The interaction of gold clusters with methanol molecules: Ab initio molecular dynamics of Au\textsuperscript{n+}CH\textsubscript{3}OH and Au\textsubscript{n}CH\textsubscript{3}OH

Roger Rousseau
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany and Steacie Institute for Molecular Science, National Research Council of Canada (NRC), 100 Sussex Drive, Ottawa, Ontario, K1A 0R6, Canada

Dominik Marx
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany

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Structural, dynamical, and electronic properties of adducts obtained by adsorbing one methanol molecule onto charged and neutral gold clusters, Au\textsubscript{n+}–CH\textsubscript{3}OH and Au\textsubscript{n}–CH\textsubscript{3}OH, are investigated using Car–Parrinello ab initio molecular dynamics as a function of the cluster size n. The absorption process occurs by the formation of a Au\textsuperscript{n+}–O coordination bond to one particular gold atom Au\textsuperscript{n+} without altering the structure of the underlying cluster. This chemical bond is much stronger for the charged metal clusters Au\textsubscript{n+} than for the neutral analogs Au\textsubscript{n}. In the charged case, the C–O stretching vibration of the interacting methanol molecule is found to increase discontinuously as the underlying cluster structure changes from two-dimensional to three-dimensional. The weaker C–O bond in the neutral species however has “insufficient strength” to be sensitive to changes in coordination number and cluster structure. This leads to a constant C–O stretching frequency as the size of the cluster increases, including the regime where the Au\textsubscript{n} cluster changes from planar to three-dimensional. © 2000 American Institute of Physics.

I. INTRODUCTION

One of the chief quests in cluster science is the determination of the real-space structures of those assemblies, which bridge the gap between the molecular level and bulk behavior.\textsuperscript{1–5} Experimentally, there has been tremendous progress in recent years concerning the investigation of size-selected clusters. This has made possible the “clean” and controlled spectroscopic investigation of thermalized atomic or molecular clusters as a function of the number of constituents. However, it is in general not possible to determine directly cluster structures from such experiments. To a great extent ab initio electron structure calculations have served as a complementary method in this endeavor. In this approach spectra are typically calculated for various rigid isomers, i.e., local minima of the potential energy surface, as obtained from the selected electronic structure theory. These theoretical spectra may then be compared with the experimental data to determine which cluster isomers are present, see Refs. 6–15 for a very incomplete compilation of recent examples. By this route valuable information about the real-space structure of clusters is obtained.

This strategy, although very successful, has its limitations. One such limitation is how does one go about obtaining, in an unbiased way, a proper ensemble of cluster structures which may be used for the ab initio property calculations? Another difficulty arises when one considers the actual shape of the potential energy landscape for metallic clusters. For metal clusters the potential surface can be sufficiently flat so that the ensemble of energetically available local minima can be relatively large. This will lead to strong anharmonic effects and in the worst possible scenario a cluster of given size can visit several local minima on the time scale of the experiment. These shortcomings can be largely diminished by the use of Car–Parrinello ab initio molecular dynamics simulations.\textsuperscript{16} This approach combines the powerful tool of molecular dynamics for sampling configuration space with first-principle electronic structure calculations. When this method is used in the “simulated annealing mode” and combined with local geometry optimization techniques it allows an efficient and to a large extent unbiased generation of cluster structures. Moreover, it is possible to obtain relevant information about the impact of thermal fluctuations, in addition to the number of available minima at finite temperatures and the isomerization pathways between them, see Refs. 17, 18 for reviews.

Another question which is emerging to the forefront of cluster science is that of probing interactions between individual molecules and size-selected clusters as a function of cluster size.\textsuperscript{3,19–23} Of course, the behavior of these adducts is diverse and one is flooded by a host of intriguing questions; how do the molecules adsorb (dissociative vs molecular, adsorption site and geometry), what is the nature of their bonding (from van der Waals interactions to covalent bonds), do the properties of the attached molecule change as the cluster grows (not at all, smoothly or discontinuous, bulk limit), and many others. Here too ab initio molecular dynamics has a valuable role. It provides an avenue by which clusters can be allowed to chemically react at finite temperatures with adsorbate molecules in a finite temperature molecular dynamics simulation. Thus, the same procedure that allowed for the
finding of preferred cluster structures may then be used to obtain adducts of these clusters with small molecules.

Along these lines we have undertaken a study of the dynamic, structural, and electronic properties of adducts formed between clusters of gold atoms and methanol. Previously in a short communication, it was shown that the structural properties of adducts formed between size-selected charged Au_n^+ (n = 1–15) clusters and methanol could be interpreted by combining experimental measurements and ab initio molecular dynamics simulations. It was found that the ‘‘internal’’ C–O stretching frequency \( \nu \) of the free methanol molecule decreased by about 60–100 cm\(^{-1} \) upon adsorption to the metal cluster. Moreover, the resulting red shift in frequency \( \Delta \nu = \nu_{\text{CH}_3\text{OH}} - \nu_{\text{Au}_{n} \text{CH}_3\text{OH}} \) decreased in a stepwise fashion as the cluster size was increased. Specifically, \( \Delta \nu \) exceeds at least 100 cm\(^{-1} \) for the smallest cluster with \( n = 1 \), reaches a plateau around 75 cm\(^{-1} \) for \( n = 3–7 \), with a second smaller but significant steplike change for \( n \geq 8 \) to a value of about 60 cm\(^{-1} \). By comparison with cluster adducts obtained from the ab initio simulations it was found that these features could be explained by a change in cluster shapes. The plateau for \( n = 3–7 \) corresponds to planar two-dimensional (2D) clusters, whereas the cluster structure is three-dimensional (3D) in the regime \( n \geq 8 \). This behavior is surprising in light of the distinctly different findings for neutral \( M_n - \text{CH}_3\text{OH} \) adducts of various metal clusters such as Fe_{5–15}, Cu_{5–11}, Ag_{3–22}, including in particular also Au_{3–13}. For these species, \( n \)-independent constant red-shifts (in the range of only 15 to a most 40 cm\(^{-1} \)) have been observed.\(^{25,26} \)

