Selective C-H bond Activation of Ethane by Free Gold Clusters

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The activation and potential dissociation of ethane mediated by small cationic gold clusters Au_x^+ ($x = 2-4$) has been explored by infrared multiphoton dissociation (IR-MPD) spectroscopy and density functional theory (DFT) calculations. The calculations show that the interaction between the gold clusters and ethane is mainly governed by the mixing of the ethane CH_3 bond-forming orbitals $\sigma(\text{CH}_3)$ with gold d-orbitals. While the C-C single bond appears to be unaffected, this mixing leads to the selective activation of up to two ethane C-H bonds and a reduction of the activation barrier for C-H bond dissociation to up to 0.82 eV, making the reaction kinetically feasible at room temperature. In agreement with this, experimental IR-MPD spectra of the complexes $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$ and $\text{Au}_2(\text{C}_2\text{D}_6)_2^+$ reveal that the dominant product is one where a single ethane C-H bond is dissociated resulting in a complex which contains an ethyl group and a bridge-bonded H atom along with a second, adsorbed C_2H_6 molecule. A similar C-H bond dissociation mechanism is theoretically predicted for the $\text{Au}_3(\text{C}_2\text{H}_6)_y^+$ ($y = 2,3$) and $\text{Au}_4(\text{C}_2\text{H}_6)_y^+$ ($y = 2,3$) complexes, albeit thermodynamically less favorable. IR-MPD spectra of $\text{Au}_3(\text{C}_2\text{H}_6)_y^+$ ($y = 2,3$) and $\text{Au}_4(\text{C}_2\text{H}_6)_y^+$ ($y = 2,3$) confirm the encounter product to be the dominant one, although the co-existence of isomers containing ethyl groups cannot be excluded. Various pathways for C-H bond activation are theoretically explored and the ethane activation mechanism is compared to the gold mediated activation of methane and ethylene.

1 Introduction

Ethane represents (besides methane) the second most abundant constituent of natural gas [1]. Nowadays it is mainly used for heating purposes as well as the production of ethylene in an energy demanding process [2, 3]. Due to the large abundance of ethane, its large scale use for the production of other chemicals such as e.g. ethanol or acetic acid would be desirable. All these mentioned processes require the activation and dissociation of one or more C-H bonds. Thus, the main challenge is the development of novel tailor-made catalytic materials that are on the one hand able to dissociate the strong ethane C-H bonds (4.38 eV [4]) and on the other hand are selective towards the desired reaction product. For the rational design of such catalytic materials, it is imperative to develop molecular level understanding of the catalyst-ethane interaction as well as of the the C-H bond activation and dissociation mechanism. In order to gain such fundamental insight the investigation of free metal atoms and small clusters as model systems for the active sites of heterogeneous and homogeneous catalysts is becoming of increasing importance [5-8]. In particular, the seminal contributions of Helmut Schwarz to this field have demonstrated the unique power of gas phase model systems for a fundamental understanding of C-H bond activation and dissociation mechanisms as well as the subsequent C-C, C-O, and C-N coupling reactions (see for example [9-16]).

So far gas phase studies of ethane activation by pure metals mainly focused on the investigation of atomic metal cations. Reactivity studies under single and multi-collision conditions as well as guided ion beam mass spectrometry revealed that the only exothermic reactions are single and double dehydrogenation of ethane (i.e. formation and elimination of H_2 and 2H_2) [17, 18]. Among the 3d and 4d metal cations merely the early metals Sc^+ , Ti^+ , Y^+ , Zr^+ , and Nb^+ have been found to dehydrogenate ethane to ethylene in an exothermic reaction [19-21], whereas this reaction

appeared to be endothermic for V^+ , Cr^+ , Mn^+ , Fe^+ , Co^+ , Ni^+ , Cu^+ , Zn^+ , Pd^+ , and Ag^+ (for studies performed before 1991, see Refs [17, 22, 23] and references therein) [24-32]. Exceptions are the late 4d metals Ru^+ and Rh^+ which catalyze the formation of $\text{MC}_2\text{H}_4^+ + \text{H}_2$ in an exothermic reaction [33-36]. Among the 5d metals, all so far studied cations, Ta^+ , Os^+ , Pt^+ , and Au^+ are able to dehydrogenate ethane in an exothermic reaction [37-42]. Furthermore, ligated platinum PtL^+ ($\text{L} = \text{CH}_2$, 2,2'-bipyridine, 2-phenylpyridine, 7,8-benzoquinoline) [43, 44] and iron FeL^+ ($\text{L} = \text{NH}$) [45] cations as well as Si^+ and La^+ were found to form H_2 from ethane [46, 47] whereas Al^+ , Lu^+ , and U^+ are unreactive [47-50].

In contrast to the numerous studies on atomic metal cations, much less is known about the interaction of metal clusters with ethane. Reaction studies of cationic iron clusters Fe_x^+ ($x = 4-13$) under single collision conditions showed that only Fe_4^+ is able to dehydrogenate ethane [51]. In contrast, platinum and rhodium clusters in a wide size range Pt_x^+ ($x = 1-21$) and Rh_x^+ ($x = 1-23$) were found to mediate the formation and elimination of H_2 [52-55]. Some of these clusters were even able to catalyze the double dehydrogenation to ethyne. Most interestingly, Rh_x^+ clusters show a strong cluster-size-dependent reaction efficiency in the whole investigated size range [55], whereas Pt_x^+ clusters have an efficiency close to 100% if they contain up to twelve atoms, and significant cluster size dependent variations are only observed for larger clusters. In an independent study the dehydrogenation cross section was shown to increase from about 30% to about 50% for Pt^+ and Pt_5^+ [56]. Furthermore, the mechanism for dihydrogen elimination appears to be fundamentally different for Pt_x^+ and Rh_x^+ (1,2-elimination to form $\text{Pt}_x^+-\text{H}_2\text{CCH}_2$ and 1,1-elimination to form $\text{Rh}_x^+-\text{CHCH}_3$, respectively) [53].

Besides these experimental studies on the interaction of ethane with cationic metal clusters, few neutral clusters have been studied theoretically. For cuboidal Ir_x ($x = 8,12,18$) clusters the cleavage of the first C-H bond yielding the inserted structure $\text{H-Ir}_x-\text{C}_2\text{H}_5$ has been found to represent the rate limiting reaction

step [57]. The activation barrier for this process appears to depend strongly on the cluster size and the ethane adsorption site, with corner atoms being most reactive. Furthermore, Al_{12}Ti in the roof-bend-like (marquee) structure binds ethane via coordination of one methyl group or via coordination with two C-H bonds from both methyl groups to the Ti atom [58]. Subsequent C-H bond cleavage is energetically more favorable than C-C bond cleavage (compare an activation energy of 0.20 eV with 0.30 eV for the triplet state and 0.06 eV with 0.30 eV for the singlet state).

