

Cluster properties in the regime in which each atom counts

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Abstract

In this contribution we address (A) size selective reactivity of anionic gold clusters relevant for catalysis and (B) femtochemistry of metallic clusters and its control by tailored laser fields. In this connection the following results will be presented. (I) General mechanism for co-adsorption of O₂ and CO based on structure–reactivity relation has been obtained using DFT method which permits to elucidate fully available experimental results. (II) Simulation of pump–probe signals in the framework of negative-to-neutral-to-positive (NeNePo) spectroscopy using combination of Wigner distribution approach and MD “on the fly” allows to determine experimental conditions under which different processes such as geometric relaxation and internal vibrational relaxation (IVR) in Ag₂Au can be observed. (III) We show that optimal control theory can be used as a tool for analysis of ultrafast processes on example of photoionization processes in NaK, since the shapes of the optimized pulses based on full quantum mechanical treatment can be used to deduce the mechanisms of the processes underlying the optimal control.

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1. Introduction

The chemical reactivity of clusters as well as ultrafast processes induced by light can be tailored by size, structures and lasers. These non-scalable properties include: (A) size selective reactivity of metal oxide clusters relevant for catalyst design and (B) femtochemistry of clusters and its control by tailored laser fields driving selected ultrafast processes towards a maximal yield and suppressing other channels. In this contribution we present theoretical results based on first principle methods obtained for prototypes of above mentioned research directions. These are: (I) structure–reactivity relation of anionic gold clusters for co-adsorption of atomic and/or molecular oxygen and CO; (II) Identifica-

tion of ultrafast processes in NeNePo (negative to neutral to positive) signals of silver–gold mixed species; (III) Use of optimal control for maximizing the yield of photoionization processes in mixed alkali dimer NaK as a tool for analysis of underlying processes.

2. Results and discussion

2.1. Reactivity of anionic gold oxide clusters as model systems for heterogeneous catalysis

The discovery of Haruta [1] that nanosized gold particles can promote the oxidation of CO has led to increased interest into the catalytic activity of gold nanoclusters [2]. We report on joint theoretical and experimental investigation on reactivity of gold oxide clusters allowing us to gain an inside into the role which molecular vs. atomic chemisorption of oxygen might

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play in catalysis, e.g. in combustion of toxic CO. Upon establishing the structure–reactivity relation for the anionic gold oxide species Au_mO_n^- ($m = 2, 3$; $n = 1-5$) [3] the reactive centers have been identified which are responsible for oxidation of CO. They are (i) peripheral O-atom, (ii) O-atom bridging two Au-atoms and (iii) molecular bound O_2 group. For each kind of active center the energetics and reaction pathways based on proposed reaction mechanisms have been determined employing density functional method with appropriate functionals, e.g. B3LYP [4–6], allowing for the calculation of reliable binding energies and energetics along the reaction pathway [7,8].

(i) For peripheral O-atom the reaction mechanism is illustrated for the reaction of Au_2O^- with CO in the doublet spin state (Fig. 1 left). First, a complex I with weakly bound CO molecule is formed. The next reaction step, which involves a charge transfer from the cluster to the CO molecule leading to a strongly bound complex II with a CO_2 subunit, is crucial for the oxidation to proceed. The corresponding transition state TS_1 competes in energy with the reactants but lies slightly below in case of Au_2O^- making the reaction favorable. The same energetic situation has been found also for AuO^- , AuO_3^- , Au_2O^- , Au_2O_3^- and Au_2O_4^- and thus oxidation reactions have also been experimentally observed for these species. In general, once this barrier has been overcome and an intermediate like complex II (cf. Fig. 1 left) with a CO_2 subunit bound with an O-atom to the gold has been formed, the following reaction steps can be easily realized due to gained internal energy from complex formation. Oxidation can be realized via two pathways which involve (a) breaking of Au–O bond and forming of an Au–C bond or (b) rotation of O–CO group leading both to emanation of free CO_2 molecule. In contrast, e.g. for AuO_2^- and Au_3O_2^- , the transition state has an

higher energy with respect to the reactants and therefore reactions could not be observed.

(ii) The reaction at bridged O-atom follows a similar reaction mechanism: Like in the case of (i) the reaction is initiated by weak association of CO molecule with the bridged O-atom and is then followed by charge transfer from the cluster to the CO molecule. We found out, that oxidation on bridged O-atom can take place as realized in the case of Au_3O^- only if no further electron acceptor groups are bound to the neighbored gold atom (like O-atom in the case of Au_3O_2^- or O_2 group in Au_3O_3^-). This is due to the fact that binding of an electron acceptor leads to a dramatic increase of the ionic character of the inner Au–O bond and thus a higher binding energy, which is illustrated in Fig. 1 (right) for binding of O_2 to Au_3O^- forming Au_3O_3^- . As a consequence the electron transfer from oxygen to CO becomes unfavorable resulting in a very high reaction barrier (~ 1 eV) and therefore no oxidation reaction is observed for Au_3O_3^- .

(iii) For reactions with molecular oxygen the reaction mechanism is completely different from the above described due to the fact that the strong O=O bond must be broken for occurrence of oxidation of CO. According to this mechanism, CO binds after bond rearrangement to the gold atom leading to intermediate complex IV with a OOCO subunit. Starting with complex IV, two reaction pathways can be followed which might be realized under different experimental conditions. The first pathway (dashed path in Fig. 2) reflects conditions in which only one CO molecule is involved. Therefore, in order to emanate the reaction product CO_2 along this path, the O=O bond in complex IV has to be broken which is connected with a very high barrier (TS_4 in Fig. 2). In contrast, this barrier can be substantially lowered, if a second CO molecule is involved (solid path in Fig. 2). This second CO weakens the O=O bond and

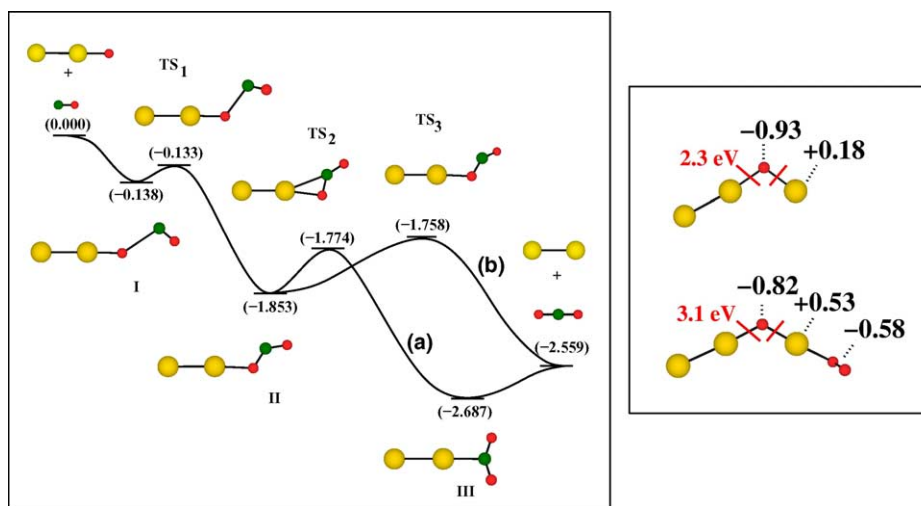


Fig. 1. Left: reaction profile for oxidation of CO by Au_2O^- in doublet spin state illustrating general reaction mechanism. Right: charges and binding energies for bridging O-atom for Au_3O^- and Au_3O_3^- .

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