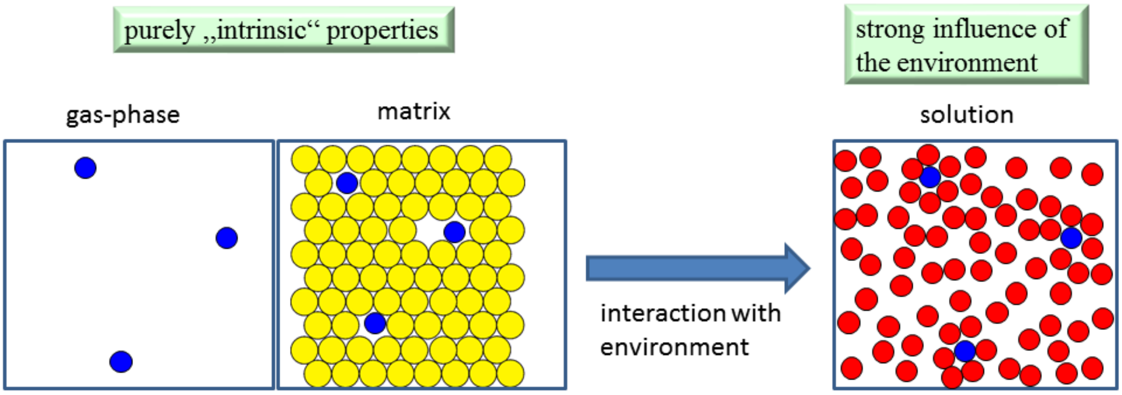
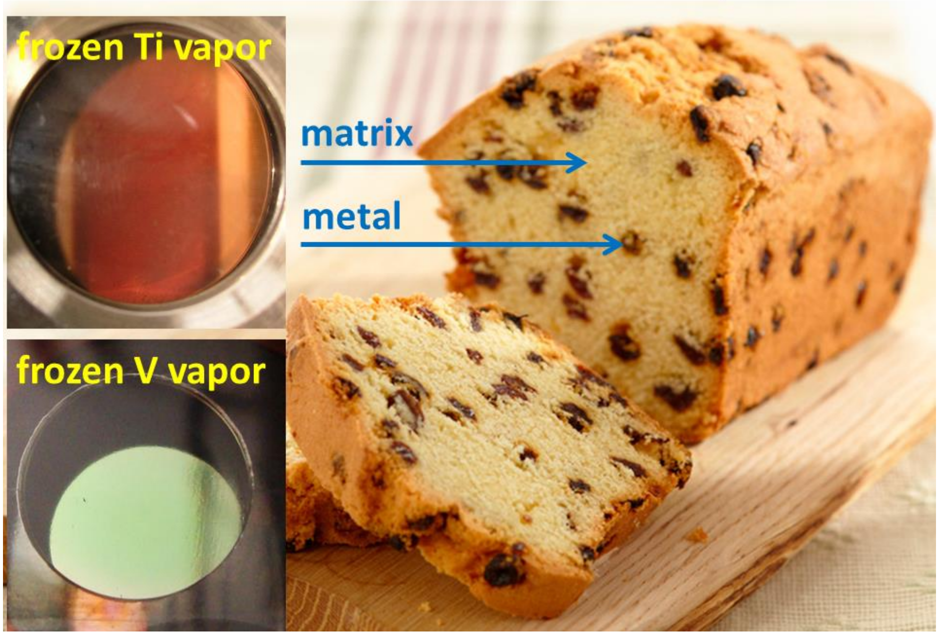
Matrix Isolation

The electronic structure and chemical properties of reactive molecular compounds and intermediates are heavily influenced by the environment (e.g. solvation, aggregation), especially if they are open-shell species. The matrix isolation technique offers the possibility to study the electronic structure and "intrinsic" properties of these species, free of any "extrinsic" influences such as solvation or aggregation. In difference to gas-phase studies, standard spectroscopic techniques could be used for this analysis, since the compounds could be kept in the matrices for several hours or even days if demanded. The clear separation of intrinsic and extrinsic effects on a chemical reaction under consideration allows detailed insight into the reaction pathway and therefore is of key importance for the development of synthetic strategies.

