Available online at www.sciencedirect.com
ScienceDirect
Chemical Physics Letters 444 (2007) 232–236
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

# Anion photoelectron spectroscopy of $Au^-(H_2O)_{1,2}$, $Au_2^-(D_2O)_{1-4}$, and $AuOH^-$

Weijun Zheng [a], Xiang Li [a], Soren Eustis [a], Andrej Grubisic [a], Owen Thomas [a], Helen de Clercq [b], Kit Bowen [a,*]

[a] Departments of Chemistry and Materials Science, Johns Hopkins University, Baltimore, MD 21218, United States
[b] Department of Chemistry, Howard University, Washington, DC 20059, United States

Received 8 June 2007; in final form 13 July 2007
Available online 21 July 2007

**Abstract**

The photoelectron spectra of $Au^-(H_2O)_{1,2}$, $Au_2^-(D_2O)_{1-4}$, and $AuOH^-$ have been measured. The anionic complexes, $Au^-(H_2O)_{1,2}$ and $Au_2^-(D_2O)_{1-4}$, were characterized as $Au^-$ and $Au_2^-$, which are respectively solvated by water molecules. The stepwise spectral shifts between adjacent size species have been quantified. The photoelectron spectrum of $AuOH^-$ exhibits considerable vibrational structure. Based on our assignment of its spectrum, the adiabatic electron affinity of AuOH was determined to be $1.771 \pm 0.015$ eV.


## 1. Introduction

When gold nanoparticles are supported on transition metal oxides, they exhibit considerable catalytic activity, even though bulk gold surfaces do not [1]. While the specific mechanism is not known, it is generally believed that charge transfer to gold nanoparticles plays a key role in this process [2]. This proposed interaction, together with the fact that gold has a high electron affinity, has motivated several studies on gold cluster anions and on the reactions of negatively-charged gold atoms and clusters with oxygen and carbon monoxide in the gas phase [3–8]. In addition, photoelectron studies have been conducted on $AuO^-$ [9–11], on $Au_nO_2^-$ [10] and on $AuS^-$ [9] in order to characterize the bonding between gold and oxygen and between gold and sulfur.

Here, we present results from our photoelectron spectroscopic study of $Au^-(H_2O)_{1,2}$, $Au_2^-(D_2O)_{1-4}$, and $AuOH^-$. The most closely related studies in the literature are those dealing with $Cu^-(H_2O)_1$, $Cu^-(H_2O)_2$, and $CuOH^-$, although the neutral $Au(H_2O)_1$ complex [12] and neutral AuOH [13] have been treated theoretically. Theoretical studies found anionic $Cu^-(H_2O)_1$ to be a planar complex with the hydrogen atoms of water oriented toward the copper atomic anion, whereas in neutral $Cu(H_2O)_1$, the oxygen atom is oriented toward the copper atom [14–16]. In the case of $Cu^-(H_2O)_2$, two different structural situations have been reported by theory. In one study, the two water molecules are hydrogen bonded to one another, while one hydrogen atom from each water molecule points toward the copper anion. In neutral $Cu(H_2O)_2$, the two water molecules are again hydrogen bonded to one another, but in this case an oxygen from one water and a hydrogen from the other interact with the copper atom [17]. In the other study, which focused only on the anionic complex, all of the hydrogen atoms of the two water molecules point toward the copper anion, but from opposite sides of the copper [14]. Extensive photoelectron and femtosecond photoelectron studies have also been conducted on $Cu^-(H_2O)_1$ and $Cu^-(H_2O)_2$ complexes [15,17–19]. These anionic complexes were characterized from their spectra as atomic copper anions interacting with water molecules. The $Cu^-(H_2O)_{1,2}$ anion complexes provide a reference point in considering our results on the $Au^-(H_2O)_{1,2}$ anion

* Corresponding author. Fax: +1 410 516 8420.
*E-mail address:* kbowen@jhu.edu (K. Bowen).