In this article and its preceding experimental complement,\(^{27} \) more complete investigations and analyses of these findings are presented. Here, we start in Sec. II by describing how ab initio simulation techniques have been employed to study the species of interest. The structure and dynamics of the Au_{2–10} (m = 0,1) clusters and their adducts with methanol is presented in Sec. III A along with a direct comparison to experimental data.\(^{26,27} \) In Sec. III B the relationship between the geometric structure of the clusters and their electronic structures with ramifications on experimental observations is worked out. Conclusions and outlook are presented in Sec. IV.

II. THEORETICAL APPROACH

Ab initio molecular dynamics, simulated annealing, and geometry optimization were performed in the Car–Parrinello scheme.\(^{16,28–30} \) With this approach the potential energy under which the nuclei move is calculated via first-principles electronic structure methods within the Born–Oppenheimer approximation as the ions move. The motion of the nuclei is assumed to be governed by classical mechanics, which is a valid approximation for ‘‘heavy atoms.’’ All simulations were performed with the Car–Parrinello Molecular Dynamics package CPMD.\(^{\text{31}} \) The electronic structure calculations are based upon Hohenberg–Kohn–Sham density functional theory.\(^{32,33} \) In particular, the local density approximation was supplemented with with Becke’s and Perdew’s gradient corrections for exchange\(^{34} \) and correlation,\(^{35} \) respectively. The core electrons for Au, C, and O are represented by norm-conserving pseudopotentials of the Troullier–Martins-type.\(^{36} \) The pseudopotential for Au is scalar-relativistic and leaves 11 electrons in the valence shell. For hydrogen a Car–von Barth pseudopotential is employed in order to smooth the Coulomb divergence. The valence orbitals are expanded in plane waves at the \( \Gamma \) point.

In particular, we have studied charged Au_n^+ clusters (\( n = 1, 3, 5, 7, 9, \) and 15 including two isomers each for the cases \( n = 5, 7, \) and 15) and neutral Au_n clusters (\( n = 4,8 \)) as well as their adducts with one methanol CH_3OH molecule attached. It is noted that clusters with only even numbers of electrons are considered in this study to avoid the unnecessary complications due to open shells, such as spin-orbit coupling, spin-contamination, etc. which may arise in systems with an odd number of electrons. This restriction is fully justified by the experimental outcome\(^{24,27} \) that no significant even–odd effects are observed, i.e., the even-electron clusters contain already all the physics.

It is not obvious how to prepare theoretically thermalized cluster–molecule adducts. Here, the procedure outlined in the following was used in order to generate the cluster and adduct structures. First, the cluster configuration was obtained by placing the required number of gold atoms into a periodic cubic box with a linear dimension of 26 atomic units; at this stage the plane wave cutoff was 50 Rydberg. Each gold atom was initially assigned an artificially small atomic mass of 17 a.u. which allows the cluster to behave more liquidlike at a given temperature. This accelerates the exploration of phase space subject to the correct potential energy surface. These starting structures were heated to 300–400 K and allowed to equilibrate. After equilibration a simulated annealing procedure was performed to a temperature which was below 10 K. Final cluster structures were obtained by performing local geometry optimizations (with a 90 Ry plane wave cutoff in a 26 a.u. cubic box with nonperiodic boundary conditions) on the final structures obtained from simulated annealing. All cluster structures reported here were obtained by this recipe except that of the planar Au_7^+ cluster. For this species entropic considerations make finding a planar species highly unfavorable in a short molecular dynamics trajectory which is initiated from a nonplanar guess. Thus, for this cluster all the atoms were constrained to lie within a plane during the initial equilibration step with molecular dynamics at 300–400 K. This constraint was released in all subsequent steps, where the cluster was found to remain planar. Finally, it is noted that we do not suppose that by this protocol the global minima of the potential energy surfaces have been obtained, especially for the larger clusters. However, the elaborate structure-finding procedure should lead to very-low-energy local minima. This is supported by several cross-checks and comparison to experiment, see Sect. III A for a discussion.

Starting from the optimized pure clusters, cluster–adsorbate adducts were subsequently obtained by adding a methanol molecule into the system away from the closest cluster atom by about 4 Å. Here again we used a periodic cubic 26 a.u. simulation cell but with a 70 Ry cutoff and the correct atomic mass for Au, 197 a.u. This higher cutoff ensures convergence of the oxygen pseudopotential with re-
spect to structural quantities. These systems were first equilibrated at a temperature of 300 K of the \( \text{Au}^+_4 \text{CH}_3\text{OH} \) adducts, where the attachment of the methanol molecule to the cluster occurred. The formed adducts were then annealed to a temperature below 10 K. The weaker cluster–methanol interaction for the corresponding neutral species required a slightly different procedure where the oxygen of the methanol was oriented directly towards the cluster in the starting configuration and a temperature of 100 K was used for equilibration. The final adduct structures were further optimized to remove residual forces using a 90 Ry cutoff in a nonperiodic 26 a.u. cubic cell.

