

# Rotationally inelastic collisions of LiH ( $X^1\Sigma^+$ ) with H: State-to-state inelastic rotational cross-section

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## Abstract

The potential energy surface describing the interaction between the hydrogen atom and the rotating LiH molecule has been calculated very accurately and presented in our previous work (J. Mol. Struct. (THEOCHEM) 678 (2004) 11). The rigid rotor potential already fitted analytically and expanded in terms of Legendre polynomials, is employed here to evaluate the pure state-to-state rotational cross-sections over a range of energies of astrophysical interest varying from 10 to 3000  $\text{cm}^{-1}$ . An exact close coupling and CS calculation of the state to state rotational cross-section was done first in the range of small energy, from 10 to 100  $\text{cm}^{-1}$ . The comparison of both results shows the good agreement between them and leads to a generalisation of such calculation for higher energy using the CS approximation. We determine the state to state rotational cross-section for transitions from  $j = 0, 1, 2, 3, 4$  to all accessible final states  $j'$ , at total energy varying between 10 and 3000  $\text{cm}^{-1}$ . The presented cross-sections were found to be very large even for low energy and large  $\Delta_{jj'}$ . Thus indicates the important probability to produce the heated LiH molecule in excited states by collisions with H and explain the strong anisotropy discussed in our previous paper.

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*Keywords:* Potential energy surface; LiH; Close coupling; Inelastic collision; Rotational cross-section

## 1. Introduction

In the primordial universe, LiH is present with lower concentration than  $\text{H}_2$  and HD. However, it is of particular astrophysical interest due to its large dipole moment,  $\mu = 5.88 \text{ D}$  [1]. Hot excited LiH molecule exhibits several intense radiative rovibrational transitions [2]. The LiH molecule can be produced through radiative association, associative detachment or transfer reaction [2–4]. Therefore, LiH may have played an important role in the radiative cooling of primordial gas clouds [5–7]. The consequences and effects of the presence of the LiH in the early universe was studied in various works [8–10]. The possibility of forming the LiH molecule in excited nuclear states is related to the efficiency of collisional transfers from the most abundant species in the interstellar medium [11] and specially through collisions of LiH with H,  $\text{H}^+$ , He and  $\text{He}^+$ .

In our previous paper [12] we have evaluated the interaction forces between LiH (in its equilibrium distance:  $r_e = 3.014 \text{ a.u.}$ ) as a target and H as a projectile, in terms of Jacobi coordinates  $V(r_e, R, \gamma)$ . We have employed the pseudopotential techniques where the  $\text{Li}^+$  core was replaced by a pseudopotential and the H–LiH system was reduced to a three electrons system. A large configuration interaction was realised and have produced accurate rigid rotor potential for a dense grid and a wide number of orientations. The good accuracy, the unusual feature, and the strong anisotropy of the potential energy surface were discussed and analysed. Thus presents an important step for the calculation of excitation efficiency of that molecule at the temperature of relevance for the interstellar medium.

Many works have been done [13–15] to study the possibility of forming the LiH in excited rotational levels by collision with the He atom. For our best knowledge, our work on the H–LiH interaction is the first work. Having an odd number of electrons, and presenting a strongly interacting system, the H–LiH presents a benchmark system for theoretical studies for both intermolecular

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potentials and collision energy transfer. To this aim the present work focuses on the calculation of the pure rotational state-to-state cross-sections using the accurate potential energy surface produced in our last paper [12].

Section 2 describes the collision theory used to evaluate the cross-section. In Section 3, we present some results of the calculated state-to-state rotational cross-sections. Finally we summarize by the conclusion.

## 2. Theoretical method

At short distances region, we interpolated the potential energy surface by the analytic form proposed by Heiliter and London [16]:

$$V(R) = Ae^{-BR} \quad (1)$$

In the region  $2.25 < R < 6$  a.u., there is an elementary transfer of charge between the three atoms showing a real chemical bond. For larger distance, the Li is charged positively, the first atom of hydrogen is charged negatively, whereas the second atom of hydrogen is neutral. In fact from this distance, we can model our system by an interaction between a dipole ( $\text{Li}^+\text{H}^-$ ) and a neutral hydrogen atom. Thus at large distances, our system is equivalent to an interaction between a dipole and a neutral entity. For a dynamic study, it is necessary to have an analytic form. Thus the curves, for all orientations, were interpolated on a very dense grid going beyond 200 a.u. Using the fact that in this region the types of strengths of interaction are of electrostatic, polarization and diffusion types, we express our potential following the analytical form

$$V(R, \gamma) = -\frac{C_3^{\text{el}}}{R^3} - \frac{C_4}{R^4} - \frac{C_6}{R^6} - \frac{C_8}{R^8} \quad (2)$$