We have recently employed small gold cluster cations as potential catalysts to mediate the selective activation of hydrocarbons such as methane [59-64] and ethylene [65]. However, to-date little is known about the interaction of gold with the C_2 alkane. Ethane was found to physisorb on an $\text{Au}(111)$ surface with a binding energy of 0.25 eV [66], which is in agreement with the theoretical value of 0.22 eV [67]. A similarly weak binding has also been reported for ethane adsorption on small neutral clusters Au_x ($x = 3-5, 10, 20$) ranging between 0.08 and 0.33 eV [68, 69]. The interaction can be considerably enhanced by exchanging one Au atom by a Ni atom [69] or by positively charging the cluster [68]. Dehydrogenation has not been reported and is rather unlikely due to the low binding energy. This is in contrast to the gold cation Au^+ which reacts under single as well as multi-collision conditions resulting in elimination of H_2 as well as AuC_2H_4^+ [40-42]. DFT calculations [32] have shown that C_2H_6 binds via Au-H interaction with a binding energy of 1.39 eV [40]. The barrier for subsequent C-H bond dissociation and formation of the inserted structure $\text{H-Au}^+-\text{C}_2\text{H}_5$ involves a barrier of only 0.19 eV whereas dissociation of the second C-H bond to form $\text{H}_2-\text{Au}^+-\text{C}_2\text{H}_4$ requires an energy of 1.26 eV and final elimination of H_2 requires 0.58 eV. However, the overall reaction is exothermic and all involved energy barriers lie below the energy of the separate reactants, thus the reaction can be observed even under single collision conditions. Schwarz and coworkers have recently studied the coupling of the gold carbene AuCH_2^+ with methane which was shown to result in the generation of ethane, bound by 1.27 eV to Au^+ [41]. Similar to the calculated pathway reported in Ref. [32], ethane was found to undergo subsequent reaction forming the insertion complex $\text{H-Au}^+-\text{C}_2\text{H}_5$ ($E_{\text{act}} = 0.24$ eV) and finally $\text{H}_2-\text{Au}^+-\text{C}_2\text{H}_4$ ($E_{\text{act}} = 1.12$ eV). Thus, the dissociation of the second C-H bond represents the rate determining reaction step which is in agreement with the reactive behavior of Pt^+ and Pt_x^+ clusters [37, 53] but in contrast to the findings for neutral cuboidal Ir clusters [57].

In this contribution we present the first experimental investigation of the interaction between small gold cluster cations Au_x^+ ($x = 2-4$) and ethane. $\text{Au}_x(\text{C}_2\text{H}_6)_y^+$ and $\text{Au}_x(\text{C}_2\text{D}_6)_y^+$ ($y = 2, 3$) complexes were produced in a flow tube reactor under multi-collision conditions and the formed products were subsequently studied with the use of infrared multiphoton dissociation (IR-MPD) spectroscopy in conjunction with first-principles simulations. The theoretical investigation of the electronic structure of $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$ reveals that the interaction between the gold clusters and ethane is mainly governed by mixing of the ethane CH_3 bond-forming orbitals $\sigma(\text{CH}_3)$ with the gold d-orbitals, which leads to the selective activation of some ethane C-H bonds. Indeed, the experimental IR-MPD spectra of the complexes $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$ and $\text{Au}_2(\text{C}_2\text{D}_6)_2^+$ show the existence of an isomeric

structure which contains an ethyl group (C_2H_5) and a bridge bonded H atom and thus proves the ability of Au_2^+ to dissociate one C-H bond of ethane at room temperature. A similar C-H bond dissociation mechanism is theoretically also predicted for $\text{Au}_3(\text{C}_2\text{H}_6)_y^+$ ($y = 2, 3$) and $\text{Au}_4(\text{C}_2\text{H}_6)_y^+$ ($y = 2, 3$) complexes, but the IR-MPD spectra indicate that the encounter complex is the dominant species formed, although contributions of isomers containing an ethyl group cannot be excluded.

2 Methods

2.1 Experimental Methods

Cationic gold clusters were produced by pulsed laser ablation of a rotating gold target using the second harmonic of a Nd:YAG laser. The ablation took place in a 3 mm diameter and 60 mm long growth channel in the presence of a short pulse of helium carrier gas. To enhance cluster growth the He buffer gas was seeded with about 5% oxygen; while this also led to the formation of Au_xO_2^+ complexes, these do not interfere due to the mass-selective detection method. Cluster-ethane complexes were formed by introducing a mixture of 1% ethane (C_2H_6 or perdeuterated C_2D_6) in helium via a second pulsed valve 50 mm downstream in a flow tube reactor. The gold cluster/ethane reaction resulted in the formation of $\text{Au}_x(\text{C}_2\text{H}_6)_y^+$ and $\text{Au}_x(\text{C}_2\text{D}_6)_y^+$ ($x = 2-4$ and $y = 1-2$) without any indication of ethane dehydrogenation in the mass spectrometric analysis.

On exiting the flow reactor, the reaction mixture was expanded into vacuum forming a molecular beam, which was collimated by a 2-mm diameter skimmer and a 8×0.45 mm horizontal slit aperture. After shaping, the ion beam entered the intracavity region where it interacted with the IR laser beam of the Free Electron Laser for Intra Cavity Experiments (FELICE) crossing it at an angle of 35° .

FELICE laser pulses are produced in a pulse train, the so-called macropulse, with a typical duration of 9 μs , consisting of ps-long micropulses at a 1 ns separation. The near transform limited radiation of FELICE covered the 240-1800 cm^{-1} spectral range and the spectral width was set to approximately 0.4% FWHM of the central frequency.

A few μs after interaction with FELICE, all clusters were extracted by a set of pulsed high voltage plates into a reflectron time-of-flight mass spectrometer and detected with a microchannel plate detector [70, 71].

In IR-MPD spectroscopy, vibrational spectra are recorded by monitoring fragmentation of a given cluster complex. Whenever the IR laser is in resonance with an IR active vibrational mode, multiple IR photons can be absorbed sequentially, leading to a heating of the complex and, when the internal energy is sufficient, to its fragmentation. This fragmentation results in a depletion of the detected signal intensity. IR-MPD spectra were recorded by measuring the cluster-complex intensity (I) in the mass spectrum as a function of the IR frequency. To correct for long term source fluctuations, the experiment was operated at twice the FELICE repetition rate, allowing for the recording of reference mass spectra (I_0) in between successive FELICE pulses. The IR-MPD spectra shown in this contribution display the ratio

Table 1: C₂H₆ to gold electron charge donation Q_q as well as C-C and C-H bond length, $d(C-C)$ and $d(C-H)$, for all theoretically investigated Au_x(C₂H₆)_y⁺ complexes.

cluster	$\mathbb{Q}^{(a)}$	Q_q/e	$d(C-C)/\text{\AA}^{(b)}$	$d(C-H)/\text{\AA}^{(c)}$
Au ₂ (C ₂ H ₆) ⁺	1	0.23	1.52	1.14, 1.12
Au ₂ (C ₂ H ₆) ₂ ⁺	1	0.16	1.52	1.17, 1.11
	2	0.16	1.52	1.17, 1.12
Au ₃ (C ₂ H ₆) ⁺	1	0.13	1.53	1.14, 1.14
Au ₃ (C ₂ H ₆) ₂ ⁺	1	0.11	1.53	1.14, 1.12
	2	0.11	1.53	1.14, 1.12
Au ₃ (C ₂ H ₆) ₃ ⁺	1	0.08	1.53	1.13, 1.13
	2	0.08	1.53	1.13, 1.13
	3	0.08	1.53	1.13, 1.13
Au ₄ (C ₂ H ₆) ⁺	1	0.16	1.53	1.13, 1.13
Au ₄ (C ₂ H ₆) ₂ ⁺	1	0.13	1.53	1.15, 1.12
	2	0.14	1.53	1.12, 1.12
Au ₄ (C ₂ H ₆) ₃ ⁺	1	0.10	1.53	1.13, 1.12
	2	0.11	1.53	1.15, 1.11
	3	0.10	1.53	1.14, 1.12

