

Charge Separation Promoted Activation of Molecular Oxygen by Neutral Gold Clusters

Alex P. Woodham,[#] Gerard Meijer,[#] and André Fielicke^{*,#,\$}

[#] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

^{\$} Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstrasse 36, D-10623 Berlin, Germany

S Supporting Information

ABSTRACT: Gold nanoparticles and sub-nanoparticles famously act as highly efficient and selective low-temperature oxidation catalysts with molecular oxygen, in stark contrast to the nobility of the bulk phase. The origins of this activity and the nature of the active species remain open questions. Gas-phase studies of isolated gold clusters hold promise for disentangling these problems. Here we address the interaction of neutral gold clusters (Au_n ; $4 \leq n \leq 21$) with molecular oxygen by probing the highly characteristic O–O vibrational stretch frequencies. This reveals that for selected cluster sizes the oxygen is highly activated with respect to the free moiety. Complementary quantum chemical calculations provide evidence for substantial electron transfer to the O_2 unit and concomitant rearrangement of the parent gold cluster structure upon binding and activation. This gives evidence for a model of the interaction between neutral gold clusters and molecular oxygen.

The now famous onset of catalytic activity as gold is reduced in size from the bulk limit toward the nano and sub-nano regimes has provoked a large body of research into the chemical properties of these species,^{1–4} as well as more fundamental, gas-phase studies into the geometric and electronic structures of the isolated bare clusters^{5–7} and their complexes with small molecules.^{8–12} Such studies of isolated systems, in addition to theoretical support, have revealed gold clusters to possess many highly unusual and unique properties, e.g., 2D structures until surprisingly large cluster sizes.^{6,13–16}

Above all others, one reaction has been the subject of much investigation: the low-temperature oxidation of CO to CO_2 with O_2 .^{17–20} Despite extensive research into this process, which serves as a model for other, technically more relevant oxidation reactions, questions still remain as to the nature of the reactive intermediates and the mechanism by which it occurs. This is especially interesting in light of the inability of bulk gold to form from O_2 the crucial O^{2-} intermediate required for an oxidation proceeding via the Mars–van Krevelen mechanism.²¹ Several mechanisms have been proposed for oxidations catalyzed by small gold particles, e.g., the reaction occurring at the three-phase boundary between the gold cluster, the support, and the gas phase.⁴ Alternatively, electron density may be transferred into the antibonding HOMO of O_2 by negatively charged gold clusters,^{1,22} resulting in a significantly weakened O–O bond, which is then

susceptible to further reaction. Indeed, a complete catalytic reaction cycle for the oxidation of CO has been mapped out for Au_2^- in the gas phase.⁹

This use of gas-phase, mass-spectrometric techniques allows for explicit investigation of the size effects on an atom-by-atom basis, and first revealed the odd–even alternation in the reactivity of the gold cluster anions with molecular oxygen²³ which ultimately led to the proposal of an activation mechanism that relies on the donation of a single, unpaired electron into the HOMO of oxygen. With subsequent spectroscopic studies, e.g., anion photoelectron spectroscopy (PES) and infrared multiple photon dissociation (IR-MPD), such a picture was confirmed.^{12,24–26}

Compared to the anionic gold clusters, experimentally very little is known about the interactions of neutral gold clusters with molecular oxygen, presumably in part due to the increased experimental difficulty associated with the neutral clusters. Fortunately, anion PES is in part sensitive to the nature of the final state, i.e., the neutral species, albeit in the geometry of the anion. Vibrational progressions in the PES seen for the even-sized anions reveal O–O stretching frequencies between 1226 and 1443 cm^{-1} .^{25,27,28} Such frequencies are indicative of a slight activation of the adsorbed oxygen. Additionally, Wang et al. also investigated the properties of the oxygen complexes of odd-sized anions and found no difference compared to the spectra of the bare Au clusters, indicating no chemical interaction between adsorbate and cluster in the anionic state.²⁵

Unlike experimental studies, theory suffers no technical difficulties concerning the study of neutral species and several, sometimes conflicting, predictions have been made on the basis of DFT and higher level calculations.^{29–35} Several key ideas do emerge: First, the reactivity is expected to be dominated by those clusters possessing an odd number of electrons, i.e., the odd-numbered clusters. This is in agreement with the observations for the anionic clusters where an unpaired electron is required for donation. Second, for most small cluster sizes, O_2 is energetically favored to be dissociatively bound, although the barriers to dissociation are expected to be large (on the order of 1 eV and greater) and thus may not be observed experimentally owing to kinetic trapping. Third, in the cases where molecular adsorption is observed, charge transfer to the molecular oxygen occurs with an increase of the O–O distance, suggesting activation toward a superoxo-like state. Finally, the extent of activation (for molecular adsorption) is

Received: December 14, 2012

Published: January 17, 2013

predicted to be less for the neutral clusters than the anionic ones.

