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Potential energy surface and molecular dynamics simulation of gold(I) in liquid nitromethane

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ABSTRACT

Potential energy functions for Au(I)-nitromethane (NM, CH_3NO_2) and NM–NM interactions were calculated by fitting analytical expressions to quantum chemically derived energies. These functions were then used in a molecular dynamics simulation of one Au(I) cation in 499 nitromethane molecules in the NVT ensemble at room temperature. A comparative simulation with a generic NM–NM potential energy function was also performed for comparison and gave the same results with respect to the calculated properties. It was found that the first solvation shell around the gold ion contains 9–10 nitromethane molecules in an environment with no strong symmetry.

Complementary, cluster calculations on $AuNM_n^+$ were performed. The especially strong binding of nitromethane in $AuNM_2^+$ and the validity of the pair approximation are discussed.

1. Introduction

A renewed interest in the properties of gold ions [1] in non-aqueous solution can be noticed and stems from various new applications and problems. New applications of gold solutions in nanotechnology and cluster science deal, for example, with gold nanowires and with the catalytic properties of gold nanoclusters. Many applications utilize the ability of gold to change easily between the oxidation states 0, 1 and 3. Potentially useful nanostructures can also be formed by self-assembly of ligands around gold ions. Gold surfaces in contact with various solvents play an important role in electrochemistry and in technology and, last but not least, gold is a biocompatible metal. On the other side, gold — like other heavy metals are — is an environmental liability. Since it is omnipresent in electronics devices it has to be separated and recovered before dumping or burning outdated boards and other scrap. Optimal processes for retrieving gold under such circumstances are still under investigation [2].

Gold exists in solutions predominantly as colloidal gold and as Au(I) and as Au(III) cations. Au cations in both of these oxidation states are normally complexed in solution and can easily transform or disproportionate into each other with Au(III) being normally the more stable and more strongly complexed oxidation state. Gold ions can also easily be reduced to neutral gold atoms which can form nanoclusters. There exist a large number of experimental works on gold ions in connection to nanotechnology but very few molecular dynamics studies on solutions of gold ions have been performed, however. Farges et al. [3] performed an EXAFS study on aqueous Au(III) chloride and found that gold exists as AuX_4 complexes (X = Cl, OH) at higher and at $AuCl_4^-$ at lower pH values. Bryce et al. [4] studied gold(I) thiosulfate in aqueous solution by means of EXAFS measurements and density functional. They found a linear S–Au(I)–S coordination. Their calculations used a continuum model for the effect of water. Concerning MD simulations of liquid nitromethane (NM) and the resulting properties we refer to a recent paper [5] where classical and Car–Parrinello simulation results are compared with diffraction data. NM is one of the good solvent of gold ions. Therefore this work investigate to study the specific properties of Au(I)–NM_n cluster via quantum chemical calculations and the behaviors of Au(I) in liquid NM by molecular dynamics simulations.

2. Theory

2.1. Quantum chemical calculations

Most of our quantum chemical calculations were performed with the LANL2DZ [6] basis set for Au and the D95V [7] basis set for N, O, C and H. This choice of basis sets was motivated by the necessity of including relativistic effects for Au and the requirement that the LANL2DZ [6] basis set and ECP which is often used successfully for Au

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[2,8] must be combined with a same-quality basis for the lighter elements. This also allows us to perform quantum chemical calculations on the larger clusters. As a method we employed Hartree–Fock (HF) and MP2. Primarily because of the use of an ECP for the Au core electrons, the BSSE (basis set superposition error) of the binding energy at the HF level is small. For calculations at the MP2 level it was found that after correcting for the BSSE, (which is larger than for HF), both HF and MP2 binding energies are very similar, which is typical for systems dominated by electrostatics. The method and basis sets as mentioned above were performed to investigate the geometry, electronic structure, and the binding energy of $AuNM_n^+$ clusters with $n = 1–10$. Because NM is a molecule with a high dipole moment (4.6 debye) its electrostatic potential (Fig. 1) is divided into a positive half-space (CH_3) and a negative one (NO_2). This defines the electrostatics qualitatively . The chemical aspects of the coordination of Au(I) to NO_2 are discussed in paragraph 3 in detailed. All quantum chemical calculations were carried out with the Gaussian 03 [9] computer program.

2.2. Au^+–NM and NM–NM potential energy surface

The Au^+–NM and NM–NM intermolecular potential functions were developed for investigating the dynamics of Au(I) in liquid NM. We constructed an analytical pair potential for Au^+–NM by fitting the parameters of functions of the interatomic distances to energies derived from quantum chemical calculations. Details of these calculations were given in Section 2.1 above. Au(I) coordinates (Fig. 2) were generated along straight lines around a rigid NM molecule. In principle, it is not important how the conformation space is sampled unless important parts of it are left out. The subdivision of the sampling coordinates into straight lines only allows for an easy visualization of the potential energy in sets of distinct curves. The q_i partial charges of NM were taken from [10] as shown in Table 3, for reasons of consistency ($q_{Au} = 1$ a.u.). The equation and its parameters describing the Au^+–NM potential energy surfaces were obtained by minimizing the least-square deviation between the energies from the analytical formula and their quantum-chemically calculated counterparts.