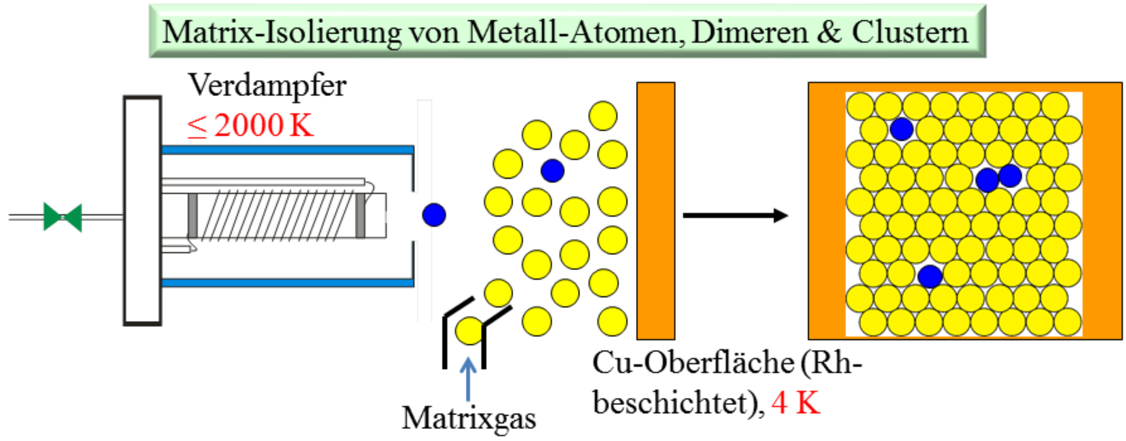


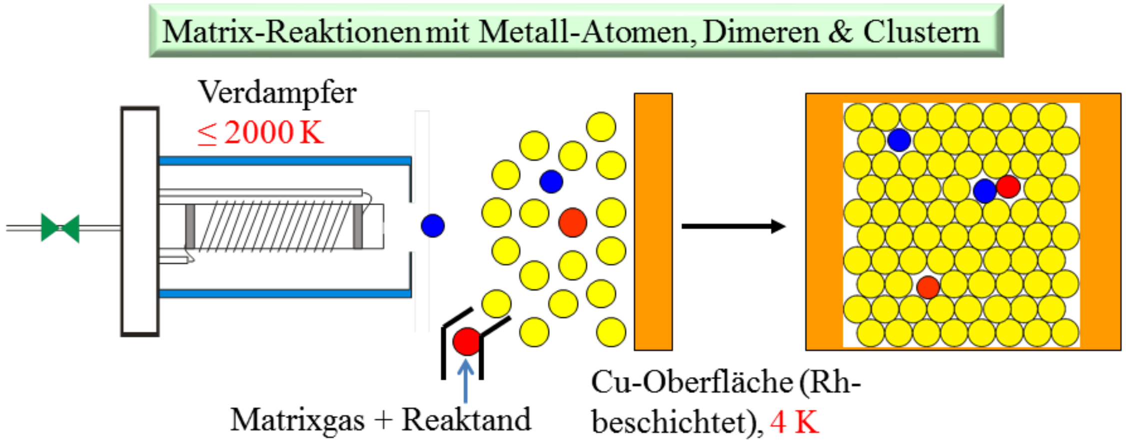
The compounds are isolated in the matrix like the raisins in a raisins cake. Hence the matrix is a special host material, in which host-guest interactions are reduced to a minimum by choice of frozen inert gases (e.g. Ne or Ar) as host materials. The metal atoms in the following picture could not aggregate to form solid metal, and their colors arise from electronic transitions that are only slightly shifted in energy with respect to the gas-phase.