The multipolar expansion was produced in our previous paper and used to explain and to analysis the strong anisotropy in the RR interactions

$$V_{\text{RR}}(R, \gamma) = \sum_{\lambda=0}^{\lambda_{\text{max}}} V_{\lambda}^{\text{RR}}(R) P_{\lambda}(\cos \gamma) \quad (3)$$

Where  $R$  is the separation between the H atom and the center-of-mass of the LiH molecule, and  $\gamma$  is the angle between  $R$  and the LiH internuclear axis.

In this work they are used in the standard close-coupling (CC) formulation of atom-rigid rotor collisions, where the determination of the required matrix elements of the potential is facilitated by the usual expansion in Legendre polynomials. In this case a large number of terms was used in order to ensure convergence in the representation of the full potential energy surface.

The CC equations describing the quantum collision between a spherical atom and a polar diatomic molecule are

expanded

$$\left( \frac{d^2}{dR^2} + k_{j'j}^2 - \frac{l(l+1)}{R^2} \right) u_{j'l'}^{j'l}(R) = \sum_{j''l''} \langle j'l'|V|j''l'' \rangle u_{j''l''}^{j'l}(R) \quad (4)$$

where

$$k_{j'j}^2 = 2\mu(E_j - E_{j'}) \quad (5)$$

and

$$E = \frac{k_j^2}{2\mu} + \varepsilon_j = E_j \quad (6)$$

is the total energy; and  $\varepsilon_j = B_j(j+1)$  is the internal energy of the  $j$ th rotational state of LiH. The coupling matrix elements include the RR anisotropic potential determined below.

The size of the coupled equations increases very rapidly in CC representation because of the  $(2J+1)$  multiplicity of the states. For small collision energy, it still possible to resolve the coupled equations and obtain exact solution. In contrast for large energies, the computing time increases rapidly and simplification have to be included. One of the various approximation methods is the coupled state (CS) decoupling scheme, introduced originally by Kouri [20]. In this approximation, the equations are written in the body-fixed rotating frame with the  $z$ -axis pointing

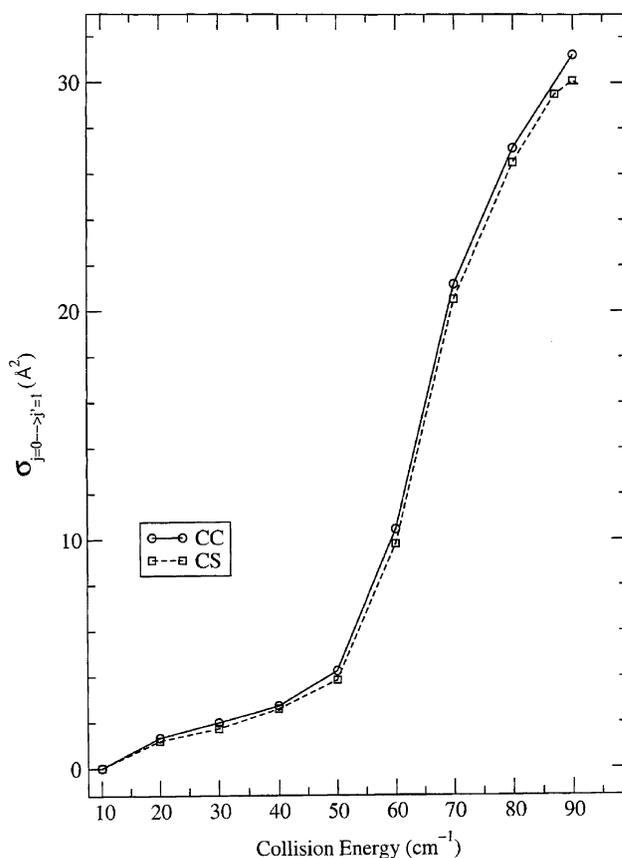


Fig. 1. Inelastic CC and CS (coupled states approximation) calculated cross-sections for low energies:  $\text{H} + \text{LiH} (j = 0) \rightarrow \text{H} + \text{LiH} (j' = 1)$ .

