Dynamics of Structural Photoinduced Relaxation of NO doped Ar solids with the use of ground and excited state *ab initio* PESs for Ar-NO complex

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Abstract

The many-body dynamics in response to photoexcitation in condensed media is of general interest in many systems, such as: biological molecules, condensed phase chemical media and solids (insulators and semiconductors. Extensive configurational rearrangements following photoabsorption are observed in such systems. Pure and doped rare gas solids have long been considered as good model systems for describing and understanding the basic principles behind such a medium response since they result amenable to modelization because of their simple structural properties and the great knowledge of their physical properties.

To this respect, molecular dynamics simulations have been used to describe simple photochemical reactions during this decade in rare gas and clusters. Such events are driven by the photoinduced intramolecular motion which induces nuclear dynamics of the surrounding cage as well as long range propagation of energy.
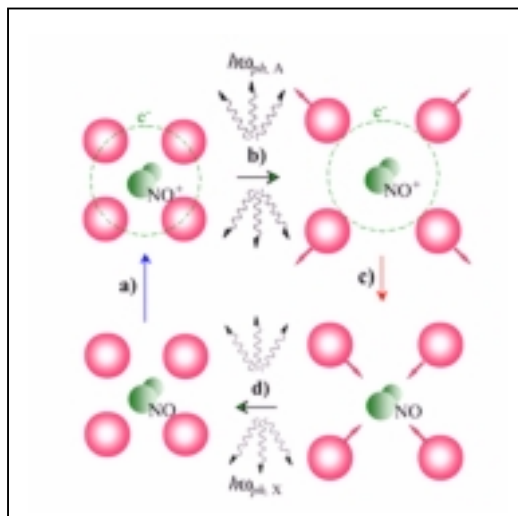
It is known that excitation of low-n Rydberg states of impurity molecules or atoms in rare gas solids leads to a large blue spectral shift in absorption, as compared to the gas phase, due to the strong short range repulsion between the Rydberg electron and the closed shell of rare gas atoms. The strong repulsion leads to a relaxation of the cage species surrounding the excited center to a new equilibrium configuration from which fluorescence occurs. The large absorption-emission Stokes shifts that are observed reveal the extensive lattice rearrangements around the excited species. The basic mechanism is considered to be a radial expansion of the cage (the so-called electronic "bubble" formation) which is also operative in rare gas liquids and clusters. The figure on the left shows a schematic representation of NO photoexcitation to its first Rydberg state when placed in a rare gas solid medium.

In the present work, Molecular Dynamics (MD) simulations are carried out to study Rydberg photoexcitation of NO in Ar solids. In order to give a more realistic characterization of this system, effects of angular variations of intermolecular Ar-NO potential energy are taken into account by means of using fully *ab intio* potential energy surfaces (PESs) for the ground and excited state of the Ar-NO complex. The dynamics of the systems using only the isotropic term of the Legendre expansion of the PESs have also been included.

Results show that the average cage radius (see figure bellow) increases after excitation up to 4 % of the equilibrium radius in the ground state, for the case of using fully *ab initio* PESs and 7.9 % when the isotropic parts are used. These results are in fare agreement with experimental results for the bubble size, namely, between 4 and 15 %. The inertial character of the first shell response is very well appreciated. It expands up to 200 fs without any answer of the other shells. The adiabatic character of the first expansion at short periods and the interchange of energy among the shells are also noticed. There is a clear dependence of the response propagation on the 110 crystallographic direction in the lattice. This is appreciated when the case of the 1st, 4th and 9th a shells, which are directionally connected, is compared with the case of the other shells. A great part of the energy is transmitted in the geometrically connected shells direction. The first medium response in time was about 0.834 ps in good agreement with 0.8 ps from experiments.
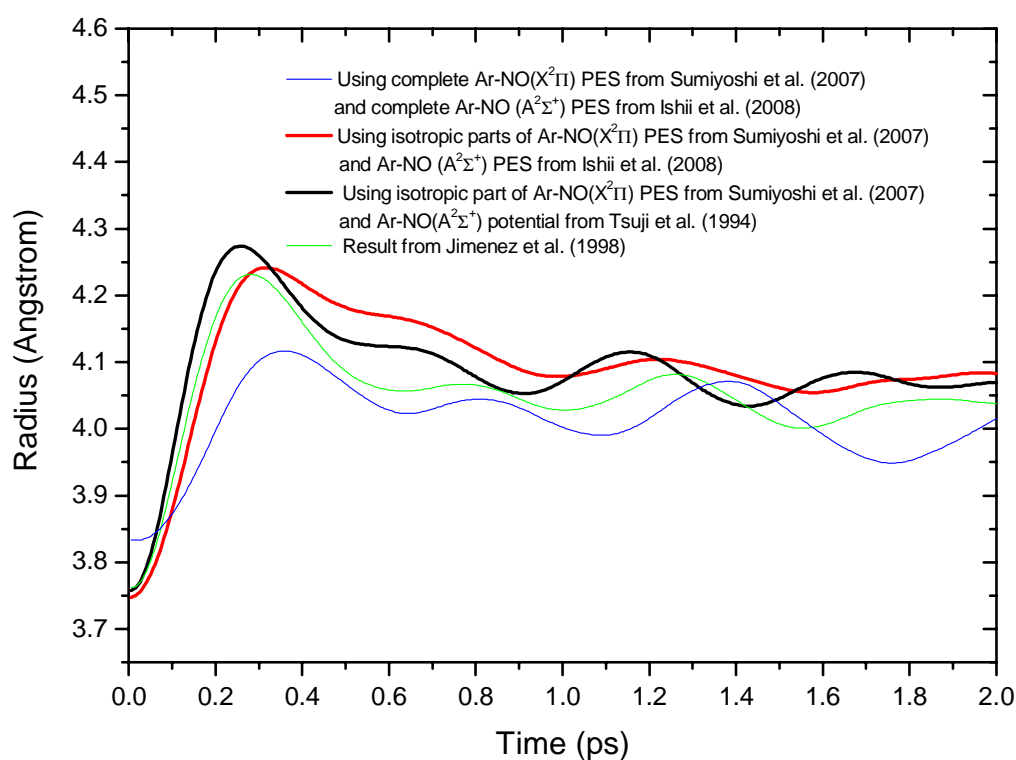
MD simulation results for the absorption peak and Stokes shift (difference between absorption and emission peaks) were also obtained. The calculated value for the Stokes shift was 610 meV in good agreement with the value of 570 meV reported in the experiments. However, when the isotropic parts were used the calculated value was 290 meV, being the anysotropy of potentials important for the determination of this quantity.