THEORETICAL SPECTROSCOPIC STUDY OF VAN DER WAALS SYSTEMS

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In these recent years, a wide interest has been lead towards the elucidation of the spectroscopy and dynamics of van der Waals (VDW) systems, not only experimental but also theoretical one. The observation and study of these molecular systems provides us a unique and clear example for energy acquisition and redistribution between different degrees of freedom. This is due to the special features presented by these complexes which the most important are dissociation energies ($10\text{--}500\text{ cm}^{-1}$) and VDW bond lengths in the range of $[3,9]\text{ \AA}$. These turn out to be very small and very large, respectively, compared with values commonly found in traditional chemical molecules. Thus, the intramolecular interaction is so weak that the constituents retain most of their individual properties. In this context, it is paid attention to photo-fragmentation of triatomic molecules (mainly, X-BC molecule where X = He, Ne, Ar, Kr, Xe and BC is a normal diatomic molecule, H_2 , N_2 , O_2 , I_2 , etc.) since they are best understood. In most of cases direct photo-dissociation is very slow due to unfavourable overlap factors and the fragmentation occurs essentially via vibrational or rotational predissociation (VP or RP, respectively). The spectrum, then, of each complex will exhibit a set of lines broadened. An experimental datum is the VP or RP rate, determined from the fluorescence excitation spectrum. Also, from the analysis of the fluorescence spectrum of the fragments, the final vibrational and rotational distributions of BC are established.

From the theoretical point of view, much effort has been devoted to VP process, but much less is known about RP one. In this conference, we present different approaches in order to study the spectroscopy of VDW molecules. In all of them, we take advantage of the difference in frequencies between VDW and chemical bond and we also investigate the rotational effects in the VP process. For incorporating these effects, a decoupling scheme related to the infinite order sudden approximation is used. We report several results for different complexes obtained by our group using approximate and exact methods for the calculations of the lifetimes.

The reverse process is also possible. The collision of the BC molecule with the X rare atom has also been experimentally studied in order to analyze the vibrational and rotational relaxation (VR and RR, respectively) of the diatomic subunit during the process. At very low collisional energies the cross section for VR increase when the relative kinetic energy decreases, whereas the RR appears to be almost independent of these energies. The presence of metaestable states or "orbiting resonances" at very low energies is responsible of the particular behaviour of the cross section. The same kind of calculations are available in this new way of describing the dynamics of these complexes.

In spite of this great theoretical progress, there are a number unexplained experimental observations. It is clear that the nature of the interaction must play a very important role in this affair. Further works are needed in order to elucidate this interesting aspect of VDW systems and therefore in the energy transfer processes.