10−11 cm3 s−1. Our corresponding rates for ΔN = −1 (see figure 9) start around 5 × 10−11 cm3 s−1 at 10 K but markedly vary with temperature up to 50 K so that they double in size up to about 10−10 cm3 s−1.

Correspondingly, the rotational heating, state-changing cross sections also seem to follow comparable patterns: in the case of OH− with He, in fact, the rotational excitation rates from the |J = 0⟩ level varied from about 10−13 cm3 s−1 at 10 K to about 5 × 10−11 cm3 s−1 at 50 K. Our calculations of figure 9 (lower panel) show the ΔN = +1 excitation rates from the |N = 1, S = +1/2⟩ to vary from 5 × 10−13 cm3 s−1 at 10 K up to about 5 × 10−11 cm3 s−1 at 50 K. The two systems therefore exhibit very similar behaviour, at least when tested through computational models. Since the experiments of [18] further indicate remarkable agreement between measurements and calculations around 15 K of trap temperature, it could also be interesting to design similar experiments for the LiH− anion under trap conditions: the calculations suggest, in fact, that the size of the state-changing probability might also turn out to be rather similar and thus also becoming observable.

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