We also calculated NM–NM energy surfaces at B3LYP/6–31 + G(d) level and constructed a NM–NM potential energy function, in the same way as described above. This served the purpose of providing an independent check since the intermolecular part of the NM potential energy function previously used for simulations of liquid NM [5,10] was derived from physical data of crystals of triazines [11,12]. Its accuracy is therefore difficult to judge and besides the issue of transferability sometimes such potential energy functions are not accurate for liquid state simulations where much more mutual orientations of neighboring molecules play a role than in the crystalline phase. We refer to this potential energy function subsequently as the 'generic NM pair potential'. The charges q_{ij} were fixed at the values given in [10] in order of being able to use the Au–NM energy function described above.

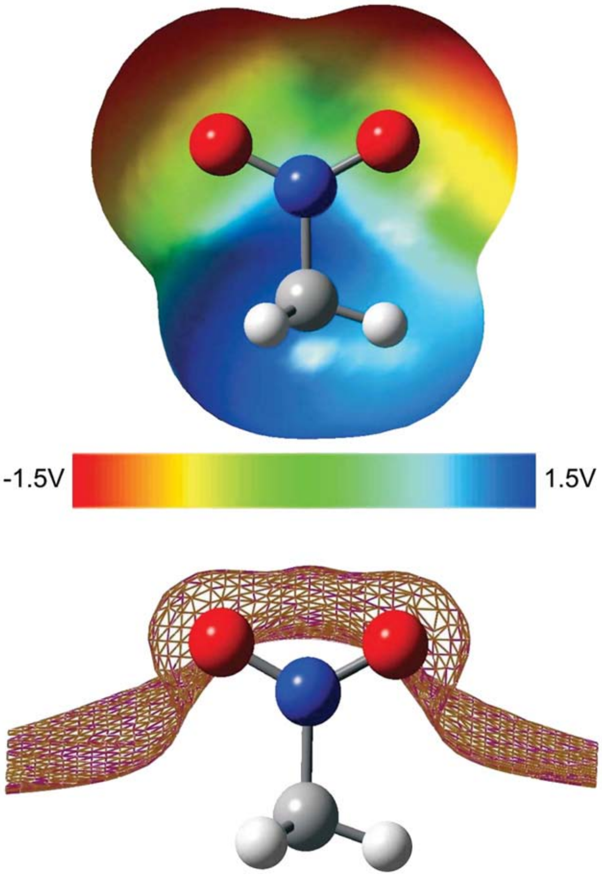

Fig. 1. Electrostatic potential of NM (upper part) and the surface of zero ESP (lower part).

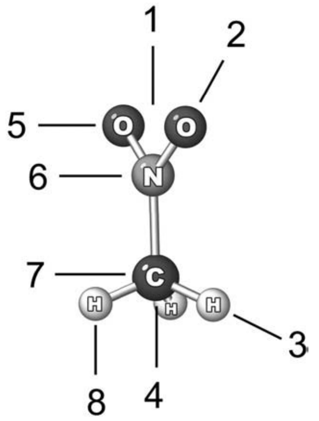

Fig. 2. Positions of Au around NM used for the construction of the Au^+–NM potential energy function. The solid lines refer to movement of Au^+. The numbers of the lines refer to the energy curves in Fig. 5.

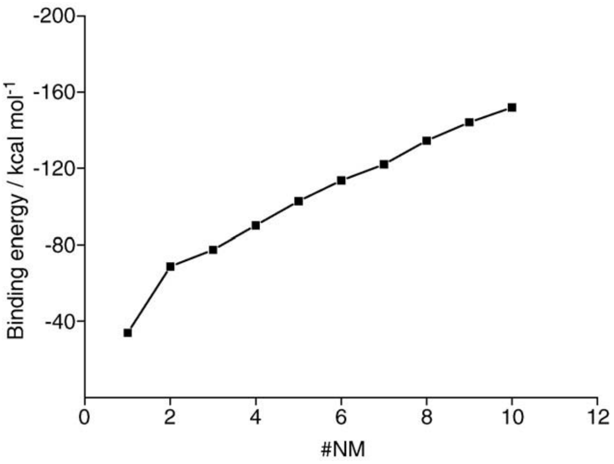

Fig. 3. Total ligand–cation binding energies defined as $E = E(Au(NM)_n^+) - E(Au^+) - nE(NM)$ in the $Au(NM)_n^+$ clusters with $n = 1$ to 10. It can be seen that for $n > 4$ the binding energies in the tri- to deca-coordinated complexes increase regularly.