^(a) Number (label) of the C₂H₆ molecule. ^(b) free C₂H₆: $d(C-C) = 1.53 \text{ \AA}$ (theoretical value), $1.54 \text{ \AA}$ (experimental value [4]). ^(c) bond lengths of the two most activated C-H bonds; free C₂H₆: $d(C-H) = 1.10 \text{ \AA}$ (theoretical value), $1.09 \text{ \AA}$ (experimental value [4]).

of the mass peak intensity obtained with (I) and without (I_0) laser light. When the light is not resonant with a vibrational transition, no fragmentation occurs and the ratio I/I_0 is 1. In case of resonant absorption of IR light, the cluster complex fragments and the ratio I/I_0 becomes smaller than 1 which appears as a ‘depletion’ in the IR-MPD spectrum. At the same time a larger cluster may fragment into the mass channel of a specific cluster complex, causing an intensity ‘gain’, which is reflected by a I/I_0 value larger than 1. Due to this fragmentation mechanism it was not possible to obtain reliable IR-MPD spectra of Au_x(C₂H₆)⁺ containing one ethane molecules only and we focus on the investigation of Au_x(C₂H₆)_y⁺ ($y = 2, 3$) in the current study.

As a consequence of the required absorption of multiple photons, the observed IR depletion intensities can deviate from the linear IR absorption intensities, as predicted by calculations [72].

2.2. Theoretical Methods

The theoretical explorations of the atomic arrangements and electronic structures of the gold clusters and their complexes were performed with the use of density functional theory (DFT) employing the Vienna ab-initio simulation package VASP [73-76]. The wavefunctions were expanded in a plane wave basis with a kinetic energy cut-off of 400 eV. The interaction between the atom cores and the valence electrons was described by the projector augmented-wave (PAW) potential [77] and the exchange-correlation potential was described by the PBE generalized gradient approximation (GGA) [78].

For all calculations, a supercell with a lattice constant of $25 \text{ \AA}$ was used to avoid any interactions between the cluster complexes and their periodic images. To further minimize the electrostatic interaction with the images a neutralizing background charge as well as dipole and quadrupole corrections to the total energy were applied [79]. For structure optimization, convergence was achieved when the change in the total free energy was smaller than 10^{-6} eV .

The character of the wavefunctions was evaluated by projecting them onto spherical harmonics (in particular $l = 0, 1, 2$) within spheres around each atom (angular momentum projected local density of states, PLDOS). The radius of the spheres was chosen as half the average bond length (covalent radius) and amounted to $1.36 \text{ \AA}$ (Au), $0.76 \text{ \AA}$ (C), and $0.31 \text{ \AA}$ (H) [80]. In Figure 1, the density of states (DOS) shown for the entire cluster complexes (gray shaded) and the C₂H₆ molecule (green shaded) is the sum of the projected contributions ($l = 0 - 2$) calculated for each of the involved atoms.

To obtain insight into the charge transfer upon complex formation the charge density difference between the complex $\mathbb{Q}[\text{Au}_x(\text{C}_2\text{H}_6)_y]^+$ and the individual components, $\mathbb{Q}[\text{Au}_x]^+$ and $\mathbb{Q}[\text{y}(\text{C}_2\text{H}_6)]$, was calculated according to $\mathbb{Q}[\text{Au}_x(\text{C}_2\text{H}_6)_y]^+ - \mathbb{Q}[\text{Au}_x]^+ - \mathbb{Q}[\text{y}(\text{C}_2\text{H}_6)]$. The net charge transfer from C₂H₆ to the gold cluster was then estimated from $\mathbb{Q}[\text{Au}_x(\text{C}_2\text{H}_6)_y]^+$ by attributing the charge on each grid point to the nearest atom and summing over all these charges.

The vibrational spectra of the cluster complexes were calculated in the harmonic approximation by determining the dynamical matrix (matrix containing the electron density response to atomic displacements from equilibrium) using density functional perturbation theory [81, 82].

3 Results and Discussion

3.1 Gold-Ethane Interaction

To gain insight into the interaction between small gold cluster cations and ethane, we have first investigated the electronic structure of the gold-ethane complexes theoretically. As an example, Figure 1 displays the electronic density of states (DOS) for (left) a free C₂H₆ molecule, (middle) the gold-ethane encounter complex Au₂(C₂H₆)₂⁺ (below referred to as iso 2,2-a), and (right) an isolated Au₂⁺ cluster. The DOS is shown separately for spin up (majority spin) and down (minority spin) electrons. Also shown are all the occupied Kohn-Sham (KS) orbitals of C₂H₆ as well as selected KS orbitals of Au₂(C₂H₆)₂⁺.

The DOS shown in the middle of Figure 1 illustrates the modification of the electronic structure of C₂H₆ and Au₂⁺ upon formation of the Au₂(C₂H₆)₂⁺ complex. As noted above, the gray filled peaks of the Au₂(C₂H₆)₂⁺ DOS correspond to the total electronic DOS of the cluster complex while the green areas correspond to the DOS localized on the C₂H₆ molecules. The two energetically lowest lying orbitals closely resemble the C-H bond forming orbitals $\mathbb{Q}^{\text{H}}(\text{CH}_3)$ and $\mathbb{Q}^{\text{H}}(\text{CH}_3)$ of free C₂H₆. Similarly, the two ethane $\mathbb{Q}^{\text{H}}(\text{CH}_3)$ orbitals and the C-C bond forming $\mathbb{Q}(\text{CC})$ orbital are mainly localized on the ethane molecule and mixing with gold d-orbitals is rather limited. In marked contrast, the two (degenerate) occupied $\mathbb{Q}^{\text{H}}(\text{CH}_3)$ orbitals of ethane appear to mix considerably with the Au₂⁺ d-like orbitals. This mixing leads to a shift of the Fermi energy (ϵ_F) of ethane to lower energies and a considerable up-shift of the Fermi energy of Au₂⁺. Most interestingly, all orbitals close to ϵ_F are mainly localized on the gold atoms, with only small contributions from the ethane molecule. Finally, the highest occupied molecular orbital (HOMO) results from interaction of the ethane $\mathbb{Q}^{\text{H}}(\text{CH}_3)$ orbital with gold orbitals of s- and d-character that lie close to the Fermi energy of Au₂⁺. In particular, both the HOMO and the LUMO (lowest unoccupied molecular orbital) of the Au₂(C₂H₆)₂⁺, show

Figure 1: Electronic structure, represented by the density of states (DOS) and isosurfaces (encompassing 90% of the electron density) of selected KS orbitals (with positive and negative values depicted in blue and pink, respectively) for (left) a free C_2H_6 molecule, (middle) the encounter complex $Au_2(C_2H_6)_2^+$, and (right) an Au_2^+ cluster. The DOS is shown separately for spin up and down electrons and the occupied states (i.e. states with energy below ϵ_F) are shown as filled features on the energy axis. The Fermi level, ϵ_F , is denoted by a dashed line. The gray filled peaks of the $Au_2(C_2H_6)_2^+$ DOS correspond to the total charge of the cluster complex while the green areas correspond to the charge localized on the C_2H_6 molecules.