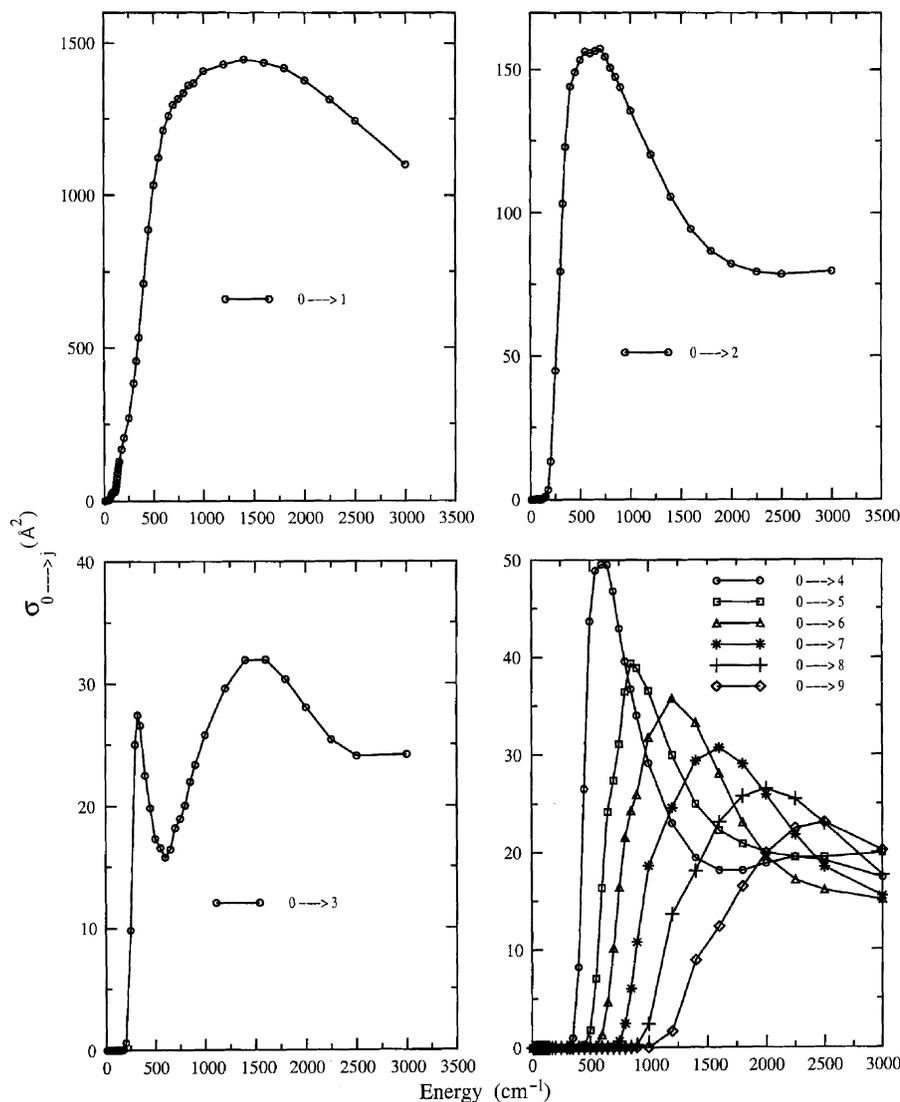


Fig. 2. Inelastic CS calculated cross-sections:  $\text{H} + \text{LiH} (j = 0) \rightarrow \text{H} + \text{LiH} (j' = 1-9)$ .

towards the incoming atom. Thus the interaction potential matrix element are diagonal in  $m_j$  and independent of  $l$ . Therefore, the Schrödinger equation is transformed into a set of coupled differential equations, indexed by a pre-selected orbital angular momentum  $\bar{l}$  and the body-frame helicity  $\Omega$ , namely [17–19]

$$\left( \frac{d^2}{dR^2} + k_{jj'}^2 - \frac{\bar{l}(\bar{l} + 1)}{R^2} \right) u_{jj'}^{\bar{l}\Omega}(R) = \sum_{j''} \langle j' \bar{l} | V | j'' \bar{l} \rangle u_{jj''}^{\bar{l}\Omega}(R) \quad (7)$$

where the coupling potential in Eq. (7) is given by

$$\langle j' \bar{l} | V | j'' \bar{l} \rangle = V_{jj'}^{\Omega}(-)^{\Omega} [(2j' + 1)(2j'' + 1)]^{1/2} \times \sum_{\lambda} V_{\lambda}(R) \times \begin{pmatrix} j' & j'' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & j'' & \lambda \\ -\Omega & \Omega & 0 \end{pmatrix} \quad (8)$$

with the usual meaning of the  $3j$  symbols [20].