Harmonic vibrational frequencies were extracted for all cluster–methanol adducts as well as their perdeuterated analogues using static finite-differences. These frequencies are estimated to be converged within about 5 cm\(^{-1}\) as a function of basis set size and residual gradient on the atomic positions. In addition, we estimated anharmonic corrections by performing (after equilibration) 2.3 ps \textit{ab initio} molecular dynamics runs for \( \text{CD}_2\text{OD} \) and the two representative adducts \( \text{Au}^+_4 \text{CD}_2\text{OD} \) and \( \text{Au}^+_4 \text{CD}_2\text{OD} \) at the experimental temperature 300 K. The relevant frequencies were obtained from Fourier transforms of the C–O stretch autocorrelation function to obtain power spectra. The anharmonic correction was calculated as the difference between the harmonic frequency C–O of the deuterated species and that obtained from the C–O stretching power spectra. We have found these anharmonic corrections to be 5.5% \((n = 3)\), 3.2% \((n = 9)\), and 4.0% (free \( \text{CD}_2\text{OD} \)). This correction for the remaining adducts was assumed to be linearly proportional to the C–O bond length (and the Au–O bond length) of the optimized species. All reported frequency shifts \( \Delta \nu = \nu_{\text{CH}_3\text{OH}} - \nu_{\text{Au}^+_4 \text{CH}_3\text{OH}} \) are based on the harmonic frequencies that were approximately corrected for the isotope effect and anharmonicity.

Standard Mulliken population analysis and Mayer bond orders\(^{37} \) are obtained by projection of the total molecular wave function obtained from the plane wave calculations onto an atom-centered (minimal atomic) basis derived from the pseudo-wave-function. Mayer’s bond orders, sometime also called multiplicity indices, reduce in straightforward cases to the classic valence picture of bonding. Within minimal basis sets this bond order is found to be unity for \( \text{H}_2 \), three for \( \text{N}_2 \) and 2.5 for CO, it is 1.0, 2.0, and 3.0 for the carbon–carbon bond in ethane, ethylene, and acetylene and close to 1.0 for carbon–hydrogen bonds in methane, ethane, ethylene, and acetylene. It is important to reiterate here that all “quantitative” measures for populations and bond orders are necessarily subject to some inherent arbitrariness, whereas trends can certainly be inferred.

As a complementary technique analysis of the electronic structure and bonding has been carried out using the electron localization function (ELF) (Ref. 38) supplemented by its topological bifurcation analysis.\(^{39,40} \) ELF can be viewed as a local measure of the Pauli repulsion between electrons due to the exclusion principle in three-dimensional space. It allows one to define regions of space which are associated with different electron pairs in a molecule or solid. The definition of ELF is given by

\[
\eta(r) = \frac{1}{1 + (D/D_h)^2},
\]

\[
D = \frac{1}{2} \sum_{i,j=1}^{N} |\nabla \psi_i|^2 - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho},
\]

\[
D_h = \frac{3}{10} (3 \pi^2)^{2/3} \rho^{5/3},
\]

\[
\rho = \sum_{i=1}^{N} |\psi_i(r)|^2,
\]

where the sum is over all singly occupied one-electron (spin-) orbitals \( \psi_i(r) \) in an \( N \)-electron system. This function \( \eta(r) \) is large in regions where the Pauli repulsion \( -D \) is small, i.e., where two electrons with antiparallel spin are paired in space. Its maxima, \( \eta^\text{max} \), can be associated with attractor basins due to electron pairing. In addition, higher \( \eta^\text{max} \) values correspond to more tightly localized electron pairs in space and as such may be used as an indicator to locate and interpret chemical bonding. ELF is normalized between zero and unity and its value for the uniform electron gas is 1/2. The normalization allows for a quantitative scale by which electron localization may be gauged within a class of systems. As such, ELF is ideal for comparative studies of bonding within chemically distinct systems composed of the same atoms types. Another set of characteristic numbers are the bifurcation values \( \eta^* \) where different attractor basins merge. For a discussion on how these quantities may be used in order to classify and interpret chemical bonding, see Refs. 39, 40. The reader is referred to reviews\(^{41} \) and previous publications\(^{42-43} \) for in-depth discussions of the properties of ELF. Finally, the present ELF and charge density analyses is focused exclusively upon the chemically relevant valence electrons.