15 character (nodeless, delocalized superatom orbital) on the Au_2^+ cluster and $\pi^*(CH_3)$ character on the adsorbed ethane molecules.

The mixing of the occupied $\pi^*(CH_3)$ orbitals with the gold orbitals results in an electron charge donation Δq from ethane to gold and a partial de-occupation of the $\pi^*(CH_3)$ orbitals. This partial de-occupation is reflected in the lowest unoccupied molecular orbital (LUMO) that is formed by interaction of the occupied $\pi^*(CH_3)$ ethane orbitals and the unoccupied s-like gold orbital. The net charge ethane-to-gold charge donation Δq is estimated from the charge difference resulting from the interaction of Au_x^+ and γC_2H_6 (cf. Section 2.2) and is summarized in Table 1 for several theoretically investigated gold-ethane complexes. These complexes represent optimized structures of $Au_x(C_2H_6)_\gamma^+$ containing intact molecularly bound ethane and will be further discussed in the following sections. As can be seen, Δq depends on the cluster size, the number of adsorbed C_2H_6 molecules, and the adsorption site. Generally, the charge transfer per molecule decreases with increasing number of adsorbed C_2H_6 molecules and is higher for Au_2^+ and Au_4^+ compared to Au_3^+ . The latter can be understood by the closed shell, spin-paired electronic structure of the Au_3^+ cluster (singlet state), which inhibits the ethane-gold charge donation.

Table 1 also gives the distance between the carbon atoms, $d(C-C)$, after adsorption on the gold cluster cations. It is observed that for all investigated complexes $d(C-C)$ does not change compared to the value of the free C_2H_6 molecule (1.53 Å). Thus, the small mixing of the C-C bond-forming $\pi(CC)$ orbital with the gold orbitals is not sufficient for a noteworthy C-C bond activation. In marked

contrast, the gold-ethane interaction is mainly governed by mixing of the occupied ethane $\pi^*(CH_3)$ orbitals with gold d-orbitals which leads to an activation of the ethane C-H bonds. However, not all C-H bonds are activated but only those in close proximity to the Au atoms. In general, only two C-H bonds per C_2H_6 molecule are activated, and the corresponding activation barriers are given in Table 2. The highest selectivity for the activation of one C-H bond is observed for $Au_2(C_2H_6)_2^+$ with one C-H bond per molecule activated to $d(C-H) = 1.17$ Å whereas the bond lengths of all other C-H bonds are below 1.12 Å.

The observed interaction between the gold cations and ethane should lead to a reduction of the activation barrier for C-H bond dissociation. Therefore, we have calculated the energy barriers

Table 2: Calculated binding energies E_b between Au_x^+ and C_2H_6 as well as activation barriers for C-H bond dissociation $E_{act,1}$ and $E_{act,2}$ for the energetically most favourable reaction pathways.

cluster	E_b / eV ^(a)	$E_{act,1}$ / eV	$E_{act,2}$ / eV ^(b)
$Au_2(C_2H_6)_2^+$	0.88	0.30	--
$Au_2(C_2H_6)_2^+$	1.82 (0.91)	0.68	--
$Au_3(C_2H_6)^+$	0.88	0.78	0.34
$Au_3(C_2H_6)_2^+$	1.64 (0.82)	0.79	0.35
$Au_3(C_2H_6)_3^+$	2.28 (0.76)	0.82	0.36
$Au_4(C_2H_6)^+$	0.65	0.67	--
$Au_4(C_2H_6)_2^+$	1.18 (0.59)	0.64	--
$Au_4(C_2H_6)_3^+$	1.65 (0.55)	0.62	--

^(a) The values in the brackets give the binding energy per ethane molecule for complexes with more than one adsorbed C_2H_6 molecule; ^(b) If C-H bond dissociation results in a terminally bound H atom, $E_{act,2}$ represents the energy barrier that has additionally to be overcome to bring the H atom in a bridge bonded position (cf. Figure 3b).

Figure 2: IR-MPD spectra of (left) $Au_2(C_2H_6)_2^+$ and (right) $Au_2(C_2D_6)_2^+$ as well as calculated spectra of two isomeric structures. The calculated red curves corresponds to isomer iso 2,2-a, and the green curve corresponds to isomer iso 2,2-b. The green spectra are vertically shifted for clarity. The dots of the experimental spectra represent the sum of typically five spectra and the solid lines are obtained by a five-point average. Structural models: Au yellow, C gray, H white. The sticks at the bottom of the spectra show the line positions of IR active (black) and inactive (gray) modes of the free C_2H_6 and C_2D_6 molecule, respectively.

for several $Au_x(C_2H_6)_y^+$ complexes and the values for the lowest energy pathways for each $Au_x(C_2H_6)_y^+$ complex are summarized in Table 2. Details of the pathways will be further discussed in the following sections. The C-H bond strength in free ethane amounts to 4.38 eV [4] and Table 2 show that this energy barrier is considerably reduced to below 0.7 eV upon adsorption on the di- and tetra-gold clusters, whereas the barriers for the tri-gold complexes are slightly larger (0.78-0.82 eV). This difference might again be caused by the closed shell nature of Au_3^+ . In addition, Table 2 shows the calculated binding energies between Au_x^+ and C_2H_6 . It should be noted, that all the energy barriers are considerably smaller than the energy gained upon formation of the encounter complexes $Au_x(C_2H_6)_y^+$, and consequently the reactions are energetically directed “downhill” and the C-H bond dissociation represents an overall exothermic reaction.

3.2 Selective C-H Bond Dissociation Mediated by Au_2^+

The theoretical evaluation of the interaction between small gold cations and ethane suggests the activation of ethane C-H bonds upon adsorption on the cluster. Subsequent C-H bond dissociation occurs in an overall exothermic reaction and all the

activation barriers are below 0.82 eV. Since it should be possible to overcome such energy barriers in room temperature gas phase experiments operated under multi-collision conditions, we have next prepared $Au_x(C_2H_6)_y^+$ complexes in a flow tube reactor and probed the potential occurrence of this bond dissociation reaction via IR-MPD spectroscopy.

The left panel of Figure 2 displays the IR-MPD spectrum of the gold dimer with two ethane molecules adsorbed, $Au_2(C_2H_6)_2^+$, in the wavenumber range of 240-1800 cm^{-1} , as well as the calculated vibrational spectra of two different isomeric structures.