### 3. State-to-state rotational computed cross-sections

It seems from the potential energy surfaces [12] that the H–LiH system is a reactive system and the interaction for small angles, where the projectile H atom approaches the H side of the LiH molecule, is attractive. However, the potential energy curve describing the interaction between the H and the LiH molecule and for small angles presents a barrier, which increases with the orientation. For all orientations, the value of this barrier is larger than the collisional energy. On the other hand and from Table 1 of our previous paper [12] the minimum of energy of the potential energy curve increases rapidly with the orientation and the difference between the energy of the minimum and the asymptotic limit decreases with the orientation. Thus shows the small probability to produce the  $\text{H}_2$  molecule for intermediate and high orientation and even for small angles. In a previous work [21] the LiH + H reaction interaction in the collinear geometry ( $\gamma = 0^\circ$ ) and producing the  $\text{H}_2$

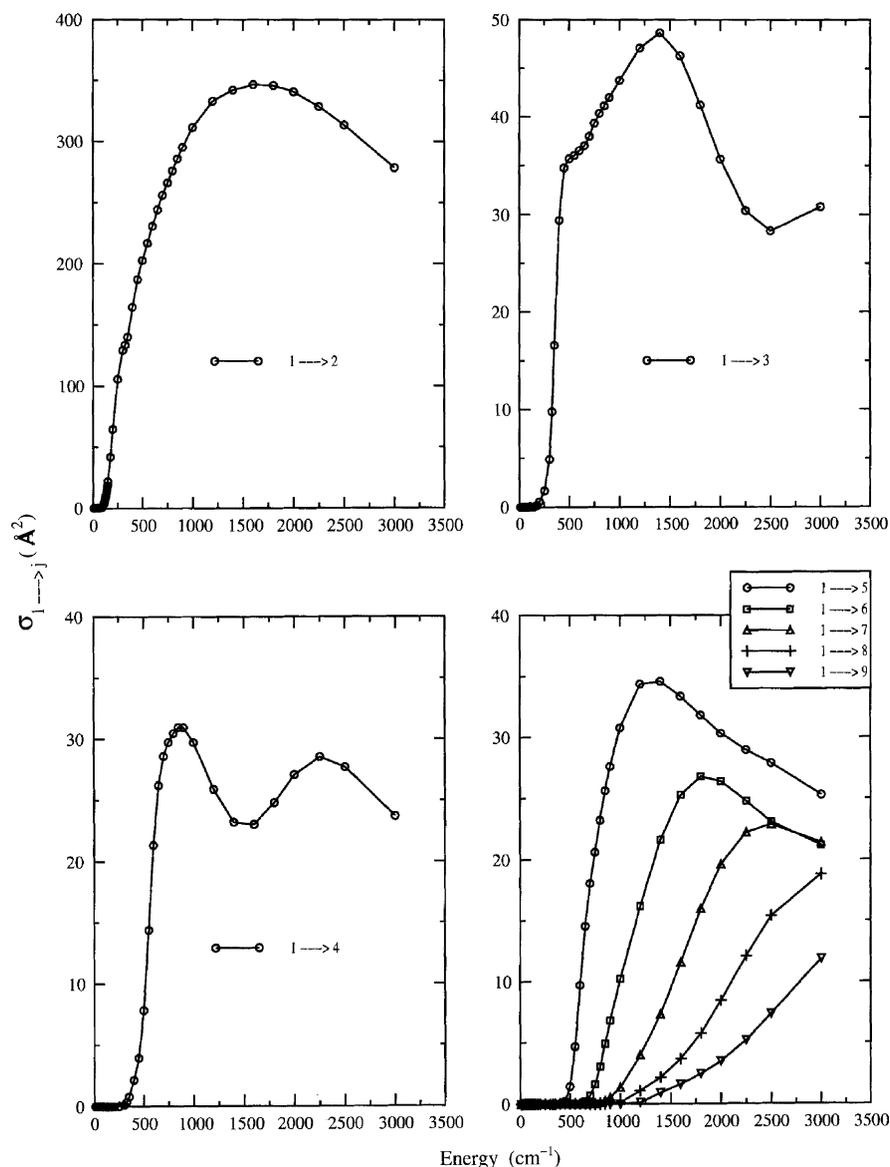


Fig. 3. Inelastic CS calculated cross-sections:  $\text{H} + \text{LiH} (j = 1) \rightarrow \text{H} + \text{LiH} (j' = 2-9)$ .