0009-2614/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2007.07.036

complexes. For both CuOH and $CuOH^-$, theory found a roughly 'L' shaped structure with the oxygen atom bonded to the copper atom [13,14].

## 2. Experimental

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of anions with a fixed frequency photon source and energy analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship $h\nu = \mathrm{EKE} + \mathrm{EBE}$, where $h\nu$ is the photon energy, EKE is the measured electron kinetic energy, and EBE is the electron binding energy. The details of our apparatus have been described elsewhere [20]. Briefly, both mass spectra and anion photoelectron (photodetachment) spectra were collected on an apparatus consisting of a laser vaporization source, a linear time-of-flight mass spectrometer for mass analysis and selection, and a magnetic bottle photoelectron spectrometer for electron energy analysis. [Its instrumental resolution is ~35 meV at 1 eV EKE and degrades as $(\mathrm{EKE})^{3/2}$.] The third harmonic (355 nm, 3.493 eV) of a Nd:YAG laser was used to photodetach the cluster anions of interest. Photoelectron spectra were calibrated against the well-known atomic lines of $Cu^-$.

$Au^-(H_2O)_{1,2}$, $Au_2^-(D_2O)_{1-4}$, and $AuOH^-$ anions were generated in a laser vaporization source. A rotating, translating rod wrapped with gold foil was utilized as the target in the laser vaporization source. It was ablated with the second harmonic (532 nm, 2.33 eV) of a pulsed Nd:YAG laser. Helium gas at ~4 atm., seeded with a trace of water vapor, was expanded through a pulsed valve into the source, thereby generating the resultant anions.

## 3. Results and discussion

### 3.1. $Au^-(H_2O)_{1,2}$

The photoelectron spectra of $Au^-$, $Au^-(H_2O)_1$, and $Au^-(H_2O)_2$ are presented and compared in Fig. 1. These were all measured with 3.49 eV photons. The photoelectron spectrum of $Au^-$ shows the transition from the electronic ground state of the atomic gold anion to the electronic ground state of the neutral gold atom [3]. This peak is centered at an electron binding energy (EBE) of 2.31 eV, which is the electron affinity of the gold atom. The main peak in the photoelectron spectrum of $Au^-(H_2O)_1$ is centered at 2.76 eV, and this value is the vertical detachment energy (VDE) of $Au^-(H_2O)_1$. This peak looks very much like that of $Au^-$, except for being shifted to higher EBE by 0.45 eV and slightly broadened. The broadened width of this peak is likely due to a combination of rotations and Franck–Condon overlap between weak bond vibrations of the anionic complex and its neutral complex. There are also three other features in this spectrum, all of which are located to the high EBE side of the main peak. The most prominent of these is located at 2.96 eV, which is 0.20 eV