The experimental IR-MPD spectrum of $Au_2(C_2H_6)_2^+$ shows five main features (labeled with Roman numerals) in the investigated wavelength region. Since three of these bands (I, III and V) reach the same depletion of 50% it must be assumed that this is the maximum depletion, limited either by temporal and spatial overlap between laser beam and ion package, or by the coexistence of multiple species in the beam. This implies that bands I, III, and V may be saturated, which could lead to a broadening. Nevertheless, some of the bands are asymmetric, which indicates the overlap of several vibrational modes.

The IR spectrum of free ethane (cf. black sticks at the bottom

of Figure 2) is dominated by a strong absorption centered at 1468 cm^{-1} with a satellite at 1379 cm^{-1} (deformation vibrations of the methyl groups perpendicular to and along the C-C bond, respectively) and a second strong band at 822 cm^{-1} (methyl rocking vibration) [83, 84]. A further band observed in the IR is the torsion at 289 cm^{-1} . The 1468 cm^{-1} and 822 cm^{-1} modes appear readily recognizable in band V and the weaker band II, whereas the torsional mode at 289 cm^{-1} could be responsible for band I centered at 330 cm^{-1} . Furthermore, the dominant band III might correspond to the C-C stretch vibration at 995 cm^{-1} (cf. gray sticks at the bottom of Figure 2). This mode is IR forbidden in free ethane, however, complexation with Au_2^+ could lead to IR activation and a blue-shift of this mode. The only band that cannot be readily accounted for is the sharp band observed around 1280 cm^{-1} .

These tentative assignments can be checked by examining the spectrum for the perdeuterated species (Figure 2, right panel). Free C_2D_6 has IR active bands at 208, 594, 1077, and 1081 cm^{-1} which could be taken to correspond to the experimental bands I, II, and IV, although band I is blue-shifted. The IR forbidden C-C stretch vibration is red-shifted to 843 cm^{-1} upon perdeuteration of the molecule and may be considered to correspond to the intense band III of the experimental spectrum.

For a further interpretation of the experimental IR-MPD spectra of $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$ and $\text{Au}_2(\text{C}_2\text{D}_6)_2^+$, we will discuss now the calculated spectra of these complexes. Figure 2 shows the spectra for a complex containing two intact C_2H_6 molecules (iso 2,2-a, red curve) and for a complex containing an ethyl group and a bridge bonded H atom in addition to one intact ethane (iso 2,2-b, green curve). The structures of these two isomers are displayed

Figure 3 (a) Calculated energy profile (solid black curve) for the dissociation of up to two C-H bonds in the di-gold-complex $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$. The dashed green curve represents the corresponding energy profile for

C-H bond dissociation in $\text{Au}_2(\text{CH}_4)_2^+$ which will be discussed in section 3.3. (b) Calculated energy profiles for the dissociation of one C-H bond in the tri-gold complexes $\text{Au}_3(\text{C}_2\text{H}_6)_2^+$ (black curve) and $\text{Au}_3(\text{C}_2\text{H}_6)_3^+$ (red curve). All energies are given with respect to the energy of the reactants. The numbers in parentheses denote the barrier height. Structural models: Au yellow, C gray, H white.

below the experimental spectrum. Comparison of the IR-MPD spectrum and the calculated spectrum of iso 2,2-a (red curve) shows that bands I, II, and V are well reproduced by the modes discussed for free C_2H_6 (torsion for band I, methyl rocking vibration for band II and CH_3 group deformations for band V). However, the theoretically obtained values are slightly blue-shifted compared to the experimental ones, which can be explained by the use of the harmonic approximation in the calculations. Furthermore, the predicted intensity for band I is clearly underestimated, whereas the predicted intensity for II is clearly overestimated. Due to the binding mode of ethane to the gold dimer, the C-C stretch hardly shifts from the value of the free molecule (compare 990 and 991 cm^{-1} for $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$ to 995 cm^{-1} for free C_2H_6 [84]). Thus, band III might indeed arise from the C-C stretch, although the IR intensity appears to be strongly underestimated. In addition, iso 2,2-a offers a possible explanation for band IV in the form of an intense band at 1235 cm^{-1} associated with the deformation mode of the methyl group, although the inconsistencies between the measured and calculated relative intensities and vibrational band frequencies make this assignment somewhat tentative.

The match between iso 2,2-a for the perdeuterated species may be judged as perhaps even less convincing, as the vibrational band that could explain band I in the perprotio system red-shifts by about 100 cm^{-1} upon deuteration while the experimental band I does not shift. A more promising alternative is offered by iso 2,2-b: here, the frequencies of essentially all bands are predicted satisfactorily. In particular, the strong band III is described most satisfactorily by the calculated mode at 1029 cm^{-1} which corresponds to the Au-H stretch mode of the bridged H, and band IV is in rather good agreement with the theoretically predicted mode at 1292 cm^{-1} corresponding to a CH_3 deformation motion of the ethyl group. Although certain inconsistencies remain - for instance in the predicted relative intensities of bands I and V, or the slightly too low frequency for the Au-D stretch at 790 cm^{-1} - we conclude that altogether the spectrum of iso 2,2-b offers a much better match to the experimental $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$ and $\text{Au}_2(\text{C}_2\text{D}_6)_2^+$ spectra.

Thus, while we cannot rule out the presence of iso 2,2-a, (notably the band that starts to appear on the high frequency side of the perdeuterated spectrum is an indicator for its existence), we assign the experimental spectrum as corresponding to iso 2,2-b. This shows directly that Au_2^+ is able to mediate the activation and dissociation of one C-H bond in ethane.

The calculated energy profile for C-H bond dissociation mediated by Au_2^+ is shown by the black curve in Figure 3a. Au_2^+ adsorbs two C_2H_6 molecules with an average binding energy $E_{b,av}$ of 0.91 eV per C_2H_6 molecule (iso 2,2-a). Dissociation of one C-H bond requires an activation energy of $E_{act} = 0.68$ eV and leads to iso 2,2-b with an ethyl group (C_2H_5) and a bridge bonded H atom. This isomer is thermodynamically more favorable by 0.33 eV than the simple encounter complex. Dissociation of a second C-H bond (of the second intact C_2H_6) involves an energy barrier of $E_{act} = 1.85$

eV resulting in complex iso 2,2-c which is 0.93 eV less stable than iso 2,2-a and 1.26 eV less stable than iso 2,2-b. This energy profile shows that the selective dissociation of the first C-H bond in $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$ is overall exothermic by 2.15 eV and thus consistent with the observation under the current experimental conditions, signaled by bands corresponding to iso 2,2-a and iso 2,2-b in the IR-MPD spectrum. The barrier of 1.85 eV for dissociation of a second C-H bond makes the formation of iso 2,2-c less likely, although the whole reaction path does not involve energies higher than the energy of the separated $\text{Au}_2^+ + 2 \text{C}_2\text{H}_6$. Based on the experimental IR-MPD spectra the formation of iso 2,2-c and its presence in the molecular beam cannot be excluded.