molecule was done. The results found show the small tendency for the reaction to occur. From a dynamical point of view [21,22] the reaction producing  $\text{H}_2$  could turn out to be rather rare event either because the ‘dynamical’ constraints in the favorable quasicollinear arrangements or because the unfavorable approaching angle of the projectile. If we accept this point of view the elastic and inelastic process between the LiH and the most abundant H atom would dominate the scattering process. To obtain a correct transition probabilities a full reactive scattering calculation has to be done. Such study constitute a very important aim and will be considered in the near future. In this work we will realise a non-reactive scattering calculation in order to get some useful information for further more exact full reactive calculation.

For our best knowledge there is neither experimental nor theoretical works on the pure rotational cross-sections. In this part we use the analytical potential surfaces, produced in the last section, within a quantum mechanical frame-work to calculate rotationally inelastic cross-sections for collisions of rigid rotor LiH with H. For low energy and where the exact CC calculation is feasible, we determine the exact pure inelastic rotational cross-sections. As the H–LiH system is characterized by a strong interaction potential and thus by a strong coupling between the fragments, it becomes particularly difficult to control the numerical convergence of the calculation and needs about hundreds of rotational open channels. The calculations were carried out using The MOLSCAT program of Huston and Green [23]. The CS approximation of McGuire and Kouri [17] was used to