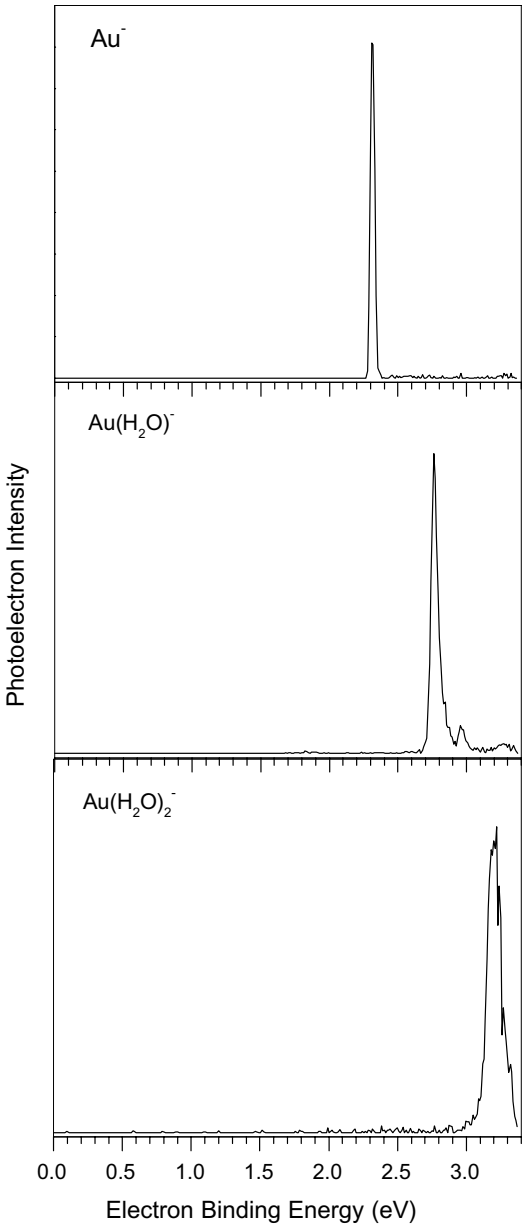


Fig. 1. The photoelectron spectra of $Au^-$, $Au^-(H_2O)_1$, and $Au^-(H_2O)_2$, all recorded with 355 nm photons.

(~1600 $cm^{-1}$) higher in electron binding energy than the main peak. Since the vibrational frequency of the bending mode of gas phase $H_2O$ is 1595 $cm^{-1}$, we assign this peak to the excitation of the water bending mode following photodetachment. The weak feature centered near EBE = 3.25 eV is located 0.49 eV (~3900 $cm^{-1}$) higher in electron binding energy than the main peak. It is assigned to the excitation of water stretches following photodetachment. We confirmed this assignment by recording the photoelectron spectrum of $Au^-(D_2O)_1$ and watching both features move to lower EBE values, i.e. to 2.91 eV (~1200 $cm^{-1}$) and to 3.09 eV (2650 $cm^{-1}$), respectively. The shoulder at 2.84 eV is reproducible and may be due to a libration of the gold/water complex, i.e. a manifestation of the overlap of weak bond vibrations mentioned above.

The photoelectron spectrum of $Au^-(H_2O)_2$ consists of a single peak, which is centered at 3.20 eV. This value is the VDE of $Au^-(H_2O)_2$. Since it is near the edge of our available energy window, we cannot see whether other peaks are present immediately to its high EBE side, and thus, we cannot determine whether the vibrations of water are excited due to photodetachment in this case. As was the case for the main peak in the photoelectron spectrum of $Au^-(H_2O)_1$, the peak in this spectrum also resembles the spectrum of $Au^-$ except for being shifted to still higher EBE and broadened. The peak in the $Au^-(H_2O)_2$ spectrum is shifted to higher EBE by 0.44 eV relative to the main peak in the $Au^-(H_2O)_1$ spectrum.

Since the fingerprint photoelectron spectrum of $Au^-$ is evident in all three spectra in Fig. 1, it is clear that $Au^-$ is the chromophore in each case. We thus characterize $Au^-(H_2O)_1$ as an atomic gold anion interacting with (solvated by) one water molecule and $Au^-(H_2O)_2$ as an atomic gold anion interacting with two water molecules, i.e. as anion-molecule complexes. While the spectral broadening increases in the order; $Au^-$, $Au^-(H_2O)_1$, $Au^-(H_2O)_2$, the sequential shift in the spectra is nearly constant at 0.45 and 0.44 eV in going from $Au^-$to $Au^-(H_2O)_1$ and in going from $Au^-(H_2O)_1$ to $Au^-(H_2O)_2$, respectively. Since the structures of copper/water anionic complexes differ from those of their corresponding copper/water neutral complexes, we anticipate analogous differences between the structures of gold/water anionic complexes and their corresponding gold/water neutral complexes. Under these circumstances, where the photodetachment process accesses a region of the neutral potential surface somewhat above its well, we can write