Matrix Isolation of Metal Vapors

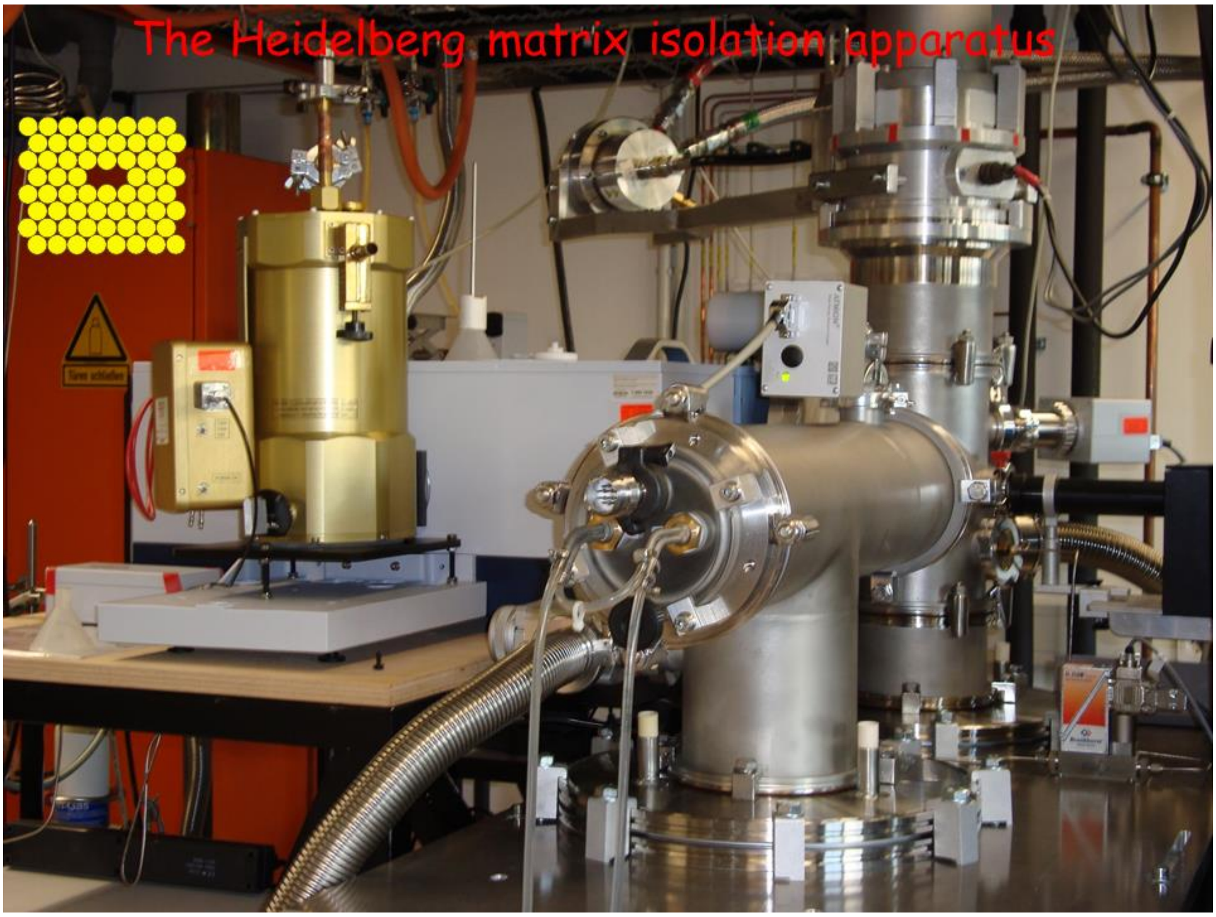


If metal atoms, dimers or clusters are isolated in the absence of a reaction partner, one could analyze their electronic structure in the ground state, and also in electronically excited states, which are most important for the understanding of their reactivity. On the other hand, if the inert gas is doped with a reaction partner, one could study the reactivity of these species. Tempering of the matrix material enables diffusion of the reaction partners. For reactions which are subjected to a reaction barrier, energy could be inscribed through irradiation of the matrix, making use of the almost complete transmissibility of the matrix material in the UV and visible region.

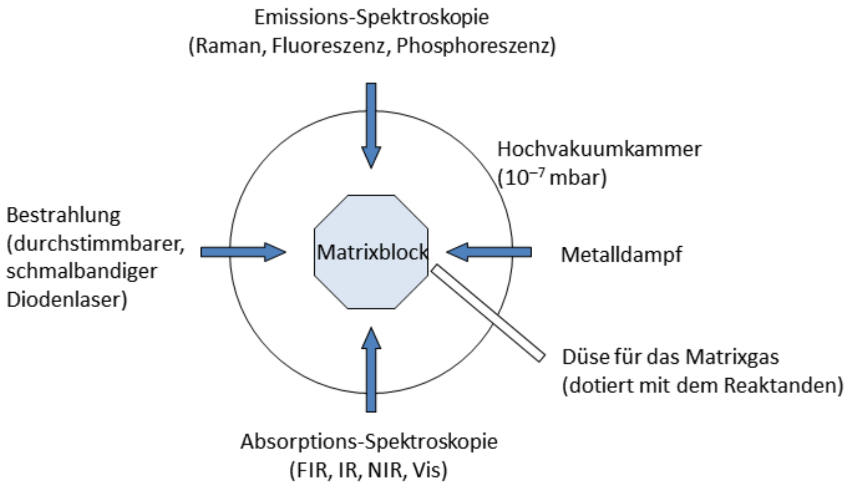




The matrix is deposited on a substrate which is cooled to a very low temperature (e.g. 4 K), generally by means of a closed-cycle cryostat. To avoid the deposition of air and moisture, the matrix is integrated in a high-vacuum system. The following picture shows the home-built Heidelberg matrix isolation apparatus and a schematic drawing which illustrates the possible spectroscopic techniques which could be applied.

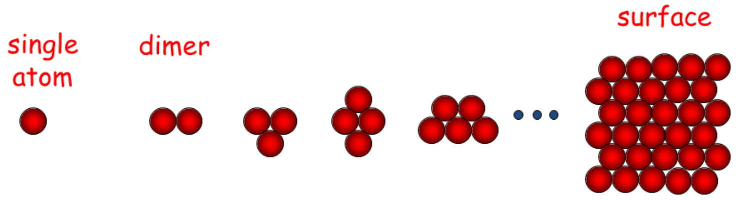


Schematic scheme of the Heidelberg matrix isolation apparatus



One important research theme in our group is the understanding of the reactivity of “naked” (ligand-free) metal atom clusters. A metal atom is surprisingly inert, which could be explained by large symmetry barriers. One would expect the reactivity to reach a maximum when the number of atoms increases. Such studies help to understand catalytic reactions involving heterogeneous catalysts, a concept which is known as “molecular surface science”.

Clustersize & (catalytic) reactivity



Trend in the reactivity?

Many studies indicate that the dimers exhibit a special reactivity. The following scheme summarizes some results of our group which underline the high reactivity of metal atom dimers.

Summary of the matrix reactivity of Ga_2 and Ti_2