### III. RESULTS AND DISCUSSION

#### A. Structure and dynamics

To begin this discussion on structural and dynamical considerations we focus on the isolated gold clusters as obtained from \textit{ab initio} molecular dynamics simulations. Since it is found that the structures of the pure clusters change only negligibly upon methanol adsorption, it is sufficient to present only the adducts in Fig. 1. \( \text{Au}^+_3 \) is an equilateral triangle with an Au–Au bond length of 2.50 Å. For both the \( \text{Au}^+_3 \) and \( \text{Au}^+_4 \) clusters 2D and 3D isomers are obtained. The distribution of Au–Au bonds is relatively uniform within a given cluster with a maximum spread of about 0.1 Å between the longest and shortest distances. For the \( \text{Au}^+_4 \) cluster the two isomers are isoenergetic within a fraction of an eV/atom. The 2D cluster has \( C_{2v} \) symmetry and consists of three edge-sharing triangles with an average Au–Au bond distance of 2.53 Å. The 3D cluster is a trigonal bipyramid (\( D_{3h} \) symmetry) but has a slightly larger 2.60 Å average Au–Au distance. Likewise the planar \( \text{Au}^+_4 \) cluster consists of edge-sharing triangles (\( C_s \) symmetry) with an average Au–Au distance of 2.56 Å, but the 3D isomer (\( C_{3v} \) symmetry) has an average Au–Au distance of 2.64 Å. The energy difference
between the 2D and 3D isomers of the \( n=7 \) cluster is again on the scale of fractions of eV/atom. The \( \text{Au}_{9}^{+} \) cluster is 3D and has an overall \( C_{2v} \) symmetry with an average 2.64 Å Au–Au distance. Two isomers of \( \text{Au}_{15} \) were also generated one having \( C_{2v} \) symmetry and a second unsymmetrical \( C_{1} \) species which is much lower in energy by 0.99 eV. In both cases the average Au–Au bond distance is 2.65 Å similar to that found for the 3D \( n=5 \) and 9 clusters. It is noted that in all cases the Au–Au bonds are shorter then the 2.88 Å found experimentally for the solid fcc gold,\(^{44} \) and longer than the 2.47 Å (Ref. 45), of the \( \text{Au}_{2} \) dimer (for which the present calculation yields 2.45 Å).

Similar findings are obtained for the two neutral gold clusters. The \( \text{Au}_{4} \) cluster (\( C_{2v} \) symmetry) is planar consisting of two triangles which are joined at an edge. Here the average Au–Au bond length is 2.54 Å (similar to that of \( \text{Au}_{5}^{+} \)) with only a slight 0.01 Å difference between the various bond lengths. The \( \text{Au}_{4}^{+} \) cluster also has \( C_{2v} \) symmetry and consists of an octahedron with two of the triangular faces capped by extra gold atoms. Like the positively charged analogues the \( \text{Au}_{4}^{+} \) cluster is found to have longer Au–Au bonds with an average length of 2.63 Å similar to that of \( \text{Au}_{5}^{+} \). The presence of a net positive charge on the \( \text{Au}^{+} \) clusters seems to have little effect on structural parameters such as bond length because this charge is spread out over the entire cluster; see Sec. III B. However, a comparison of the spectroscopic data\(^{26,27} \) shows that this charge does play an important role upon the chemical reactivity of the clusters.

Injection of one methanol molecule into the simulation cell leads to the formation of cluster–molecule adducts. The cluster–molecule interaction is mediated via a direct Au–O bond between a single atom Au* of the gold cluster and the hydroxyl group of the methanol molecule, see Fig. 1 for illustration of these species and Table I for relevant structural parameters. The energetically preferred adsorption site Au* turns out to be the lowest-coordinated gold atom that is available for a given cluster size. This finding gets support from the dynamical behavior observed during the attachment process itself, which is exemplified here for three isomers of \( \text{Au}_{5}^{+} \). After placing the molecule with the oxygen pointing directly towards the 4C site were we able to obtain a second adduct with planar \( \text{Au}_{5}^{+} \). However, this isomer, where Au* is bound to four other gold atoms, is 0.33 eV higher in energy then

![FIG. 1. Structures of \( \text{Au}^{+} \text{CH}_{3} \text{OH} \) and \( \text{Au}_{n} \text{CH}_{3} \text{OH} \) adducts obtained from \textit{ab initio} molecular dynamics simulations as described in Sec. II. Atoms are represented as spheres: Au (black) O (dark gray) C (medium gray) H (light gray).](https://example.com/fig1.png)

### Table I

<table>
<thead>
<tr>
<th>Species</th>
<th>C( \text{Au}^{+} )</th>
<th>C–O (Å)</th>
<th>Au*–O (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Au}^{+} \text{CH}_{3} \text{OH} ) Ground state</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n=1 )</td>
<td>1</td>
<td>1.49</td>
<td>2.04</td>
</tr>
<tr>
<td>( n=3 )</td>
<td>2</td>
<td>1.48</td>
<td>2.09</td>
</tr>
<tr>
<td>( n=5 )</td>
<td>2</td>
<td>1.48</td>
<td>2.09</td>
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<td>( n=7 )</td>
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<td>2.10</td>
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<td>( n=9 )</td>
<td>4</td>
<td>1.47</td>
<td>2.13</td>
</tr>
<tr>
<td>( n=15 )</td>
<td>4</td>
<td>1.47</td>
<td>2.14</td>
</tr>
<tr>
<td>( \text{Au}<em>{n} \text{CH}</em>{3} \text{OH} ) Other isomers</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>( n=5 )</td>
<td>4</td>
<td>1.48</td>
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<td>( n=7 )</td>
<td>3</td>
<td>1.47</td>
<td>2.15</td>
</tr>
<tr>
<td>( n=15 )</td>
<td>6</td>
<td>1.47</td>
<td>2.12</td>
</tr>
<tr>
<td>( \text{Au}<em>{n} \text{CH}</em>{3} \text{OH} ) ( n=4 )</td>
<td>2</td>
<td>1.46</td>
<td>2.17</td>
</tr>
<tr>
<td>( n=8 )</td>
<td>3</td>
<td>1.46</td>
<td>2.17</td>
</tr>
<tr>
<td>( \text{CH}_{3} \text{OH} ) fl</td>
<td>…</td>
<td>1.43</td>
<td>…</td>
</tr>
</tbody>
</table>

| a2D cluster. |
| b3D cluster. |
after adsorption at the lowest-coordination 2C site. In addition, the 3D Au$^+$ isomer has two 3C sites forming the apexes of the bipyramid and three 4C sites at the trigonal equator, see Fig. 1, and methanol readily attached itself to one of the lower-coordinated sites. However, this adduct is higher in energy by 0.71 eV then the adduct obtained from the 2D cluster is found again to be more stable by about 0.96 eV then the adduct obtained from the 3D cluster, see Fig. 2.

