DISSOCIATION DYNAMICS OF THE He-I$_2$-Ne VAN DER WAALS COMPLEX

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ABSTRACT. The vibrational predissociation (VP) process of the van der Waals complex He-I$_2$-Ne, where the diatomic subunit is initially in an excited vibrational level of the electronic B state, is studied using an approximate quantum mechanical model and also a quasiclassical trajectory (QCT) method.

Only coplanar configurations of the complex have been considered. The potential surface is assumed to be the addition of atom-atom interactions that are described by Morse functions. A good agreement between QCT and quantal calculations is found for the total rate of predissociation.

I. INTRODUCTION

In recent years the predissociation of van der Waals (vdW) molecules is receiving an increasing attention as it becomes widely realized that van der Waals molecules provide tractable model systems for state-to-state studies of intramolecular energy redistribution. The greatest part of the experimental and theoretical studies on this field have been devoted to systems with one vdW bond and one or more chemical bonds$^{(1)}$, providing a detailed knowledge about their structure and dynamics and contributing to the understanding of intramolecular energy transfer and photodissociation processes. Also some complexes of I$_2$ with two or more rare gas atoms have been studied$^{(2,3)}$ in order to elucidate such questions as the importance of correlation between different dissociative steps and the competition in the flowing of energy from the diatomic molecule to each weak bond.

In this paper we study the VP of the He-I$_2$-Ne van der Waals complex for collinear and perpendicular (coplanar) configurations. The hamiltonian may be expressed in relative coordinates as the sum of a hamiltonian for the "free" I$_2$ subunit and two triatomic hamiltonians corresponding to He-I$_2$ and Ne-I$_2$, plus a crossed kinetic term and the He-Ne interaction.

As it was pointed out$^{(3)}$ a rigorous quantal treatment of four-body systems is prohibitively difficult. Hence, we use some reasonable
approximations in Quantal and Classical Mechanics.

In the quantum mechanical model, and for low and intermediate vibrational diatomic excitations, \( v \lesssim 40 \), we may apply a diabatic distorted wave approach to describe the iodine vibrations within the complex. Representing the \( v \)-averaged Hamiltonian in a basis formed by the products of discrete solutions corresponding to He-I\(_2\) and Ne-I\(_2\), we can obtain after a diagonalization the tetraatomic discrete levels. As regards the continuum wavefunctions we shall consider two different continua, each one of them representing the breaking up of one vdW bond. Thus, we assume in the model that the interaction between both continua is negligible. Finally, the predissociation rates are obtained in the "Golden Rule" framework.

Concerning with the quasiclassical model, we use the energy of the quasibound state obtained in the quantal model in order to get the initial conditions for the trajectories. The relevant result of these calculation is again the rate of predissociation of the vdW complex.(4,5) For obtaining this magnitude, an exponential law of decay is assumed.

Concerning the potential energy, we express it as a sum of pairwise atom-atom interactions, where each one of them is a Morse function. This is a reasonable assumption because the VP process is mainly sensitive to the region of the well.

In next Section we describe in detail the quantal model, while Section III is devoted to the quasiclassical model and in Section IV the potential energy used in both models is presented. Finally, the calculations and results obtained through both models are discussed.

II. Quantal model

The hamiltonian for nuclear motion, after separation of the center of mass of the whole system, when He-I\(_2\)-Ne is in collinear or in perpendicular (coplanar) configurations, may be written as

\[
H = -\frac{\hbar^2}{2\mu_{I_2}} \frac{\partial^2}{\partial r^2} + V_{I_2}(r) - \frac{\hbar^2}{2\mu_{He,I_2}} \frac{\partial^2}{\partial R_1^2} + u_{He,I_2}(r,R_1)
\]

\[
- \frac{\hbar^2}{2\mu_{Ne,I_2}} \frac{\partial^2}{\partial R_2^2} + u_{Ne,I_2}(r,R_2) + \frac{\hbar^2}{2m_I} \frac{\partial^2}{\partial R_1 \partial R_2} +
\]

\[
+ W_{He,Ne}(R_1,R_2)
\]

where \( r \) is the internuclear distance for \( I_2 \), \( R_1 \) and \( R_2 \) are the distances between He or Ne and the center of mass of \( I_2 \), respectively. \( V_{I_2}(r) \) is the intramolecular potential interaction for the "free" diatomic molecule \( I_2 \) while \( u_{He,I_2} \), \( u_{Ne,I_2} \), \( W_{He,Ne} \) are the van der Waals interactions between He and \( I_2 \), Ne and \( I_2 \), and He and Ne respectively.