In general, we can confirm this predicted reactivity of neutral gold clusters with molecular oxygen. Figure 1 shows a mass

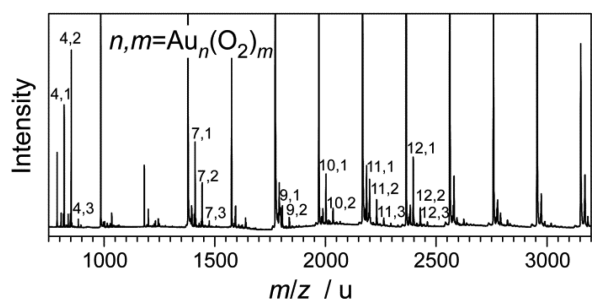


Figure 1. Sample mass spectrum for the Au_4 – Au_{16} clusters after reaction with O_2 . Ionization was done with the 7.9 eV output of an F_2 laser. The oxygen complex peaks are marked with n,m labels indicating their composition. Additional signals are due to H_2O contaminations.

spectrum obtained by single-photon ionization (at 7.9 eV) of a cluster complex distribution formed by addition of O_2 to the preformed gold clusters at ~ 173 K. The odd-sized (open-shell) clusters Au_7 , Au_9 , Au_{11} , and Au_{21} show addition of molecular oxygen, in agreement with the single-electron transfer model. Contrary to this, however, there are also mass peaks corresponding to the reaction of even-sized (i.e., closed-shell) clusters Au_4 , Au_{10} , and Au_{12} , as well as a noticeable absence of reaction for the odd-sized clusters Au_5 and Au_{13} – Au_{19} .

As the nature of the molecular oxygen–gold cluster interaction greatly influences the bond order of the complexed O_2 , and thus the O–O stretching frequency, we have used the output of an IR free electron laser to perform IR-MPD spectroscopy and directly probe the neutral molecular oxygen–gold cluster complexes. By comparing the observed band positions with known reference data³⁶ for the different charge states of oxygen, we can begin to unravel the nature of the interaction between the small gold clusters and molecular oxygen.

Figure 2 shows the IR-MPD spectra recorded from the mass channels of $Au_n(O_2)_m$ ($n = 4, 7, 9, 11,$ and 21) between 1000 and 1700 cm^{-1} (band positions can be found in the Supporting Information). The spectra show two distinct motifs, one being absorption at around 1060 cm^{-1} which is only observed for the odd-sized clusters, and the second at approximately 1500 cm^{-1} , only observed for $Au_7(O_2)_{1,2}$ and $Au_4(O_2)_{1,2,3}$. As no other vibrational fundamentals are expected at these wavelengths, they are attributed to the O–O stretch vibrations of a superoxo (O_2^-) and a slightly activated O_2 species (cf. $\nu(O-O) = 1556\text{ cm}^{-1}$ for free O_2), respectively. All of the bands correspond to around 70% depletion, with the exception of $Au_7(O_2)_{1,2}$, which splits roughly 60:40 between the two modes. The observation of a superoxo stretch for all of the odd-sized clusters is in agreement with theoretical predictions. It is also interesting to note that the observed stretching frequencies are similar to those of the anions,¹² suggesting a similar degree of activation by the neutral clusters, contrary to the theoretical predictions.

