MODELLING LIGHT DIATOMICS TRAPPED IN RARE GAS MATRICES: H₂, HD and D₂ in Ar, Kr and Xe

B. SILVI
Dynamiques des Intéractions Moléculaires (URP271), Université Pierre et Marie Curie, 4 Place Jussieu, 75230 Paris Cedex, France

V. CHANDRASEKHARAN
Laboratoire de Photophysique Moléculaire du CNRS, Bâtiment 213, Université Paris Sud, 91405 Orsay, France

M.E. ALIKHANI
Laboratoire de Spectrochimie Moléculaire (URA508), Université Pierre et Marie Curie, 4 Place Jussieu, 75230 Paris Cedex, France

R.D. ETTERS
Physics Department, Colorado State University, Fort Collins, CO 80523, USA

Abstract

The different models allowing the calculations of the rovibrational frequency shifts with respect to the free molecule of a molecular impurity embedded in a rare gas crystal are reviewed. It is shown that models which account for the translational motion of the impurity yield reliable results, the effects of the rare-gas translation seem to be less important. The different models currently used are described in detail and the computational procedures are discussed. Finally, it is shown that for heteronuclear diatomics, the translation–rotation coupling could play an important role.

1. Introduction

Molecules or atoms embedded in rare gas matrices constitute a large body of systems for which extensive spectroscopic studies have been reported. The matrix isolation technique has been developed since the pioneering works of Pimentel [1]. It allows the observation and identification by spectroscopy experiments of unstable species, such as Van der Waals complexes, ion pairs, radicals and reaction intermediates. The applications of this technique have recently been reviewed by Perchard [2].

The interaction between the solute impurity and the host crystal, "the solvent", is generally very weak, and therefore the frequencies of the spectral lines of the matrix isolated systems are very close to their gas phase values. The calculation of the matrix shifts is carried out by a perturbational technique, and the overall quality of the theoretical results is mainly related to the accuracy of the solute–solvent potential for which it constitutes a probe.
For most matrix isolated systems, the mass of the impurity is large and its centre of mass is assumed to be fixed. The translation of the impurity in the cage is, in this case, a classical motion which is not coupled with the rotation and the vibration. In the case of light impurities, this assumption is no longer valid and one has to design specific methods to calculate the frequency shifts which are able to take into account the quantified translation and its coupling with the other motions.

For most molecular impurities, the rotational motion is hindered and is alternatively called libration. For the hydrogen molecule, pure rotational states are observed in the matrix. For the hydrogen rare gas pairs, there exist accurate potentials derived from gas phase experiments on the 1:1 complexes by Leroy et al. [3]. These potentials are expressed as a power series of the intramolecular stretching coordinate. Moreover, hydrogen being light has a large centre of mass zero point motion. The hydrogen molecule \( \text{H}_2, \text{HD}, \text{D}_2 \) in rare gas \( \text{Ar}, \text{Kr}, \text{Xe} \) has been the subject of numerous experimental studies [4–13] as well as theoretical calculations [14–18].

The aim of this contribution is to describe in detail and rationalize the methods used by our group to calculate the frequency shifts of the vibrational and rotational states of a light diatomic impurity trapped in rare gas crystals.

2. Coordinate system and expression of the Hamiltonian

2.1. COORDINATES

The system of interest is made up of a diatomic impurity \( X \), and of a set of \( N \) atoms of the rare gas \( A \) spherically distributed around the impurity. In principle, this system is described by \( 6 + 3N \) coordinates. In the case of a host crystal, \( N \) tends to infinity. The coordinates used in the following are depicted in fig. 1.

Two frames are necessary. A fixed frame \((x, y, z)\) with its origin at the substitutional site and its axis arbitrarily chosen along the lattice directions is used to define the instantaneous position vectors of the rare gas atoms \((r_i)\) and of the impurity centre of mass \((r_0)\). The vectors \( R_i \) define the classical positions (fixed nuclei) of the rare gas atoms and of the impurity centre of mass, which implies in particular \( R_0 = 0 \). The diatomic impurity is described by three other coordinates: on the one hand is the internuclear distance \( r \), and on the other hand are the angular coordinates \( \theta, \phi \) of the bond with respect to the axis of a local frame \((x', y', z')\), parallel to the fixed frame but with its origin at the centre of mass of the diatomic.

The dimensionless stretching coordinate \( \xi \) defined by:

\[
\xi = \frac{r - r_e}{r_e},
\]

in which \( r_e \) denotes the equilibrium bond length, will be used instead of \( r \).