The clusters, both charged and neutral, retain their overall shape when methanol is attached and even the Au–Au bonds changed by only 0.02 Å on average. Moreover, the change in Au–Au bonds is not found preferentially around the Au$^+$, as one could expect as a first guess, but occurs throughout the entire cluster. There are only a few structural parameters which seem to have any great dependence on either cluster size or charge. The Au–O bond distance in the lowest-energy adduct is shortest for $n=1$ with 2.04 Å, increases to 2.09–2.10 Å for the planar $n=3,5,7$ species, and finally levels off to about 2.13–2.14 Å for the 3D $n=9,15$ clusters, see Fig. 2(a) and Table I. The longest Au$^+$–O distance 2.17 Å is found for the neutral Au$_n$CH$_3$OH $n=4$ and 8 adducts. Concurrent to the lengthening of the Au$^+$–O bond we observed that the C–O bond shortens in the Au$_n$CH$_3$OH species from 1.49 Å for $n=1$ to 1.48 Å for $n=3,5$ to 1.47 Å for $n=7,9,15$ but remains constant at 1.46 Å for Au$_n$CH$_3$OH for both $n=4$ and 8. However, all these bonds are longer then the 1.43 Å found within free methanol using the same methodology.

These systematic trends in bond length variation are expected to affect also the associated force constants as a function of cluster size $n$, which in turn should be detectable by vibrational spectroscopy of mass-selected adducts. The vibrational probe used in the experiment$^{27}$ is the C–O vibrational stretching frequency $\nu$ of the methanol molecule.
Thus, direct contact between experimental observables and calculated properties can be established via this frequency as a link. The experimental and calculated frequency shift relative to that of free methanol, \( \Delta \nu = \nu_{\text{CD}_3\text{OD}} - \nu_{\text{CH}_3\text{OH}} \), is plotted in Fig. 2(b) as a function of cluster size \( n \). As expected, the C–O frequency is lower in the adducts than in free methanol signaling the expected weakening of the C–O bond due to the interaction with the cluster. This correlates nicely with the increase in C–O bond length observed in the static species, see Table I. For the \( \text{Au}_n^+ \text{CH}_3\text{OH} \) adducts the largest experimental red-shift \( \Delta \nu \) [filled circles Fig. 2(b)] is observed in the limit of \( n = 1 \). Due to experimental limitations, see Ref. 27 for details, only a lower bound of about 100 cm\(^{-1}\) could be derived from the spectra. The red shift reaches a plateau around 75 cm\(^{-1}\) in the range \( n = 3 \)–7, with an abrupt second step-like change where \( \Delta \nu \) levels off at about 60 cm\(^{-1}\) for \( n \geq 8 \). The largest cluster produced. This scenario in stark contrast to the behavior of neutral \( \text{Au}_n\text{CD}_3\text{OD} \) adducts as a function of cluster size \( n \) [filled triangles Fig. 2(b)]. In this case, \( n \)-independent constant red-shifts in the range of 25–30 cm\(^{-1}\) were observed for cluster sizes from \( n = 3 \) up to \( n = 15 \). It is interesting to note that no odd–even effect in the cluster size \( n \) is observed within the experimental resolution for both charged and neutral adducts.

The calculations for the charged adducts using the lowest-energy species [open circles Fig. 2(b)] reproduce essentially quantitatively the significant drop from \( n = 1 \) to the plateau for \( 3 \leq n \leq 7 \) as well as the less pronounced step from there to the saturation regime for \( n \geq 9 \). Furthermore, the calculations for the neutral \( \text{Au}_n\text{CD}_3\text{OD} \) adducts [open triangles Fig. 2(b)] display a constant shift of only about 25 cm\(^{-1}\), which is again in accord with experiment (i.e., 25 cm\(^{-1}\) for \( \text{CD}_3\text{OD} \)).

Moreover, the values obtained for \( \Delta \nu \) from the higher energy \( n = 5, 7, \) and 15 adducts [open diamonds, Fig. 2(b)] are not in accord with the experimental trends. This suggests that the clusters analyzed in the experiment are indeed well thermalized low-energy isomers. It is interesting to compare the trend in \( \Delta \nu \) [Fig. 2(b)] with that of the \( \text{Au}^+ \text{O} \) bond length [Fig. 2(a)]. The symmetry between these two curves is readily apparent. For the neutral adducts the \( \text{Au}^+ \text{O} \) bond is constant (at 2.17 Å) as is \( \Delta \nu \). The charged adducts all exhibit shorter \( \text{Au}^+ \text{O} \) bonds and larger values of \( \Delta \nu \), and \( \Delta \nu \) decreases as the \( \text{Au}^+ \text{O} \) bond length increases. What is most notable is that the step-like behavior in the frequency shift \( \Delta \nu \) is found also to occur in the \( \text{Au}^+ \text{O} \) bond length. The \( \text{Au}^+ \text{O} \) bond length is directly related to the dimensionality of the cluster via the available lowest-coordinated binding site \( \text{Au}^+ \). Thus, the step-like discontinuity at \( n = 7 \) coincides with a change of dimensionality of the underlying cluster structure from 2D to 3D. Therefore, the frequency change must also be related to the dimensionality of the cluster and the methanol molecule may be considered to be acting as a probe on this property, but only for the charged clusters. Finally, experiment (performed for all \( n \) values up to \( n = 10 \)) complements theory (based on odd-\( n \) clusters only) in that the change of dimensionality can be located to occur from \( n = 7 \) to \( n = 8 \), see Fig. 2(b).

