

Coupling between dipole-bound and valence states: the Nitromethane anion

T. Sommerfeld

Universität Heidelberg

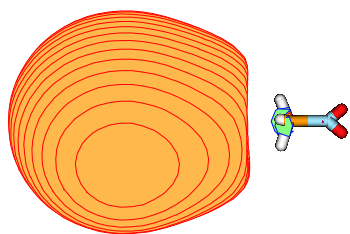
Theoretische Chemie, Physikalisch-Chemisches Institut

Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

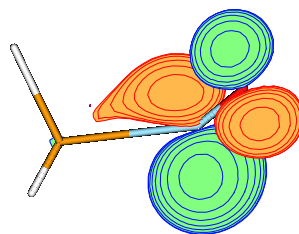
E-mail: Thomas.Sommerfeld@urz.uni-heidelberg.de

Nitromethane is a prototypical example for a polar molecule that can bind excess electrons in two fundamentally different ways. On the one hand, dipole-bound anions can be formed where the extra electron is essentially attached to the electrostatic dipole potential of the neutral system. The associated binding energies are small, and the dipole-bound electron occupies an extremely diffuse orbital. On the other hand, the extra electron can occupy a compact valence orbital, and a stable, conventional or valence anion with a notably changed equilibrium structure is formed.

Dipole-bound state



Valence state



The classification of these electronic states as dipole-bound or valence does in fact suggest a diabatic viewpoint, and we investigate the coupling

between these two electronic states of the nitromethane anion. The electronic coupling element W is extracted from a one-dimensional cut through the two lowest adiabatic potential energy surfaces by fitting of a simple avoided crossing model potential. In other words, W is effectively approximated as half the smallest splitting.

Aiming for high level ab initio calculations of the two states along the cut, there are two important questions: how can one achieve a reasonably balanced description, and how should one include the region where the upper adiabatic state is a resonance? Regarding the former issue, it is essential to include electron correlation effects at a high level, and we discuss how a balance between the two very different electronic states can be achieved using either configuration interaction or propagator based methods. In the second place, the autodetachment lifetime following vertical electron attachment to the neutral is computed, but the calculation of the resonance state turns out to be very expensive, and so far, we include the second adiabatic state only at geometries where it lies below the neutral potential energy surfaces.

We find a coupling matrix element of 30 meV. On the one hand, this value is much smaller than the vertical excitation energies underlining the need for a diabatic picture. On the other hand, this value suggests rapid transitions on a mass spectrometric timescale substantiating the notion that the dipole bound state provides an efficient doorway for attachment to the valence state.