Dmitry S Bezrukov et al., J Phys Chem Biophys 2017, 7:4(Suppl)
DOI: 10.4172/2161-0398-C1-026

Modeling of electronic spectra of matrix-isolated atoms: Comparison of theoretical approaches

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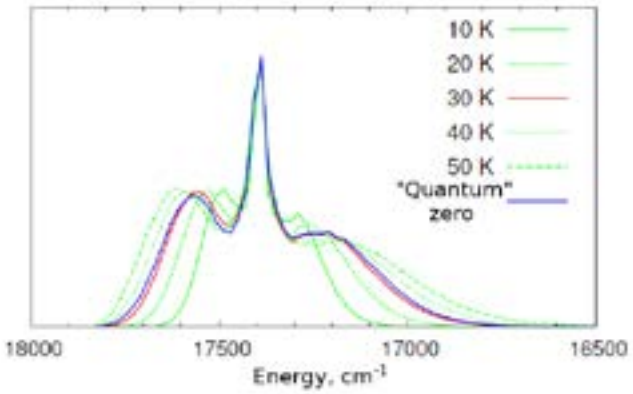
Applicability of different theoretical approaches to model the positions and shapes of the electronic absorption and emission bands for matrix-isolated atoms is considered. Comparison of the theoretical predictions with experimental spectra is currently the most straightforward way of determining structure of atomic trapping sites in matrix. Usually, modeling of the potential energy surfaces for excited states is based on the diatomic-in-molecule (DIM) method, though other approaches like quantum mechanics/molecular mechanics or effective core potentials are also currently in use. The Frank-Condon principle with thermal Boltzmann averaging for initial nuclear positions is mostly used to model spectral line shapes. The effects of spin-orbit interaction have recently been taken into account. In this work, the performance of different approaches to model electronic transition bands is studied for the examples of Yb, Na and Ba atoms trapped in rare gas matrices. The effects of thermal motions are investigated for nearest rare gas atoms forming first coordination polyhedron of the trapped atom, as well as for the more distant rare gas atoms. The problem of consistency between classical, quantum and real temperature in the modeling of the nuclear distribution in low-temperature matrix is discussed. Within the DIM model parameterized by the *ab initio* data, the dependence of transition dipole moment on the matrix atom coordinates and the effects of spin-orbit interaction are taken into account and their implications to the band positions and shapes are considered. Applicability of the Lax model which accounts for vibrational structure in the ground and excited electronic states to matrix isolated species is discussed. All results are compared to existing experimental data. The role of different interactions and factors in the modeling of positions and shapes of electronic spectral bands of matrix-isolated atoms is assessed and discussed. Spectral simulations confirm the structures of the stable trapping sites obtained by our approach proposed recently for estimating thermodynamics stability of the trapping sites.



Biography

Dmitry Bezrukov is the Senior Research Scientist of Skolkovo Institute of Science and Technology in Moscow, Russia and an Associate Professor in Department of Chemistry at Moscow State University. His research interests are connected with the developing numerical approaches for solving problems in quantum chemistry and molecular modeling, and studying states of atoms and small molecules in inert gas matrices.

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