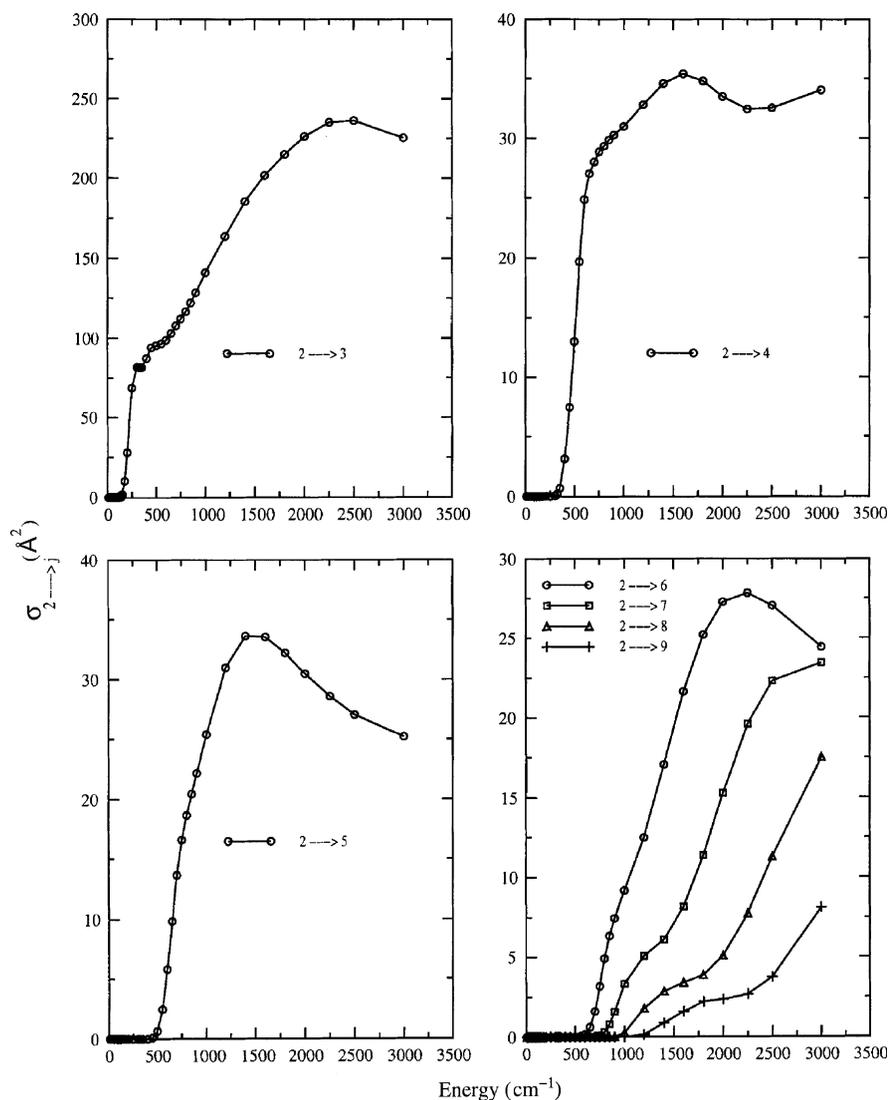


Fig. 4. Inelastic CS calculated cross-sections:  $\text{H} + \text{LiH} (j = 2) \rightarrow \text{H} + \text{LiH} (j' = 3-9)$ .

determine the inelastic state-to-state cross-sections. The efficiency of this method was demonstrated in many works [14,24–26] and it should become accurate as the collision energy increases.

Before generalising the calculation many tests were done to ensure the convergence of the CC and CS calculated cross-sections and the channel bases were large enough to ensure the convergence of the desired S matrix elements. All the rotational channels were included with  $J_{\text{max}} = 20$  corresponding to at least one closed channel for the highest collisional energy ( $3000 \text{ cm}^{-1}$ ).

Fig. 1 presents the rotational cross-sections from  $j = 0$  to  $j' = 1$  calculated using CC and CS methods for low energy varying between 10 and  $100 \text{ cm}^{-1}$ . It seems that there is a very good agreement between the two calculations. We concluded that the CS calculation is accurate and we determined the rotational cross-sections, for transitions from

$j = 0, 1, 2, 3, 4$  to all energetically accessible final states, at total energy varying between 10 and  $3000 \text{ cm}^{-1}$  using the CS approximation. The observation of the Fig. 1 shows that even at very low collision energy the cross-sections from  $j = 0$  to  $j' = 1$  are very large reflecting the extreme anisotropy of the potential.

Fig. 2 presents the CS cross-sections for transitions from  $j = 0$  to  $j' = 1-9$  for a wide interval of collision energy: from 10 to  $3000 \text{ cm}^{-1}$ . The transition from  $j = 0$  to lower-lying rotational levels is the most level to be relevant in the atmospheres of the interstellar clouds. The cross-section due to the transition  $j = 0$  to  $j' = 1$  is the most large with a spread maximum around  $1300 \text{ cm}^{-1}$ . The second transition from  $j = 0$  to  $j' = 2$  is also large and have a broad peak around  $600 \text{ cm}^{-1}$  related to a resonance. The transition  $j = 0$  to  $j' = 3$  presents two broad peaks. The first is around  $400 \text{ cm}^{-1}$  and the second

