



# Dynamic fluxionality and enhanced CO adsorption in the presence of coadsorbed H<sub>2</sub>O on free gold cluster cations



Xiaopeng Xing<sup>a,1</sup>, Xi Li<sup>a,2</sup>, Bokwon Yoon<sup>b</sup>, Uzi Landman<sup>b,\*\*</sup>, Joel H. Parks<sup>a,\*</sup>

<sup>a</sup> Rowland Institute at Harvard, Harvard University, Cambridge, MA 02142, USA

<sup>b</sup> School of Physics, Georgia Institute of Technology, Atlanta, GA 30332-0430, USA

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## ABSTRACT

This paper presents mass spectrometry measurements of the saturated adsorption of CO in the presence of coadsorbed H<sub>2</sub>O on gas phase gold cluster cations, Au<sub>n</sub><sup>+</sup>,  $n = 3-20$ , stored in a quadrupole ion trap. Initial mass spectra obtained at 150 K for specific cluster ion sizes as a function of CO pressure and reaction time, indicate increased CO saturation levels correlated with the coadsorption of background H<sub>2</sub>O vapor. Subsequent to these low temperature experiments, measurements were made of CO and H<sub>2</sub>O coadsorbed on Au<sub>6</sub><sup>+</sup> as a function of reaction time at 300 K. These mass spectra indicate that the reaction rate at constant CO pressure increases by an order of magnitude for a constant H<sub>2</sub>O pressure. First-principles density-functional theory calculations in conjunction with the above measurements allowed identification of energy barriers that control dynamic structural fluxionality between adsorption complexes that depends strongly on preadsorbed water. The calculations revealed that in the presence of H<sub>2</sub>O the energy barrier for the transition state between ground-state triangular and the incomplete hexagonal isomers of the [Au<sub>6</sub>(CO)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> complex is reduced to ~0 eV and the exothermicity is increased by 0.43 eV. The theoretical results also identified kinetic pathways exhibiting a transition of the incomplete hexagonal isomer of [Au<sub>6</sub>(ih)(CO)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> to the final saturated complex, Au<sub>6</sub>(ih)(CO)<sub>4</sub><sup>+</sup>. The energetics and kinetic pathway calculations are consistent with increased formation rates of Au<sub>6</sub>(CO)<sub>4</sub><sup>+</sup> as observed in mass spectra. The insights gained from these theoretical results not only explain measurements of the CO saturated adsorption on Au<sub>6</sub><sup>+</sup> in the presence of water, but also assist in rationalizing coadsorption results obtained over the broader range of cluster size at 150 K.

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## 1. Introduction

We begin with a brief historical introduction pertaining to the topic of catalytic reactions driven by gold nanoparticles, intended to relate the present research to results in that field. For a comprehensive background we refer to several available reviews of this subject [1–6].

Observation made in the late 1980s [6–8] about the catalyzed oxidation of CO on supported gold nanoparticles initiated extensive research efforts aimed at uncovering the origins and mechanisms

underlying the reactivity and catalytic activity of gold. Initially, the measurements of the catalytic reactivity were made for hemispherical gold particles with diameters of about 4–10 nm deposited on metal oxide surfaces. Further measurements indicated that the level of catalytic reactivity was strongly enhanced by coadsorbed water [9–12]. A decade later, to better understand the nature of the catalytic activity of supported gold particles, investigation of CO oxidation reactions were performed on atomically well-defined surfaces [13]. These measurements associated the catalytic activity with bilayer gold islands of 1–6 nm diameter supported on the surface of TiO<sub>2</sub>; with special emphasize of the role of periphery sites of these islands. Measurements of the effects of water on these controlled surfaces concluded that the enhancement of catalytic reactivity by H<sub>2</sub>O was due to an increased activation of molecular oxygen [14,15].

The development of instrumentation [16] with the capability to soft-land mass selected gold clusters of 1–20 atoms on metal oxide films and apply surface analysis techniques to study cluster–molecule interactions, introduced a new direction to the study of catalytic reactivity. These techniques provided the capability to compare measurements of reactivity with tractable

\* Corresponding author. Tel.: +1 617 497 4653; fax: +1 617 497 4627.