**B. Electronic structure**

In the previous subsection the theoretically obtained cluster adducts were used to draw a conclusion regarding what was transpiring to lead to the observed experimental trends for C–O stretching frequency shifts. Here the focus will shift to an in-depth investigation of the underlying physical principles which can explain these observations. On the outset, there are two possible explanations for the discontinuous behavior of the frequency shift \( \Delta \nu \) for the charged \( \text{Au}_n^+ \text{CH}_3\text{OH} \) adducts. First, this may be due to the closing of electronic shells of the cluster as proposed for the interaction of the CO molecule with copper clusters.\(^{23}\) But this does not explain why there is an absence of this effect in the neutral species. This is further ruled out by the finding that the 3D \( \text{Au}_3^+ \) cluster forms an adduct which is much higher in energy than its 2D analog despite the fact that the two clusters themselves are isoenergetic besides being isoelectronic. Another possibility is a purely electrostatic interaction yet it is not clear how this could explain the discontinuous variation of structural quantities such as the \( \text{Au}^+ \text{O} \) or C–O bond lengths as a function of cluster size \( n \). Thus, it is necessary to understand the detailed electronic structure of these adducts and how it relates to the trends in the structural and spectroscopic parameters which were examined in the previous subsection.

First, consider the ELF, see Sec. II for definition and discussion, of these species which is represented as a series of isosurfaces (with decreasing value from top to bottom) in Fig. 3 for the isolated \text{CH}_3\text{OH} (upper three panels in left column) and \text{Au}_n (lowest panel in left column) fragments as well as the neutral \text{Au}_n\text{CH}_3\text{OH} (middle column) and charged \text{Au}_n^+\text{CH}_3\text{OH} (right column) adducts. A valuable tool to aid in the interpretation of ELF is the bifurcation hierarchy\(^{40}\) which is represented diagrammatically in Fig. 4. For pure methanol it is found that ELF displays three attractors associated with the methyl C–H bonds (with very high values \( \eta_{\text{max}} = 0.99 \) at their maxima), one attractor stemming from the alcohol O–H bond (\( \eta_{\text{max}} = 0.97 \)), and two attractors ascribed to the two lone-pairs of electrons of the hydroxyl group (\( \eta_{\text{max}} = 0.93 \)). At \( \eta_{\text{max}} = 0.85 \) the attractor of the C–O bond emerges on the carbon–oxygen bond axis, but it is slightly displaced towards the more electronegative oxygen atom. At a bifurcation value of about \( \eta = 0.78 \) the four attractor basins around the hydroxyl group merge and form one basin and the corresponding confluence of the methyl moiety basins is established at \( \eta = 0.73 \). The merging of the ELF basins of the the methyl and hydroxyl basins occurs at only \( \eta = 0.55 \), which is close to the reference value 1/2 of the homogeneous electron gas. Thus, the methyl and hydroxyl groups are clearly separated down to low ELF values which nicely reflects the fundamental concept of functional groups in organic chemistry.

The corresponding analysis of the charged and neutral \( \text{Au}_n^+ \) (\( m = 0.1 \)) pure clusters is much less involved as can be inferred from Fig. 4. All attractor maxima occur at essentially the same value of \( \eta_{\text{max}} = 0.41 \) followed by the coalescence of all basins at about \( \eta = 0.25 \). This is the same for both neutral \( m = 0 \) and positively charged \( m = 1 \) clusters and indicates that in the bare clusters the charge does not have a
The electron localization function (ELF) represented as a series of isosurfaces \( \eta = 0.84, 0.75, 0.42 \), and 0.30. In the left column the \( \eta = 0.84, 0.75, \) and 0.42 isosurfaces of methanol (upper three subpanels) are shown and that of the Au_8 cluster (lower subpanel) is shown at \( \eta = 0.30 \). ELF of Au_8CH_3OH (center column) and Au_9CH_3OH (right column) are shown at all four values of \( \eta \). Note that no change in the ELF bifurcation hierarchy is seen in methanol below \( \eta = 0.50 \) and that \( \eta_{\text{max}} = 0.41 \) for bare Au_8, compare also to Fig. 4. Shading code of atoms is identical to Fig. 1.

FIG. 3. The electron localization function ELF represented as a series of isosurfaces \( \eta = 0.84, 0.75, 0.42 \), and 0.30.