The considerable increase of the energy barrier for dissociation of a second C-H bond can be partly understood by a change of the electronic structure of the complex caused by the dissociation of the first C-H bond. In iso 2,2-a C_2H_6 binds via electron donation of about 0.16 e per molecule. This leads to an elongation of one C-H bond in each molecule to $d(\text{C-H}) = 1.17 \text{ \AA}$. Dissociation of this C-H bond changes the electronic structure in such a way that the charge transfer from the intact ethane molecule is reduced to about 0.12 e which results in $d(\text{C-H}) = 1.14 \text{ \AA}$. Thus, one may surmise that dissociation of one C-H leads to deactivation of the second C-H bond, reflected in the above-noted 0.03 $\text{\AA}$ decrease in the C-H bond length. This process may contribute to the predicted increase of the activation barrier for a second C-H bond dissociation, but is not likely to be the determining factor. Rather, we believe that the deformation of the linear geometry of the iso 2,2-b species that accompanies the second C-H bond activated dissociation (see Fig. 3a), leads to a later transition state, thus resulting in a higher second C-H bond activated dissociation barrier.

3.3 Comparison of Au_2^+ Mediated Activation of Ethane, Methane, and Ethylene

In recent studies we have explored the interaction of small gold cations with methane [59-64] and ethylene [65], and now with ethane. All three molecules have very stable C-H bonds (4.54 eV for CH_4 , 4.38 eV for C_2H_6 , and 4.82 eV for C_2H_4 [4]) whose activation requires either high temperature or highly active catalysts.

Recently, we have shown that binding of ethylene to Au_2^+ is governed by mixing of the ethylene $\text{C}=\text{C}$ double bond forming orbitals, $\sigma(\text{CC})$ and $\sigma(\text{CC})$, with Au_2^+ orbitals, while the C-H bond forming orbitals, $\sigma(\text{CH}_2)$, $\sigma(\text{CH}_2)$, $\sigma(\text{CH}_2)$, and $\sigma(\text{CH}_2)$, hardly mix with the gold orbitals [65]. This mixing leads to a net charge donation from the molecule to the gold cluster, and the $\text{C}=\text{C}$ double bond is activated, while the C-H bonds appear to be unaffected. This gold-ethylene interaction is in marked contrast to the gold-ethane interaction, which, as discussed above, is governed by the mixing of the occupied C-H bond-forming $\sigma(\text{CH}_3)$ orbitals with the gold orbitals resulting in a net charge donation from ethane to gold and a selective activation of some C-H bonds whereas the C-C single bond appears to be unaffected. Thus, in the C_2 alkane the gold cluster cations activate the C-H bond, whereas in the C_2 alkene it is the $\text{C}=\text{C}$ bond that gets activated.

The smallest alkane, methane, binds via mixing of C-H bond-forming orbitals and Au orbitals, leading to a net charge transfer from methane to the gold cluster and an activation of the C-H bond [59, 61, 63]. However, dissociation of a first C-H bond

appears to be energetically more favorable for ethane than for methane. For example, the calculated barrier for C-H bond dissociation upon adsorption of one molecule amounts to 0.63 eV for $\text{Au}_2(\text{CH}_4)^+$ [65] while it is only 0.30 eV for $\text{Au}_2(\text{C}_2\text{H}_6)^+$ (cf. Table 2). This finding is in accord with previous single gold cation studies on the Au^+/CH_4 and $\text{Au}^+/\text{C}_2\text{H}_6$ couples. Au^+ does not form any reaction products with methane under single collision conditions which indicates the formation of only a weakly bound encounter complex Au^+-CH_4 [42, 85] without exothermic C-H bond dissociation and formation of $\text{H-Au}^+-\text{CH}_3$. In marked contrast, reaction with ethane leads to facile dehydrogenation which is most likely caused by reduced activation barriers for C-H bond dissociation [41, 42].

The energetics for C-H bond dissociation upon adsorption of two molecules are shown in Figure 3a for $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$ (solid black curve) and $\text{Au}_2(\text{CH}_4)_2^+$ (dashed green curve), respectively. While dissociation of a first methane C-H bond requires an energy of 0.80 eV [59], this value is reduced to 0.68 eV for dissociation of a first ethane C-H bond. The lower activation barrier for ethane is linked to the increased stability of the resulting ethyl complex, which is considerably more stable than the encounter complex (-0.33 eV); the methyl complex is almost isoenergetic with the corresponding encounter complex (with a mere energy difference of -0.02 eV). However, the dissociation of a second methane C-H bond is energetically more favorable (activation barrier: $E_{\text{act}} = 1.39 \text{ eV}$) than the dissociation of a second ethane C-H bond ($E_{\text{act}} = 1.85 \text{ eV}$, see Fig. 3a). Thus, while

Figure 4: IR-MPD spectra of (top row) $\text{Au}_3(\text{C}_2\text{H}_6)_2^+/\text{Au}_3(\text{C}_2\text{D}_6)_2^+$ and (bottom row) $\text{Au}_3(\text{C}_2\text{H}_6)_3^+/\text{Au}_3(\text{C}_2\text{D}_6)_3^+$ as well as calculated spectra of intact isomeric structures iso 3,2-a and iso 3,3-a (red curves) and singly dissociated isomers iso 3,2-b and iso 3,3-b (green curves, vertically shifted for clarity). The dots of the experimental spectra represent the sum of typically five spectra and the solid lines are obtained by a five-point average. Structural models: Au yellow, C gray, H white.

the dissociation of a first methane C-H bond is slightly more energy demanding than the dissociation of a first ethane C-H bond, the dissociation of a second C-H bond is energetically more feasible for methane. This barrier of 1.39 eV has previously been shown to be overcome in a room temperature gas phase

experiment, leading to the subsequent formation and elimination of H₂ and ethylene [59].

As in the case of reactions involving methane adsorbed on Au_x⁺ [63], zero-point energy (zpe) corrections to the aforementioned energies reduce them by about 0.1–0.15 eV; for example iso 2,2-b is more stable than iso 2,2-a by -0.42 eV when including zpe correction (-0.33 eV without zpe correction) and the barriers for C-H bond dissociation are reduced from 0.68 eV and 1.85 eV to 0.57 eV and 1.71 eV, respectively, when including zpe corrections.

3.4 Ethane Activation by Au₃⁺

To gain insight into a possible cluster size effect of the ethane C-H bond activation we have investigated the complexes Au₃(C₂H₆)_y⁺ (y = 2,3). Two C₂H₆ molecules bind to Au₃⁺ with an average binding energy of 0.82 eV per molecule forming the encounter complex Au₃(C₂H₆)₂⁺ (iso 3,2-a). The black curve in Figure 3b shows that dissociation of one C-H bond requires an activation energy of 0.79 eV leading to iso 3,2-b. In contrast to the gold-dimer complex iso 2,2-b, the gold-trimer complex iso 3,2-b is thermodynamically less favorable by 0.78 eV than the simple encounter complex iso 3,2-a. Furthermore, dissociation of a C-H bond mediated by Au₂⁺ results in a bridge bonded H atom whereas the abstracted H atoms is terminally bound to Au₃⁺. Bringing the H atom in a bridge position requires to overcome a second activation barrier of 0.35 eV and leads to an energetically even less stable iso 3,2-c. The energetics for C-H bond dissociation hardly changes for the complex Au₃(C₂H₆)₃⁺ containing three ethane molecules (cf. red curve in Figure 3b). It should be noted that both reaction paths proceed at energies well below the energy of the separated reactants Au₃⁺ + y C₂H₆, and the activation reactions are thus thermodynamically feasible. Further isomeric structures containing ethyl groups were found to be less stable than iso 3,2-b and 3,3-b and are shown in Figure S1 and S2 of the supporting information.