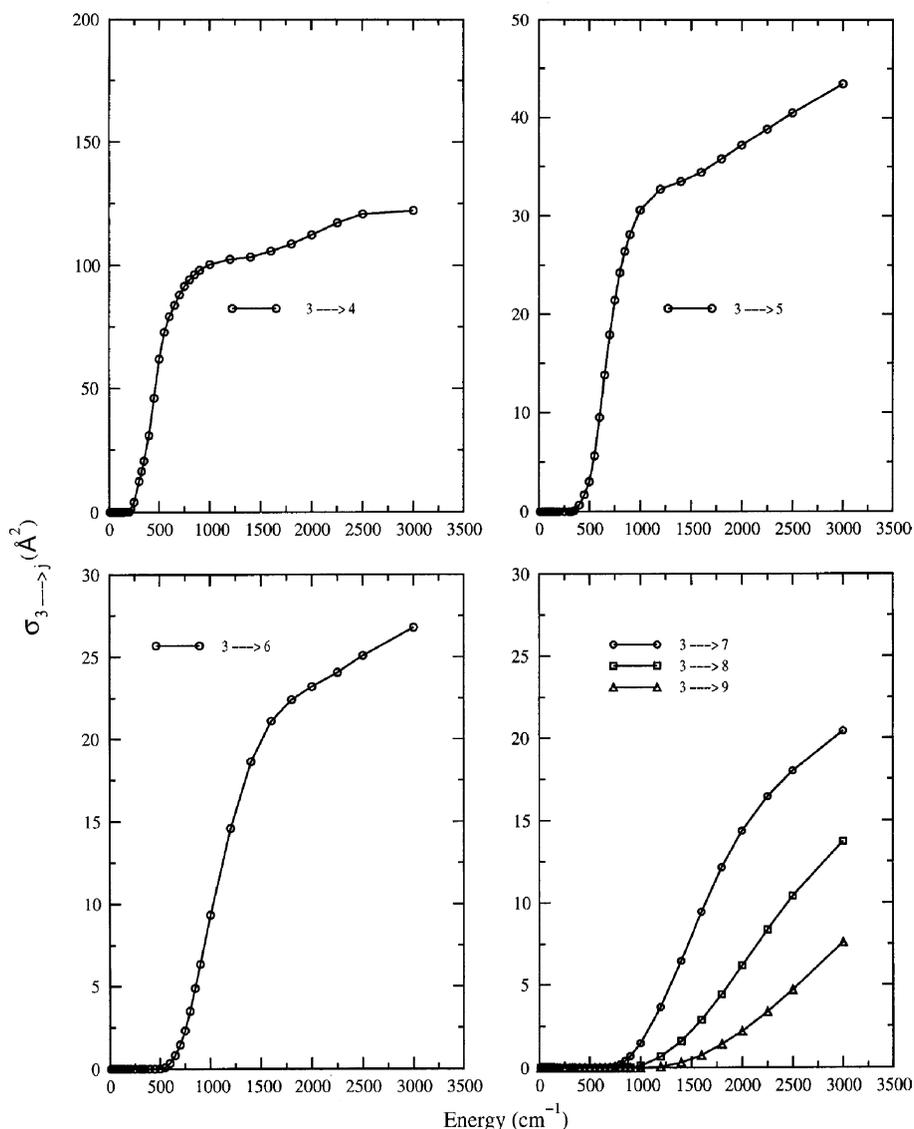


Fig. 5. Inelastic CS calculated cross-sections:  $\text{H} + \text{LiH} (j = 3) \rightarrow \text{H} + \text{LiH} (j' = 4-9)$ .

one is around  $1600 \text{ cm}^{-1}$ . The higher transitions  $j = 0$  to  $j' = 4, 5, 6, 7, 8,$  and  $9$  are presented in the same graph. Their cross-sections still large and a relatively slow fall is observed. We remark for all of them the presence of broad peak related to resonant effects. Such peaks are shifted to the higher energies when  $\Delta_{jj'}$  increases. The higher transitions are less important at the same energies, however, they grow with the energy. It's evident from Fig. 2 that the inelastic cross-sections for the first rotational channel, are large even at low energies indicating a strongly coupled system in which the H projectiles act as a strong perturber of the LiH molecule. Fig. 3 presents the rotational cross-sections for  $j = 1$  to  $j' = 2-9$ . The same general feature seen in Fig. 2 is observed in Fig. 3 for same  $\Delta_{jj'}$ . We remark, specially, the double peak in the  $j = 1$  to  $j' = 4$  transition graph located, respectively, around  $850$  and  $2250 \text{ cm}^{-1}$ .

We remark, also, the shift in the position of the peaks to higher energies when  $\Delta_{jj'}$  increases. Figs. 4–6 present, respectively, the rotational cross-sections from  $j = 2, 3, 4$  to  $j' = j + 1-9$  and for the same interval of energy. For all figures, we remark that the cross-sections corresponding to the transition  $j \rightarrow j + 1$  are the most important but the higher transitions remain also important. The presence of very large excitation cross-sections, and specially for  $\Delta j = 1$ , shows again the strong anisotropy of the interaction between the hydrogen and the LiH molecule mentioned several times.

Our calculation have thus shown that the excitation efficiency from collisional process is indeed very large in this system, thereby indicating that hydrogen projectiles under kinetic collisions frequencies could provide an important source for the production of 'heated' LiH molecules.

