Theoretical view on atomic mobility in rare gas matrices

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There is a lot of experimental studies indicating the activation of the matrix-isolated atoms at distinct and sharp temperature thresholds. The most are observed for light atoms, such as hydrogen, nitrogen, oxygen, etc., though some observations suggest that the same phenomena also occur for heavier atoms including the d-elements. Theoretical attempts to describe tempearture-activate migrations had also been going on for a long time, but the complexity of the problem prevented the simple models to reach even qualiative agreement with the experimental data.

In this work, we describe more sophisticated approach for theoretical investigation of the mobility of hydrogen and oxygen atoms in argon, krypton and xenon matrices. It relies on the the previously proposed method for determining the stable atomic trapping sites in inert gas crystals [1,2], the molecular-mechanical approach and accurate non-empirical data for the diatomic systems. Using this approach, we study the A@RG systems (A = H, O, RG = Ar, Kr, Xe) with the different numbers of RG atoms removed from the lattice to find their equilibrium geometries and energies. Using the thermodynamic concept of the convex shells, we determine what trapping sites are thermodynamically stable. The number of stable trapping sites found for each atom in each matrix is fully consistent with the available experimental data and with generic theoretical prediction [3] at the given parameters of the diatomic interaction potentials. In the case of atomic hydrogen, the results are also verified against the electron spin resonance data. The numerical estimations of the shifts of the hyperfine structure constant are obtained assuming the additivity of the Fermi contact interactions. The dependences of the isotropic components of the hyperfine structure constant and the g-tensor on the H-RG systems distance are calculated *ab initio*. The additive approximation is tested for the first coordination polyhedron by the direct *ab initio* calculations for the HRG_n subsystems.

Possible migration paths between the stable trapping sites found, as well as between crystal vacancies, are investigated using the nudged elastic band technique and then refined by the intrinsic reaction coordinate method. The barriers found for both H and O atoms are in good correspondence with the measured the confirming different migration mechanisms and pathways proposed theoretically.

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