The top panels of Figure 4 show the IR-MPD spectra obtained on the mass of Au₃(C₂H₆)₂⁺ (left) and Au₃(C₂D₆)₂⁺ (right), respectively. The experimental spectrum is accompanied by calculated spectra for the minimum energy structure iso 3,2-a (red curve) and of iso 3,2-b (green curve). In the spectral region below 900 cm⁻¹ the IR-MPD spectra recorded on the mass of Au₃(C₂H₆)₂⁺ is dominated by I/I₀ values slightly larger than 1. This is likely caused by fragmentation of a heavier complex, into the mass channel of Au₃(C₂H₆)₂⁺. Such a fragmentation process can - depending on the relative signal intensities of the complexes as well as the exact frequency and oscillator strength of the vibrational modes - cancel the depletion signals of Au₃(C₂H₆)₂⁺. Such cancellations can complicate the interpretation of the observed spectra, thus, this spectral region will not be further considered in the following.

The IR-MPD spectrum of Au₃(C₂H₆)₂⁺ shows four distinct bands in the wavenumber region between 900 and 1750 cm⁻¹, of which band I, III and IV strongly reminisce the absorption band III, IV and V in the Au₂(C₂H₆)₂⁺ spectrum. Band III in that spectrum was intense, and judged diagnostic for the presence of a bridge-bonded Au-H-Au; in the current spectrum band I is found at the same frequency, but it is rather weak and could be due to the C-C stretch vibration. For the perdeuterated system (where we neglect the spectrum below 800 cm⁻¹, as it is likely contaminated

by signal gain from Au₃(C₂D₆)₃⁺, discussed below) a similar observation can be made: bands I, II, and III are at very similar frequencies as bands III, IV, and V of the Au₂(C₂D₆)₂⁺ spectrum, with the intensity of band I strongly reduced (as in the undeuterated case discussed above). Combined with the increased depletion strength of band III (compared to the Au₂(C₂D₆)₂⁺ band V) the spectrum points to an increased contribution of the encounter complex. Indeed, when considering the experimental spectrum of Au₃(C₂H₆)₂⁺, all four bands appear in good agreement with the calculated spectrum of iso 3,2-a, where the width of band IV in combination with the relative strength of the predicted band at 1478 cm⁻¹ likely points at saturation. Bands II and III can also be described by modes predicted for iso 3,2-b but their predicted intensity ratio is reversed from the observed one; the calculated mode at 940 cm⁻¹ (corresponding to a joint motion of the C₂H₅ unit and the terminal H atom) is predicted to be somewhat red-shifted by 40 cm⁻¹ from the experimental band I. However, a contribution of this vibrational mode to the IR-MPD spectrum could explain the high intensity of the experimental band I, as well as the extension of band IV to the blue. Similarly, the main features in the IR-MPD spectrum of Au₃(C₂D₆)₂⁺ (right spectrum in the top panel of Figure 4) are mirrored in the calculated spectrum of iso 3,2-a. Here, indications of the presence of iso 3,2-b are limited to the broadening of band II at the blue edge. Calculated spectra of further isomeric structures are shown in Figure S1 of the supporting information. Based on the IR-MPD spectra contributions of these isomers cannot be definitely excluded.

The lower panels of Figure 4 show the IR-MPD spectra obtained for Au₃(C₂H₆)₃⁺ (left) and Au₃(C₂D₆)₃⁺ (right), respectively. Again, calculated vibrational spectra of iso 3,3-a (red curve) and iso 3,3-b (green curve) are displayed for comparison. The IR-MPD spectrum of Au₃(C₂H₆)₃⁺ shows six distinct bands over the measured spectral region. Comparison to the spectrum of Au₃(C₂H₆)₂⁺ shows great similarities for both perprotio and perdeuterated systems, with the exception of band II for Au₃(C₂H₆)₃⁺ (no counterpart for Au₃(C₂H₆)₂⁺) and bands I, II and III for the perdeuterated species. The absence of these bands for Au₃(C₂H₆)₂⁺/Au₃(C₂D₆)₂⁺ can be disputed, as depletions in Au₃(C₂H₆)₃⁺/Au₃(C₂D₆)₃⁺ appear mirrored in signal gain for Au₃(C₂H₆)₂⁺/Au₃(C₂D₆)₂⁺, with signs of superimposed depletion for Au₃(C₂D₆)₂⁺ at 300 cm⁻¹.

The spectra of both isotopologues are in good agreement with the calculated ones for the minimum energy isomer iso 3,3-a, containing only intact ethane molecules. However, we cannot rule out contributions from iso 3,3-b, for instance through the intense mode at 947 cm⁻¹, red-shifted by 40 cm⁻¹ from the experimental band III for Au₃(C₂H₆)₃⁺ or hidden in the high-frequency tail of band I. Similarly, the IR-MPD spectrum of Au₃(C₂D₆)₃⁺ could show signs of iso 3,3-b through its predicted mode at 910 cm⁻¹ red-shifted by 30 cm⁻¹ from the experimental band V, through observation of band II, or through the strong broadening of band IV.

The calculated spectra of two further isomeric structures iso 3,3-c and iso 3,3-d are shown in Figure S2 of the supporting information. The presence of iso 3,3-c can be excluded due to the very strong vibration at 1681 cm⁻¹ which is not observed in the experimental spectrum, while contributions from iso 3,3-d cannot

be excluded on basis of the IR-MPD spectra.

To summarize, the IR-MPD spectra of $\text{Au}_3(\text{C}_2\text{H}_6)_y^+$ ($y = 2,3$) and $\text{Au}_3(\text{C}_2\text{D}_6)_y^+$ ($y = 2,3$) are in very good agreement with the calculated spectra of the minimum energy structures iso 3,2-a and iso 3,3-a containing intact ethane molecules only. All of the theoretically predicted modes are also observed in the experimental spectra. There are some indications for contributions from the higher energy isomers iso 3,2-b and iso 3,3-b with one ethyl group and a Au-H bond to the experimental spectra, although their presence is not unambiguous. We conclude that co-existence of the higher energy isomers (also those shown in Figure S1 and S2) in the molecular beam cannot be excluded. However, based on the IR-MPD spectra, as well as the energy profile for C-H bond dissociation shown in Figure 2b, it can be expected that iso 3,2-a and iso 3,3-a represent the dominant species.