\*\* Corresponding author. Tel.: +1 404 894 3368; fax: +1 404 894 7747.

E-mail addresses: [xingxp@tongji.edu.cn](mailto:xingxp@tongji.edu.cn) (X. Xing), [xi\\_li@fudan.edu.cn](mailto:xi_li@fudan.edu.cn) (X. Li), [bokwon.yoon@physics.gatech.edu](mailto:bokwon.yoon@physics.gatech.edu) (B. Yoon), [uzi.landman@physics.gatech.edu](mailto:uzi.landman@physics.gatech.edu) (U. Landman), [parks@rowland.harvard.edu](mailto:parks@rowland.harvard.edu) (J.H. Parks).

<sup>1</sup> Current address: Department of Chemistry, Tongji University, No. 1239, Siping Road, Shanghai 200092, PR China.

<sup>2</sup> Current address: Department of Environmental Science and Engineering, Fudan University, No. 220, Handan Road, Shanghai 200433, PR China.

theoretical models. This direction has been greatly advanced by the development of computational methodologies for first-principles calculations and simulations of the properties and interactions of clusters [17] (metal clusters in particular). Of special relevance to the present study is the demonstrated ability of these calculations to predict the optimal structures of the ground- and isomeric-states of gold clusters [18]. These combined experimental and theoretical investigations resulted in deep insights into the chemical catalytic activity and atomic and electronic structures of surface-supported (mass-selected and soft-landed) and gas-phase (stored in a trap) gold (and other metal) clusters, and, most importantly, the mechanisms, dynamics and pathways of reactions catalyzed by these clusters [4b,19–24]. Pertinent to the investigations reported in the present paper we highlight the following findings from previous work:

- (1) The catalytic activity of gold clusters has been theoretically predicted and experimentally measured to be highly dependent on cluster size. In particular, in earlier work [19] on size-selected surface-supported gold clusters it has been theoretically predicted, and experimentally observed, that the catalytic activity of gold clusters emerges in clusters containing about 10 atoms having a three-dimensional structure; indeed in the initial work on magnesia-supported gold clusters the gold octamer has been found to be the smallest size cluster to catalyze the low-temperature oxidation of carbon monoxide to form CO<sub>2</sub>. This prediction, that has been supported initially by mass-spectrometric temperature programmed reaction measurements in the late 1990s [19], has been confirmed several years later in investigations employing aberration-corrected high-resolution electron microscopy [25]. Here we also highlight investigations aimed at exploring the effect of gold cluster dimensionality on the catalytic activity, and of ways to manipulate the dimensionality of supported gold clusters through controlled preparation of metal-oxide thin-films adsorbed on metal substrates (for example magnesia films on Mo(100) or Ag(100)) [23].
- (2) First-principles theoretical simulations have revealed and identified dynamic structural fluxionality as an important contributing factor to the catalytic activity of metal (gold in particular) nanoclusters [4b,20], whereby transition state activation barriers of catalyzed reactions are lowered by structural deformations of the cluster in the course of reaction. The concept of structural cluster fluxionality developed, as discussed above, in the context of surface-supported nanocluster catalysis, has been further investigated in studies of adsorption and reactions of hydrogen and oxygen on gas-phase gold cluster cations [24c]. Particularly pertinent to the current paper is the theoretical prediction, supported by the experimental mass-spectrometric data, pertaining to structural fluxionality of Au<sub>6</sub><sup>+</sup> induced by the adsorption of hydrogen molecules, and resulting in isomerization from a ground-state triangular structure to an incomplete hexagonal one. The theoretical results for hydrogen saturation coverages and reaction characteristics between the coadsorbed hydrogen and oxygen molecules were found to agree with the experimental findings. The joint investigations provided insights regarding hydrogen and oxygen cooperative adsorption effects and consequent reaction mechanisms [24c]. The concept [20] of structural fluxionality of clusters (SF), and dynamical SF (DSF), has been employed in a number of investigations. Examples include: (i) probing the structure of gas-phase metallic clusters via ligation energetics, through the use of measured equilibrium ligand-binding energies and entropies to unambiguously obtain structural information for the sequential addition of C<sub>2</sub>H<sub>4</sub> to Ag<sub>*m*</sub><sup>+</sup> (*m* = 3–7) clusters, where it been shown that