The presence of two vibrational fundamentals for Au_7O_2 suggests that there are one or more isomers of the cluster, either in the parent gold structure or in the binding geometry of the oxygen molecule. Such isomerism has been observed previously for dioxygen bound to anionic gold clusters.^{12,26}

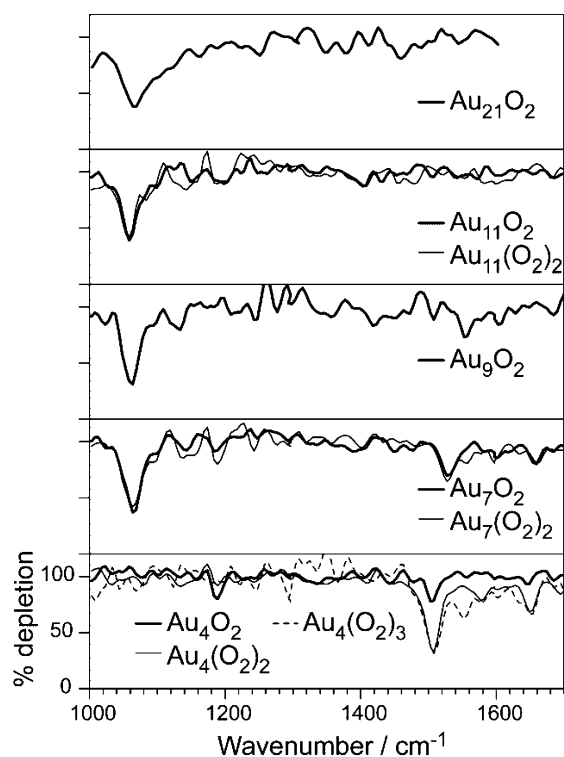


Figure 2. IR-MPD spectra for the O_2 complexes of neutral gold clusters. The spectra are smoothed with a five-point running binomial filter; the raw data have been omitted for clarity.

Similarly, the absorption band of $Au_{21}O_2$ is significantly broader than for the lighter clusters and possesses a distinct shoulder to the blue of the main peak, again perhaps an indication of isomers within the beam. The spectra for Au_9O_2 and $Au_{11}O_2$ have no such additional features or broadening and thus are assumed to come from a single isomer species.

In addition to these odd-sized clusters, Au_4 , Au_{10} , and Au_{12} were also found to react, adding up to three O_2 units. The IR-MPD spectra recorded in the $Au_4(O_2)_m$ mass channels are given in Figure 2 and are dominated by an absorption feature corresponding to a slightly activated O_2 (1507 cm^{-1}), which is significantly less activated than the frequencies measured from anion PES.^{25,27,28} For Au_{10} and Au_{12} , no IR-MPD bands have been observed. These species are then interpreted as either arising from a very weakly bound O_2 such that the perturbation of the formally IR-inactive O–O stretch is insufficient to observe excitation, or showing that these species involve dissociated O_2 and thus do not have vibrational fundamentals at the investigated wavelengths. Indeed, the presence of dissociated oxygen complexes cannot be ruled out for any of the investigated species, although for the complexes showing a $\nu(O-O)$ band, the amount of IR-induced depletion observed limits the abundance of such species to no more than 30% of the total complex intensity. For now, we cannot differentiate between these two scenarios.

To support the experimental results, quantum chemical calculations have been performed. Owing to the increasing difficulty of calculations with increasing cluster size, we have limited our investigations to the cluster complexes of Au_4 , Au_7 , and Au_9 with a single O_2 . As with previous theoretical investigations,^{29–35} we find that complexes corresponding to dissociated O_2 are the putative ground-state structures for all the investigated cluster sizes. However, while we cannot

preclude the formation of such species, they have no bearing on the experimental results reported herein. Additionally, work by other groups has suggested that, despite these dissociated complexes being the global minima, they tend to lie behind large (1 eV and greater) barriers, in agreement with our observation of superoxo species accounting for up to 70% of the observed complex intensity.

Figure 3 presents a summary of the results obtained from the quantum chemical calculations (detailed structural information