3.5 Ethane Activation by Au_4^+

Finally, we have studied the tetra-gold-ethane complexes with two and three adsorbed ethane molecules. Au_4^+ has a planar rhombic structure with two different adsorption sites, corresponding to 2-fold coordinated (2c) and 3-fold coordinated (3c) gold atoms [86-89]. Thus, intact adsorption of two ethane molecules on Au_4^+ leads to three different isomeric structures (cf. Figures 5 and S3a). One possibility is the adsorption of one molecule on a 3c and one on a 2c gold atom with an average binding energy of 0.59 eV for each molecule (iso 4,2-a, cf. Figure

stable isomer (iso 4,2-a'', +0.10 eV). Adsorption of a third ethane molecule on Au_4^+ leads to two isomeric structures (cf. Figures 5 and S5a). In the minimum energy structure two C_2H_6 molecules bind to the 3c Au atoms and one to a 2c Au atom (iso 4,3-a, 0.55 eV average binding energy per C_2H_6 ; cf. Figure 5) whereas the structure with two C_2H_6 molecules bound to the 2c Au atoms and one to a 3c Au atom (iso 4,2-a') is 0.12 eV higher in energy. Thus, the coexistence of all these isomers in the molecular beam is most likely, although they cannot be distinguished in the IR-MPD-spectrum due to the similarity of their vibrational spectra.

As a result of these energetically close lying isomers, several pathways for C-H bond dissociation are possible (cf. Figures S3b and S5b). For $\text{Au}_4(\text{C}_2\text{H}_6)_2^+$ the pathway with the lowest activation barrier (0.64 eV) starts from iso 4,2-a and results in a structure with an H atom bridging the two C_2H_6 binding Au atoms (iso 4,2-b, cf. Figure 5). An only slightly larger energy of 0.67 eV is required for C-H bond dissociation starting from iso 4,2-a'' whereas C-H bond dissociation in iso 4,2-a' requires at least 0.79 eV. Some of the studied dissociation reactions even cause a dimensionality (two-dimensional, 2D $\rightarrow$ three-dimensional, 3D) transition of the gold cluster. For $\text{Au}_4(\text{C}_2\text{H}_6)_3^+$ the pathway with the lowest activation barrier ($E_{\text{act}} = 0.62$ eV) starts from isomer iso 4,3-a' and results in iso 4,3-b with an ethyl group bound to a 3c Au atom and the H atom bridging two C_2H_6 binding Au atoms (cf. Figure 5). The lowest reaction pathway starting from the minimum energy isomer iso 4,3-a requires an energy of 0.78 eV. All reaction pathways proceed at energies well below the energy of the separated molecules and are thus exothermic.

The top panel of Figure 5 displays the IR-MPD spectra obtained on the mass of $\text{Au}_4(\text{C}_2\text{H}_6)_2^+$ (left) and $\text{Au}_4(\text{C}_2\text{D}_6)_2^+$ (right), and the bottom panel displays the IR-MPD spectra of $\text{Au}_4(\text{C}_2\text{H}_6)_3^+$ (left) and $\text{Au}_4(\text{C}_2\text{D}_6)_3^+$ (right). The red and green curves in the top panel of Figure 5 represent the calculated vibrational spectra of iso 4,2-a and iso 4,2-b and the ones in the bottom panel represent the calculated spectra of iso 4,3-a and iso 4,3-b.

Upon comparison of the experimental spectra for $\text{Au}_3(\text{C}_2\text{H}_6)_{2,3}^+/\text{Au}_3(\text{C}_2\text{D}_6)_{2,3}^+$ and $\text{Au}_4(\text{C}_2\text{H}_6)_{2,3}^+/\text{Au}_4(\text{C}_2\text{D}_6)_{2,3}^+$ their striking similarities stand out, suggesting that also for Au_4^+ the encounter complex is the dominant product. Indeed, all features of the experimental spectra are nicely predicted by the calculated spectra of the minimum energy isomers (iso 4,2-a and iso 4,3-a) containing intact C_2H_6 molecules. Just as for the Au_3^+ systems, we cannot rule out minor contributions from isomers iso 4,2-b and iso 4,3-b, containing an ethyl group and a bridge-bonded H atom, or further isomeric structures (for which calculated vibrational spectra are shown in Figures S4 and S6 of the supporting information). Thus, we conclude that the encounter product is dominant, although the co-existence of isomeric structures containing an ethyl group cannot be excluded. This is in agreement with the calculated reaction pathways (cf. Table 2 and Figures S3b and S5b) that suggest that C-H bond dissociation and formation of ethyl groups should be possible under the given experimental conditions.

4 Conclusion

We have employed IR-MPD spectroscopy in conjunction with density functional theory calculations to elucidate the interaction between small gold cations and ethane. Investigation of the

Figure 5: IR-MPD spectra of (top row) $\text{Au}_4(\text{C}_2\text{H}_6)_2^+/\text{Au}_4(\text{C}_2\text{D}_6)_2^+$ and (bottom row) $\text{Au}_4(\text{C}_2\text{H}_6)_3^+/\text{Au}_4(\text{C}_2\text{D}_6)_3^+$ as well as calculated spectra of intact absorption products iso 4,2-a and iso 4,3-a (red curves) and singly dehydrogenated products iso 4,2-b and iso 4,3-b. (green curves, vertically shifted for clarity). The dots of the experimental spectra represent the sum of typically five spectra and the solid lines are obtained by a five-point average. Structural models: Au yellow, C gray, H white.

5). Adsorption of the C_2H_6 molecules on the two 3c Au atoms (iso 4,2-a') is isoenergetic with iso 4,2-a, whereas adsorption of the C_2H_6 molecules on the two 2c Au atoms leads to a slightly less

electronic structure of $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$ reveals that the gold-ethane interaction is mainly governed by mixing of the ethane C-H bond-forming orbitals $\sigma^*(\text{CH}_3)$ with gold d-orbitals. This leads to a net ethane to gold electron charge donation and the selective activation of some C-H bonds.

Calculated reaction pathways for subsequent C-H bond dissociation show that for all investigated complexes $\text{Au}_x(\text{C}_2\text{H}_6)_y^+$ the overall reaction is exothermic, and that the activation barriers range between 0.3 eV and 0.82 eV, i.e. the reaction could proceed under thermal conditions at room temperature. In agreement with these findings, the measured IR-MPD spectra of $\text{Au}_2(\text{C}_2\text{H}_6)_2^+$ and $\text{Au}_2(\text{C}_2\text{D}_6)_2^+$ show strong indications for the co-existence of two isomeric structures, one with intact C_2H_6 molecules only, and one with an ethyl group and a bridge bonded H atom. The $\text{Au}_3(\text{C}_2\text{H}_6)_y^+$ ($y = 2,3$) and $\text{Au}_4(\text{C}_2\text{H}_6)_y^+$ ($y = 2,3$) IRMPD are dominated by the encounter complex, although the formation of singly dehydrated isomers cannot be excluded.

This investigation shows that fundamental molecular level insight into the activation of C-H bonds can be gained by IR-MPD spectroscopy in combination with first-principles theoretical simulations of the electronic, vibrational, and geometrical structures, and of the reaction and the activation mechanisms of alkanes (here ethane) adsorbed on small gold clusters, and the pathways of these reactions. In particular, the understanding and fundamental insights gained here through fundamental experiments and theoretical explorations of small cationic gold clusters interacting with alkanes, the chemical reactivity mediated by these small clusters, its selectivity and cluster size dependence, aim at adding to the growing knowledge base. This knowledge targets the charting of new avenues in catalysis research, and the formulation of rational design principles of catalysts that would enable effective selective activation and dissociation of C-H bonds and the subsequent beneficial conversion of abundant hydrocarbons into valuable chemicals.

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