Experimental evidence of vibronic interactions on molecular structures determined by gas electron diffraction

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Vibronic coupling theory shows that the cause for spontaneous instability in systems presenting a degenerate as well as nondegenerate ground state (the Jahn-Teller and pseudo-Jahn−Teller effects, respectively) [1, 2] and thus its study can be extremely helpful to understand the structure and intramolcular dynamics of molecules. The study of intramolecular rearrangements is fruitful from the point of view of gaining insight into the mechanisms of chemical reactions which are supposed to involve transient species. This report reviews advances of modern gas electron diffraction (GED) method combined with high-resolution spectroscopy and quantum-chemical calculations in studies of the impact of vibronic interactions in free molecules on their structures and nuclear dynamics. Some recently developed approaches to the electron diffraction data interpretation, based on direct incorporation of the adiabatic potential energy surface (APES) parameters to the diffraction intensity, are described. It is suggested that by using the proposed approaches, it is possible to develop a common “language” with spectroscopy and computation methods. In this way, complementary data of different experimental and computational methods can be directly combined for solving problems of the molecular structure and its dynamics. The possibility to evaluate some important parameters of the APES–vibronic interaction constants from electron diffraction intensities in solving the inverse GED problem is demonstrated on several examples. With increasing accuracy of the electron diffraction intensities and the development of the theoretical background of electron scattering and data interpretation, it has become possible to investigate complex nuclear dynamics in vibronic systems by the GED method.

The creation of molecular-size devices displaying two (or more) states with distinguishable properties (i.e. *spin-up/spin-down*) at room temperature, and which are switchable under an external perturbation will pave the way towards a number applications in fields like high-density information storage, quantum-computation or molecular spintronics. While several classes of these bistable systems exist [3], single molecule magnets where each state represents a different magnetization that relaxes very slowly are, perhaps, the ones that have attracted highest expectations for practical applications [4].

With increasing accuracy in measurements of electron diffraction intensity and development the theoretical background of electron scattering and data interpretation for the latest two decades, it became possible to investigate complex nuclear dynamics in fluxional systems by GED method combined with high-resolution spectroscopy and quantum chemical calculations.

References

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