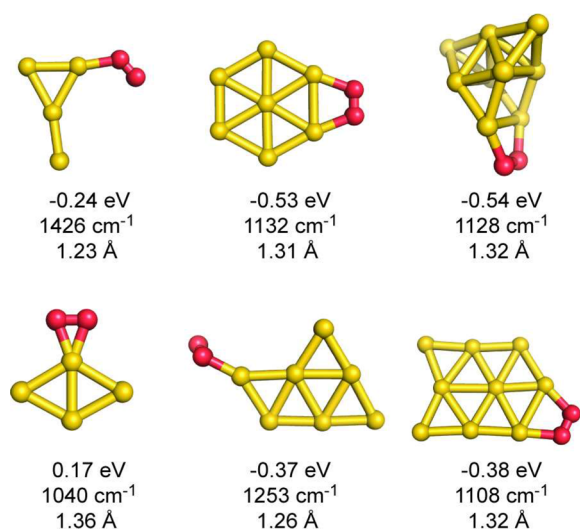


Figure 3. Structures, energies of complexation (ΔE_C), $\nu(\text{O}-\text{O})$ stretching frequencies, and $d(\text{O}-\text{O})$ bond distances for Au_4O_2 , Au_7O_2 , and Au_9O_2 . The upper structures are the identified (molecularly bound) lowest energy structures, which are believed to give rise to the experimentally observed vibrations, while the lower ones show the favored binding position with the gold cluster core in the geometry of the bare neutral cluster and are for comparison only.

can be found in the Supporting Information). The upper structures in Figure 3 are the most stable complexes, containing a molecular O_2 unit. For Au_4O_2 this favored structure involves a distorted Y-shaped gold cluster with the O_2 bound in a μ_1 mode to a two-coordinate Au atom similar to the structure reported for Au_4O_2^- .^{12,28} In Au_7O_2 and Au_9O_2 , the O_2 is bound in a μ_2 mode to the gold cluster. The cluster core for both sizes has a structure similar to those observed by Kappes et al.¹³ for the corresponding cations. Au_7^+ has the structure of a centered hexagon, while Au_9^+ forms a 3D bicapped trigonal prism of C_{2v} symmetry. The latter structure has been identified as an isomer which can be frozen out at low temperature,³⁷ and here is clearly stabilized by the interaction with the O_2 . The structures reported for bare neutral gold clusters are markedly different;^{7,16} for instance, neutral Au_9 is planar. The complex formation energies ($\Delta E_C = E[\text{Au}_n\text{O}_2] - E[\text{Au}_n(\text{neutral})] - E[\text{O}_2]$) are given for all species: in the favored structures for Au_7O_2 and Au_9O_2 the oxygen is bound by ~ 0.5 eV, while for Au_4O_2 this is significantly reduced to 0.24 eV. In the lower row of Figure 3, the most stable structures with the gold cluster core in the geometry of the bare neutral are given. Despite the lack of rearrangement required, the calculated formation energies are lower for these species, with Au_4O_2 even showing a positive value, i.e., unfavorable binding.

In agreement with the experiment, the calculated stretching frequencies for the lowest energy isomers (top row Figure 3) are similar for Au_7O_2 and Au_9O_2 while that of Au_4O_2 shows a

marked blue shift. The larger deviation between theoretical vibrational frequency and the experimental one for Au_4O_2 may be due to the known difficulties of DFT in correctly describing physisorbed $\text{Au}-\text{O}_2$ binding.³⁸ The differences between Au_7 , Au_9 , and Au_4 are further borne out when comparing the calculated $\text{O}-\text{O}$ bond lengths: for Au_4O_2 this is 1.23 Å, which is only slightly elongated compared to the free O_2 value of 1.21 Å; Au_7O_2 and Au_9O_2 , however, have $\text{O}-\text{O}$ distances of 1.31 and 1.32 Å, respectively. The second vibrational frequency observed in the spectra of $\text{Au}_7(\text{O}_2)_{1,2}$ (1527 cm^{-1}) is only very slightly shifted compared to that of free O_2 and may be due to an isomer containing O_2 which is essentially physisorbed.

