Electronic Aspects of Molecular Auger Decay

Reinhold F. Fink

Institut für Theoretische Chemie, Universität Düsseldorf, D-40225 Düsseldorf, GERMANY

Whereas theoretical methods for energy positions and line shapes in molecular and solid-state Auger transitions are well established, it is much less clear how the corresponding transition rates can be obtained with reasonable precision.

Different theoretical approaches are compared with each other with particular emphasis on the simplest *ab initio* method: the one-centre approximation. A systematic investigation of transition rates shows that they depend strongly on the quality of the bound part of the intermediate and final state wave functions. It is shown that the one centre approximation is generally well justified for molecular Auger decay rates and that very accurate wave functions
should be employed for methods of higher theoretical level. A simple formulation of the one center-approximation is presented, which allows to calculate KVV and $L_{2,3}VV$ Auger transition rates for normal as well as for resonant Auger decay by hand. Some qualitative rules are derived from this formulation.

We show that partial Auger decay rates may show a substantial dependence on the geometry of the molecule and discuss this effect on the basis of newly measured resonant Auger electron spectra of the CO, O_2, and NO molecules.

The importance of core hole orientation in molecular-field split 2p core hole states on total and partial Auger decay rates is discussed and the possibility of selective dissociation of 2p core excited states due to this orientation is discussed.