The ELF topology of all the adducts species is essentially identical, therefore it serves the present purpose to consider only two representative examples, namely, the Au_8CH_3OH and Au_9CH_3OH adducts. The chemical bonding is easily rationalized by comparing their ELF topology to that of the isolated fragments, see Figs. 3 and 4. The methanol molecule is arranged such that one of the hydroxyl lone pairs points directly towards the Au* site for both clusters, which is most clearly seen in the upper subpanels of Figs. 3. A corresponding attractor appears on the line connecting Au* with O very close to the oxygen atom. It has a less pronounced maximum electron pairing \( \eta_{\text{max}} = 0.89 \) for \( n = 8 \) and \( \eta_{\text{max}} = 0.88 \) as the unperturbed lone pair in the free methanol molecule \( \eta_{\text{max}} = 0.93 \). Thus one lone pair of methanol is transmuted into a Au*–O bond but leaves the electronic structure of the rest of the methanol molecule qualitatively untouched. As to the gold atoms, methanol adsorption enhances the electron pair localization at Au* \( \eta_{\text{max}} = 0.43 \) for both adducts vs \( \eta_{\text{max}} = 0.41 \) for the bare clusters, whereas the rest of the cluster remains essentially unperturbed (lower subpanels Figs. 3). The increased pairing at Au* is not spherical, see the halos appearing around Au* for both the neutral and charged adducts in the \( \eta = 0.42 \) isosurface plot in Fig. 2, suggesting its polarization within the cluster due to the cluster–molecule interaction.

This scenario matches well with an interpretation of the adsorption process occurring by the formation of an Au*–O coordination bond where a “main group molecule” (methanol) donates one of its lone pairs to a positively charged metal center (Au*). This assertion is further supported by the observation that coordination compounds containing gold atoms in the oxidation state one typically have Au(I)–O bonds of about 2.04–2.10 Å which is similar in length to the Au*–O bonds studied here, compare with Table I. The directionality of the coordination bond is due to its partial covalent nature. In general, these bonds are strongly polarized towards the main group element which reflects a large electrostatic contribution. There is little variation in the values of \( \eta_{\text{max}} \) (value at the attractor maximum) and \( \eta^* \) (value at the bifurcation/confluence) amongst the adducts regardless of their charge. Thus, it may be assumed that the type of
bonding is the same in both species though the structural parameters clearly indicate that the Au*–O bonds are stronger in the charged species.

To understand further details of the coordination bonding scheme for these adducts we now complement the ELF analysis by other measures of electronic properties. We start this part of the discussion with the Mulliken charges \( q \) (given in units of \( |e| \)) of the Au* and oxygen atoms before and after adduct formation are collected in Table II. As an illustration, take for example the Au\(^{+}_{9}\) CH\(_{3}\)OH adduct. The Au* atom in Au\(^{+}_{9}\) increases in positive charge from 0.11 to 0.17 \( |e| \) upon adduct formation with a corresponding decrease in the negative charge on the oxygen atom to \(-0.67|e|\) as compared to \(-0.73|e|\) in free methanol. On the other hand, the remaining eight gold atoms in the Au\(^{+}_{9}\) cluster all decrease their positive charge by about 0.03 \( |e| \). In agreement with the ELF analysis this simple scheme based upon atomic charges shows that the cluster electron density is polarized in order to provide a local positively charged site at which the methanol binds. In all cases where \( n \geq 5 \) the positive charge on Au* is increased by an average of 0.07 \( |e| \) from its value for the bare clusters whereas the remaining Au atoms decrease this charge by about 0.04 \( |e| \). The small number of Au atoms within the \( n = 3 \) species and in particular the \( n = 1 \) limit do not strictly follow this pattern. For the latter, there is only electron donation from the methanol which reduces the positive charge on the single gold atom from unity to 0.66 \( |e| \). For the former, the large charge to atom ratio leaves the charge on Au* the same after adsorption but does allow for the remaining two Au atoms to decrease their charge as in the larger clusters. Another important finding which is in agreement with the ELF analysis is that the same polarization mechanism occurs for the adducts formed from the neutral species, Au\(_{n}\) and Au\(_{0}\), with the important distinction that the net positive charge on the binding site is slightly smaller than those for the charged clusters. It follows that the Au*–O interaction will be stronger for charged clusters, which already have a positive charge and need only to concentrate it at one particular atom, but weaker for the neutral clusters where the presence of this charge is actually induced by the adsorbed methanol. This conclusion gets furthermore strengthened by the observation that the Au*–O bond becomes longer and weaker as the charged cluster grows: the positive charge is more evenly distributed over all \( n \) atoms, and thus the amount of positive charge localized on one particular gold atom is smaller. The Au*–O bond is the strongest for the \( n = 1 \) charged adduct because the single atom represents the greatest concentration of positive charge. Moreover, the 2D clusters are less able to screen out the positive charge build up at Au* then the 3D clusters and thus the Au*–O interaction is slightly stronger for the former as opposed to the latter.

How does this affect the C–O bond, which establishes the link with experiment? To address this problem, bond orders based upon the scheme of Mayer\(^{37}\) are presented in Table III for the C–O, Au*–O, and O–H bonds. The bond order of the C–O bond is found to increase towards the “saturation value” 0.91 of a free methanol molecule as the gold cluster in the charged adducts grows and is largest for the neutral adducts with \( \approx 0.85 \). Concurrently, the bond order of the O–H bond also grows and reaches the value in the free methanol molecule, 0.67, for both neutral adducts. This strengthening of the C–O and O–H bonds is accompanied by a weakening of the Au*–O bond as the cluster grows; its bond order gets halved from the \( n = 1 \) to \( n = 15 \) charged adducts. In addition, its value is significantly smaller for the neutral adducts, which means that here the cluster–methanol interaction is weaker. Furthermore, the net decrease in charge at the oxygen atom due to the donation of electrons to Au* in conjunction with a smaller secondary response from the carbon atom should result in a decrease in the dipole moment of the C–O bond. This is actually born out experimentally.\(^{27}\) As a consequence of the trend of weakening the O–H bond upon adsorption, thus making this proton the “acidic,” formation of methoxy CH\(_{3}\)O species should be possible in presence of a sufficiently strong metal–oxygen coordination bond. This correlates well with the observation of methoxy species on metal clusters made of iron\(^{48}\) which has rich coordination chemistry with oxygen unlike gold.

