Theoretical Quantum Study of the Molecular System XLi$_2$, with X=D,T, and Mu

Ricardo Gargano, Thiago F. da Cunha, Henrique V. R. Vila, Wiliam F. da Cunha, Luciano A. Leal & Geraldo M. e Silva

Introduction

This work presents an exact quantum investigation of the reactive scattering process X+Li$_2$→LiX+Li, with X=D, T, and Mu in the fundamental state with total angular momentum equal zero. The study has been carried out with a recently developed potential energy surface (PES) [1], which has been fitted from the ab initio energies determined through a full CI calculation for the 6-311G (2df, 2pd) basis set and also through a pseudo potential representing the Li.

Methods

Analytical representations of the X+Li$_2$ PES, with X=D, T and Mu, were obtained using a Bond Order (BO) polynomial expansion for both two and three-body terms, in agreement with the standard many-body method. Due to the fact that the considered reaction is highly exothermic (yielding an amount of energy of about 33.66 kcal/mol), a great number of rovibrational states and quadratures has been taken into account (even for low energies) in order to accurately describe its dynamical properties. The time-independent nuclear Schrödinger equation has been solved by means of the ABC program [2]. This code is ideally suited to calculating detailed state-to-state quantities - such as the state-resolved differential crosssections - in which the quantum states of the reactants, as well as those of the products, are specified at the same time. ABC simultaneously expands the wave functions of all three possible chemical arrangements in the Delves hyper-spherical coordinate system.

Results and Discussion

The obtained results show the isotope effects in promoting the reactivity of the H+Li$_2$ reaction and the reproduction of the physical behavior expected by the eigenvalues of the adiabatic vibrational functions to demonstrate the reliability of the expansion of the nuclear wave function. In both purely excitation rotational and vibrational, the system reactivity is higher when the translational energy of the reagent and low. The isotopic systems follow the trend of the studies for the hydrogen atom and also, the studies by da Cunha at. al [3] on the HLi$_2$ system and its isotopic variants, ie, both the vibrational excitation as the rotational influence the reactivity XLi$_2$ the system.

Figure 1. Reaction probabilities as a function of the translational energy of reactant Deuterium for the purely rotational excitation of the molecule Li$_2$.
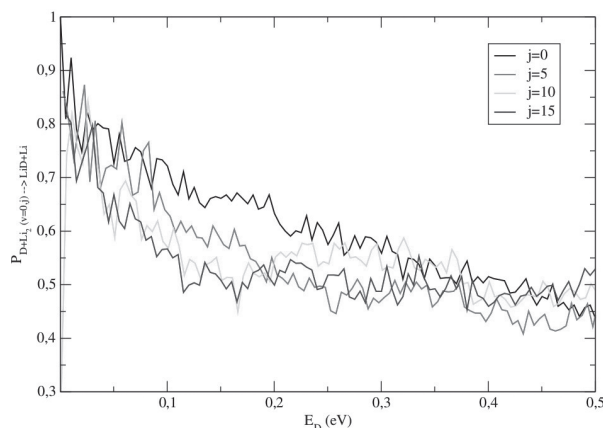
Figure 2. Reaction probabilities as a function of the translational energy of reactant Deuterium for the purely vibrational excitation of the molecule Li_2.

On analysis of the energy distribution is observed that for higher values of total energy E there are more ro-vibrational states of products, but with lower probability of reaction in these cases.

Conclusions

These results show us that the probability of reaction of $D+Li_2$ and $T+Li_2$ systems is greater at low translational energies of the reactant and also, when the reagent Li2 is in the fundamental state ro-vibracional.

From these results, we conclude also higher reduced mass of the reaction diatoms ($T+Li_2 \rightarrow LT+Li$), the greater the reactivity of the system. This result is consistent with the fact that the greater the mass of the system, the greater the coupling and the bonding of rovibracionais states of reactant and product participating in the reaction.

This has also influence in energy distribution. It is observed in energy distribution of the products that the energy yield of the product is greater when the molecules products are more massive, or in isotopic systems with more massive nuclei.

Acknowledgments

1. Maniero A. M., Acioli P. H., e Silva G. M., Gargano R. Chemical Physics Letters, v.490, p.123-126, (**2010**).

2. D., Castillo J. F., Manolopoulos D. E. Computer Physics Communications, v.133, p.128, (**2000**).

3. Da Cunha W. F., Leal L. A., Da Cunha T. F., E Silva G. M., Martins J. B. L., Gargano R. Journal of Molecular Modeling, v.20, p.2315, (**2014**).

Ricardo Gargano*, Thiago F. da Cunha, Henrique V. R. Vila, Wiliam F. da Cunha, Luciano A. Leal & Geraldo M. e Silva

Instituto de Física, Universidade de Brasília. CP04455, Brasília, DF, CEP 70919-970, Brazil

*E-mail: Gargano@Unb.Br