The presence of superoxo (O_2^-) species must arise from an electron transfer from the gold cluster into the oxygen, similar to the binding observed for the anionic clusters.^{22,25,26} Energetically the cost of the ionization is compensated by the resulting ion-ion interaction of the final complex. Indeed a simple “back of the envelope” calculation shows that two oppositely charged particles with a separation of 1.8–2 Å have an interaction energy of 7.2–8 eV, which, coupled with the electron affinity of O_2 (0.44 eV),³⁶ energetically offsets the ionization energies (IEs) of the small gold clusters, which are between 7.25 and 7.80 eV for the superoxo-forming clusters identified here.³⁹ Such a charge transfer is also supported by the results from the DFT calculations in which we see that the gold cluster preferentially adopts the geometry of the cationic species upon complexation with O_2 and formation of the superoxo species. Further, an NBO analysis of the calculated species reveals a partial electron transfer of -0.56 and -0.6 e into the O_2 in Au_7O_2 and Au_9O_2 , respectively. Conversely, in Au_4O_2 , where weaker binding and less activation is seen, the geometry of the parent gold cluster is not that of the cation, and this is explained by the significantly higher IE of Au_4 (8.60 eV),³⁹ rendering such an electron transfer unfavorable. Again an NBO analysis confirms this, showing a charge transfer of only -0.12 e into the O_2 . Indeed, owing to the well-known odd-even effect in gold clusters, it seems, for the smallest clusters at least, the reactivity should be dominated by the odd-sized clusters as they represent local minima in the IEs, particularly for Au_7 and Au_9 , which form magic electron systems upon ionization (6 and 8 being magic numbers for planar clusters).⁴⁰ With increasing cluster size, it appears reasonable to expect that the Coulomb energy will decrease as the charge is able to be distributed over a larger number of atoms, perhaps explaining the absence of oxygen complexes of $\text{Au}_{13}-\text{Au}_{19}$ with Au_{21} having a noticeably lower IE (7.60–7.70 eV vs 7.25 eV), again due to the magic shell closing of Au_{21}^+ .

In conclusion, we have presented spectroscopic evidence for the formation of a charge-transfer complex in odd-sized Au_nO_2 ($n = 7, 9, 11, 21$), resulting in the formation of a superoxo (O_2^-) species bound to a formally cationic gold cluster. The even-sized clusters, conversely, are found to be largely unreactive with the exceptions of Au_4 , Au_{10} , and Au_{12} , the former of which slightly activates oxygen upon complexation. DFT calculations suggest that the charge transfer induces significant rearrangement of the gold cluster such that it more closely resembles the structure of the cation. Such a binding mechanism highlights the importance of structural flexibility for oxygen activation by small gold particles.

■ ASSOCIATED CONTENT**■ Supporting Information**

Experimental details, xyz coordinate files, and table of experimentally observed band positions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION**Corresponding Author**

fielicke@physik.tu-berlin.de

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the support of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) for providing beam time on FELIX, and the FELIX staff for their skilful assistance, in particular Dr. B. Redlich and Dr. A. F. G. van der Meer. This work is supported by the Cluster of Excellence "Unifying Concepts in Catalysis" coordinated by the Technical University Berlin and funded by the Deutsche Forschungsgemeinschaft.

■ REFERENCES

- (1) Yoon, B.; Häkkinen, H.; Landman, U.; Wörz, A. S.; Antonietti, J.-M.; Abbet, S.; Judai, K.; Heiz, U. *Science* **2005**, *307*, 403.
- (2) Corma, A.; Serna, P. *Science* **2006**, *313*, 332.
- (3) Herzing, A. A.; Kiely, C. J.; Carley, A. F.; Landon, P.; Hutchings, G. J. *Science* **2008**, *321*, 1331.
- (4) Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T. *Science* **2011**, *333*, 736.
- (5) Li, J.; Li, X.; Zhai, H.-J.; Wang, L.-S. *Science* **2003**, *299*, 864.
- (6) Häkkinen, H.; Yoon, B.; Landman, U.; Li, X.; Zhai, H.-J.; Wang, L.-S. *J. Phys. Chem. A* **2003**, *107*, 6168.
- (7) Gruene, P.; Rayner, D. M.; Redlich, B.; van der Meer, A. F. G.; Lyon, J. T.; Meijer, G.; Fielicke, A. *Science* **2008**, *321*, 674.
- (8) Wallace, W. T.; Whetten, R. L. *J. Am. Chem. Soc.* **2002**, *124*, 7499.
- (9) Socaciu, L. D.; Hagen, J.; Bernhardt, T. M.; Wöste, L.; Heiz, U.; Häkkinen, H.; Landman, U. *J. Am. Chem. Soc.* **2003**, *125*, 10437.
- (10) Fielicke, A.; von Helden, G.; Meijer, G.; Simard, B.; Rayner, D. M. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3906.
- (11) Fielicke, A.; von Helden, G.; Meijer, G.; Simard, B.; Rayner, D. M. *J. Phys. Chem. B* **2005**, *109*, 23935.
- (12) Woodham, A. P.; Meijer, G.; Fielicke, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 4444.
- (13) Gilb, S.; Weis, P.; Furche, F.; Ahlrichs, R.; Kappes, M. M. *J. Chem. Phys.* **2002**, *116*, 4094.
- (14) Furche, F.; Ahlrichs, R.; Weis, P.; Jacob, C.; Gilb, S.; Bierweiler, T.; Kappes, M. M. *J. Chem. Phys.* **2002**, *117*, 6982.
- (15) Dong, Y.; Springborg, M. *Eur. Phys. J. D* **2007**, *43*, 15.
- (16) Assadollahzadeh, B.; Schwerdtfeger, P. *J. Chem. Phys.* **2009**, *131*, 064306.
- (17) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, *16*, 405.
- (18) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, *115*, 301.
- (19) Häkkinen, H.; Landman, U. *J. Am. Chem. Soc.* **2001**, *123*, 9704.
- (20) Bernhardt, T. M.; Hagen, J.; Lang, S. M.; Popolan, D. M.; Socaciu-Siebert, L. D.; Wöste, L. *J. Phys. Chem. A* **2009**, *113*, 2724.
- (21) Mars, P.; van Krevelen, D. W. *Chem. Eng. Sci.* **1954**, *3* (Suppl. 1), 41.
- (22) Salisbury, B.; Wallace, W.; Whetten, R. *Chem. Phys.* **2000**, *262*, 131.
- (23) Cox, D. M.; Brickman, R.; Creegan, K.; Kaldor, A. *Z. Phys. D* **1991**, *19*, 353.
- (24) Huang, W.; Wang, L.-S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 2663.