global structures can be obtained from temperature-dependent equilibrium data. Moreover, the method was found to be sensitive to ligand-induced SF of the clusters [26]; (ii) density functional studies of the reactivity of medium size gold cluster, Au<sub>*n*</sub>, (*n* = 14, 25, 29) with molecular oxygen, showing a strong dependence on SF [27]; photoelectron spectroscopy and first-principles calculations of [Au<sub>7</sub>(CO)<sub>*n*</sub>]<sup>−</sup> (*n* = 1–4), exhibiting SF manifested by structural dimensionality crossovers [28]; first-principles investigations of the collision processes between Au<sub>6</sub><sup>−</sup> and Ag<sub>6</sub><sup>−</sup> clusters and O<sub>2</sub>, where SF has been found to play an important role, and the higher sticking probabilities of the molecule to the silver anions were attributed to inherently different dynamical processes connected with the higher structural rigidity of Au<sub>6</sub><sup>−</sup> vs the floppy-like behavior of Ag<sub>6</sub><sup>−</sup> [29]; electronic structure investigation of the SF pathways emerging when transition metal anion clusters, W<sub>3</sub>O<sub>6</sub><sup>−</sup> and Mo<sub>3</sub>O<sub>6</sub><sup>−</sup>, react with hydrogen sulfide and ammonia. This study reported effects on the SF pathway due to different spin states of the anionic metal oxide cluster (doublet vs quartet), and the nature of the nonmetal in the small molecule (O vs S vs N) [30].

- (3) Theoretical calculations [22] have uncovered molecular mechanisms of water-induced (low humidity) enhancement of the gold catalyzed combustion of CO, entailing the activation of O<sub>2</sub> through formation of an hydroperoxyl intermediate.

The relationship between saturated adsorption and cluster structure has been studied previously in cluster beams for CO on clusters of Ni<sub>*n*</sub> (*n* = 2–20) [31]. The saturation of Ni<sub>*n*</sub>(CO)<sub>*m*</sub> suggested changes in the geometric structure induced by CO adsorption that could accommodate additional CO molecules. Studies of the adsorption of a single CO on isolated gold cluster cations in a Fourier transform ion cyclotron resonance mass spectrometer enabled measurements of the CO binding energy over a wide range of cluster sizes [32]. Calculations [32] of the Au<sub>*n*</sub>CO<sup>+</sup> structures for *n* = 3–9 found that a single adsorbed CO molecule can result in a different structure of the cluster complex than that corresponding to the lowest energy of the bare cluster. Adsorption studies [33] of gold cation beams combined measurements of saturation adsorption with infrared spectroscopy, aiming at interpretation of the data with the use of quantum-chemical calculations [34]. The data recorded for the gold cation beam, Au<sub>*n*</sub><sup>+</sup> (*n* = 3–10) [33], suggests that successive adsorption of CO molecules can cause distortion of the cluster structure. The only previous measurements [35] and calculations of the coadsorption of H<sub>2</sub>O and CO on free gold clusters have been performed for binary Ag<sub>*n*</sub>Au<sub>*m*</sub><sup>+</sup> cluster cations of very small size (*n* + *m* = 3).

In this paper, we present experiments and first-principles density-functional theory (DFT) calculations on mass-selected gas phase gold cluster cations, aiming at understanding the variation of CO saturated adsorption levels observed in the presence of water molecules. In addition, adsorption on gas phase cluster cations provides a well defined experimental configuration to observe and interpret dynamic structural fluxionality, suggested [20] to be a viable mechanism for enhancing reaction rates in nanocatalysis [4b,20].

Initial measurements were made for the saturated adsorption of CO on Au<sub>*n*</sub><sup>+</sup> at 150 K as a function of cluster size over the range of *n* = 3–20 atoms. These measurements identified interesting changes in the saturation levels introduced by H<sub>2</sub>O coadsorption from a residual water background pressure. These low temperature experiments were followed by controlled measurements at 300 K of CO adsorption on Au<sub>6</sub><sup>+</sup>, with and without the coadsorption of H<sub>2</sub>O, to aid the interpretation of the dynamics of these processes. Density-functional theory calculations identified the mechanism

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