### Table II. Mulliken charges \( q \) in units of \( |e| \) as obtained from population analysis for Au* and the oxygen atom of the CH\(_{3}\)OH fragment for the lowest-energy adducts and the corresponding bare clusters without methanol.

<table>
<thead>
<tr>
<th>Species</th>
<th>( q_{\text{Au}} ) (cluster)</th>
<th>( q_{\text{Au}} ) (adduct)</th>
<th>( q_{\text{O}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(^{+}<em>{9}) CH(</em>{3})OH</td>
<td>(+1.00)</td>
<td>(+0.66)</td>
<td>(-0.61)</td>
</tr>
<tr>
<td>( n = 1 )</td>
<td>(-0.33)</td>
<td>(-0.32)</td>
<td>(-0.67)</td>
</tr>
<tr>
<td>( n = 5 )</td>
<td>(-0.16)</td>
<td>(-0.22)</td>
<td>(-0.67)</td>
</tr>
<tr>
<td>( n = 7 )</td>
<td>(+0.11)</td>
<td>(+0.18)</td>
<td>(-0.67)</td>
</tr>
<tr>
<td>( n = 9 )</td>
<td>(+0.11)</td>
<td>(+0.17)</td>
<td>(-0.67)</td>
</tr>
<tr>
<td>( n = 15 )</td>
<td>(+0.03)</td>
<td>(+0.10)</td>
<td>(-0.67)</td>
</tr>
<tr>
<td>Au(<em>{9}) CH(</em>{3})OH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n = 4 )</td>
<td>(-0.06)</td>
<td>(+0.03)</td>
<td>(-0.66)</td>
</tr>
<tr>
<td>( n = 8 )</td>
<td>(-0.04)</td>
<td>(+0.05)</td>
<td>(-0.66)</td>
</tr>
<tr>
<td>CH(_{3})OH</td>
<td>( \cdots )</td>
<td>( \cdots )</td>
<td>(-0.73)</td>
</tr>
</tbody>
</table>

### Table III. Mayer bond orders as obtained from population analysis for the C–O, Au*–O, and O–H bonds for the lowest-energy adducts and pure methanol.

<table>
<thead>
<tr>
<th>Species</th>
<th>C–O</th>
<th>Au*–O</th>
<th>O–H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(^{+}<em>{n}) CH(</em>{3})OH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n = 1 )</td>
<td>0.78</td>
<td>0.56</td>
<td>0.62</td>
</tr>
<tr>
<td>( n = 3 )</td>
<td>0.81</td>
<td>0.34</td>
<td>0.64</td>
</tr>
<tr>
<td>( n = 5 )</td>
<td>0.82</td>
<td>0.32</td>
<td>0.65</td>
</tr>
<tr>
<td>( n = 7 )</td>
<td>0.82</td>
<td>0.31</td>
<td>0.65</td>
</tr>
<tr>
<td>( n = 9 )</td>
<td>0.83</td>
<td>0.29</td>
<td>0.65</td>
</tr>
<tr>
<td>( n = 15 )</td>
<td>0.84</td>
<td>0.28</td>
<td>0.65</td>
</tr>
<tr>
<td>Au(<em>{n}) CH(</em>{3})OH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n = 4 )</td>
<td>0.85</td>
<td>0.23</td>
<td>0.67</td>
</tr>
<tr>
<td>( n = 8 )</td>
<td>0.86</td>
<td>0.24</td>
<td>0.67</td>
</tr>
<tr>
<td>CH(_{3})OH</td>
<td>0.91</td>
<td>( \cdots )</td>
<td>0.67</td>
</tr>
</tbody>
</table>
IV. CONCLUSIONS AND OUTLOOK

What has been learned in this investigation goes beyond the realm of gold-cluster methanol adduct formation. It is found that the interactions between a neutral adsorbate molecule (methanol) and small metal clusters (Au\textsubscript{n} as well as Au\textsubscript{n+}) may be well understood in terms of coordination chemistry. The bond formed between the lone pair of the hydroxyl group in methanol and the gold clusters is quite stiff and directional. As such cluster and adduct geometry can have effects upon the chemical and physical properties. In particular, it is found that the experimentally observed changes of the C–O stretch frequency of the methanol molecule as a function of cluster size \( n \) is related to the coordination number of the adsorption site, which in turn goes hand in hand with the dimensionality of the cluster. A necessary step in the process of chemisorption of neutral closed-shell molecules onto metal clusters is the formation of a positively charged site where adsorption occurs. Electrostatic interactions play an important role and as a general rule the strength of the adsorption interaction is dependent upon the amount of positive charge concentrated at the adsorption site. This can have pronounced effects on the bond strengths within the adsorbed molecule and can lead eventually to bond rupturing in the adsorbate. Thus, future investigations along the lines of reacting charged clusters of oxophilic metals such as iron or tungsten and molecules like methanol may yield interesting phenomena as the charge to atom ratio of the cluster changes. Another avenue would be to substitute thioles for alcohol and again react this with charged gold clusters. Performed as a function of molecular coverage and cluster size, this approach might shine new light on the controversy concerning the gold–thiole interactions.

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