- (25) Huang, W.; Zhai, H.-J.; Wang, L.-S. *J. Am. Chem. Soc.* **2010**, *132*, 4344.
- (26) Pal, R.; Wang, L.-M.; Pei, Y.; Wang, L.-S.; Zeng, X. C. *J. Am. Chem. Soc.* **2012**, *134*, 9438.
- (27) Stolcic, D.; Fischer, M.; Ganteför, G.; Kim, Y. D.; Sun, Q.; Jena, P. *J. Am. Chem. Soc.* **2003**, *125*, 2848.
- (28) Sun, Q.; Jena, P.; Kim, Y. D.; Fischer, M.; Ganteför, G. *J. Chem. Phys.* **2004**, *120*, 6510.
- (29) Mills, G.; Gordon, M. S.; Metiu, H. *Chem. Phys. Lett.* **2002**, *359*, 493.
- (30) Franceschetti, A.; Pennycook, S.; Pantelides, S. *Chem. Phys. Lett.* **2003**, *374*, 471.
- (31) Ding, X.; Li, Z.; Yang, J.; Hou, J. G.; Zhu, Q. *J. Chem. Phys.* **2004**, *120*, 9594.
- (32) Fernandez, E. M.; Ordejan, P.; Balbás, L. C. *Chem. Phys. Lett.* **2005**, *408*, 252.
- (33) Prestianni, A.; Martorana, A.; Labat, F.; Ciofini, I.; Adamo, C. *J. Phys. Chem. B* **2006**, *110*, 12240.
- (34) Boronat, M.; Corma, A. *Dalton Trans.* **2010**, *39*, 8538.
- (35) Shi, Y.-K.; Li, Z. H.; Fan, K.-N. *J. Phys. Chem. A* **2010**, *114*, 10297.
- (36) Huber, K.; Herzberg, G. *NIST Standard Reference Database*, Number 69; National Institute of Standards and Technology: Gaithersburg, MD, 2011.
- (37) Weis, P.; Bierweiler, T.; Vollmer, E.; Kappes, M. M. *J. Chem. Phys.* **2002**, *117*, 9293.
- (38) Fang, H. C.; Li, Z. H.; Fan, K.-N. *Phys. Chem. Chem. Phys.* **2011**, *13*, 13358.
- (39) Jackschath, C.; Rabin, I.; Schulze, W. *Ber. Bunsen-Ges.* **1992**, *96*, 1200.
- (40) Janssens, E.; Tanaka, H.; Neukermans, S.; Silverans, R. E.; Lievens, P. *New J. Phys.* **2003**, *5*, 46.