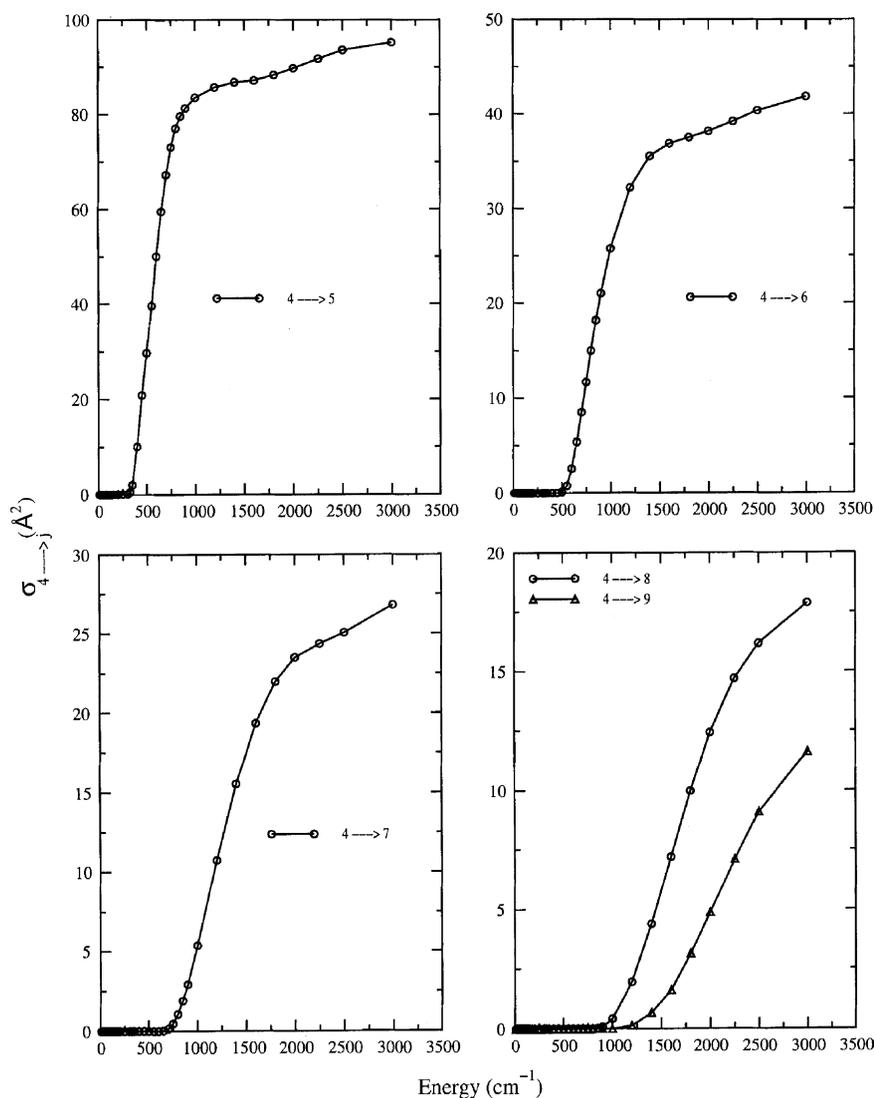


Fig. 6. Inelastic CS calculated cross-sections:  $\text{H} + \text{LiH} (j = 4) \rightarrow \text{H} + \text{LiH} (j' = 5-9)$ .

#### 4. Conclusion

The rigid rotor potential energy surface of the interaction between LiH and H is employed in the calculation of rotationally inelastic state-to-state cross-sections. At the temperatures, which are of interest in astrophysical processes, we have calculated the CC and CS rotational cross-sections. For low energy (from 10 to 100  $\text{cm}^{-1}$ ) we have carried out the exact CC and CS  $j = 0$  to  $j' = 1$  rotational cross-section. A good agreement between the two calculations was observed and a generalisation of the calculation was done for higher energy using only the CS approximation. The  $j = 0-4$  to all energetically accessible final states, at collisional energy varying from 10 to 3000  $\text{cm}^{-1}$  are presented for the first time for our best knowledge. The computed cross-sections are very large and specially the cross-sections related to the transition  $j = 0$  to  $j' = 1$ , which is the most important one. The higher

transitions remain also important but the transitions corresponding to  $\Delta_{jj'} = 1$  are the most important. The higher  $\Delta_{jj'}$  rotational cross-sections still important showing the strong anisotropy of the interaction between H and LiH. Our calculations show that the state-to-state rotational cross-sections even for low energies is large. Thus indicates the important probability to produce 'heated' LiH molecule in excited states by collisional energy transfer and specially through collisions with H.

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