$$\mathrm{VDE}[Au^-(H_2O)_1] - \mathrm{EA}[Au] = D_0[Au^- \ldots H_2O] - D_0[Au \ldots H_2O]^*, \quad (1)$$

where $\mathrm{VDE}[Au^-(H_2O)_1]$ is the vertical detachment energy of $Au^-(H_2O)_1$, EA[Au] is the electron affinity of Au, $D_0[Au^- \cdot H_2O]$ is the dissociation energy of the $Au^-(H_2O)_1$ anion breaking into $Au^-$ and $H_2O$, and $D_0[Au \cdot H_2O]^*$ is the dissociation energy of neutral $Au(H_2O)$ [at the structure of the $Au^-(H_2O)$ anion] breaking into Au and $H_2O$. Making the assumption described above, $D_0[Au \cdot H_2O]^*$ is likely to be very small and can be neglected. Then, by utilizing the values of $\mathrm{VDE}[Au^-(H_2O)_1]$ and EA[Au] in Eq. (1), we can compute the value of $D_0[Au^- \cdot H_2O]$, finding it to be approximately 0.45 eV, i.e. essentially equal to the shift between the spectra of $Au^-$ and $Au^-(H_2O)_1$.

It is interesting to compare the photoelectron spectra of $Au^-(H_2O)_1$ and $Au^-(H_2O)_2$ with those of $Cu^-(H_2O)_1$ and $Cu^-(H_2O)_2$ [18]. Both systems are anion-molecule complexes in which the atomic anion is the photodetachment chromophore. That is, the spectra of both systems are essentially those of their perturbed atomic anion states. Also, both show the same pattern of successive spectral broadening. In addition, both exhibit peaks due to the excitations of the bending mode of water. However, while the copper/water system does not show evidence of water stretching modes, the gold/water system does (see above). The sequential spectral shifts in both systems primarily reflect the energy required to remove a water molecule from each cluster species, and while those of the gold/water system are a little larger than those of the copper/water system, their values are comparable. In particular, the $Au^-$ to $Au^-(H_2O)_1$ shift is 0.45 eV versus 0.40 eV for the $Cu^-$ to $Cu^-(H_2O)_1$ shift, whereas the $Au^-(H_2O)_1$ to $Au^-(H_2O)_2$ shift is 0.44 eV versus 0.37 eV for the $Cu^-(H_2O)_1$ and $Cu^-(H_2O)_2$ shift. The vertical detachment energies of the two systems are quite different, however, with the VDE of $Au^-(H_2O)_1$ being 2.76 eV, while the VDE of $Cu^-(H_2O)_1$ is 1.64, and with the VDE of $Au^-(H_2O)_2$ being 3.20 eV, while the VDE of $Cu^-(H_2O)_2$ is 2.00 eV. Since both of these cluster anions are atomic anion-molecule complexes with similar sequential shifts, the differences in their VDE's must be primarily due to the difference in their metal atom electron affinities. Gold has a higher electron affinity than copper due to relativistic effects, viz. 2.31 eV versus 1.24 eV, respectively.

### 3.2. $Au_2^-(D_2O)_{1-4}$

The photoelectron spectra of $Au_2^-(D_2O)_{1-4}$ are presented in Fig. 2. At the resolution of a magnetic bottle electron energy analyzer, the photoelectron spectrum of $Au_2^-$ in our energy window appears as a single broadened peak centered at 1.94 eV. This is consistent with the earlier measurement of Lineberger and coworkers, who determined the adiabatic electron affinity of $Au_2$ to be 1.938 eV [3]. The spectra of $Au_2^-(D_2O)_{1-4}$ all resemble the spectrum of $Au_2^-$, but with each of them having been shifted to successively higher electron binding energies and broadened. Thus, just as in the cases of $Au^-(H_2O)_{1,2}$ clusters, $Au_2^-(D_2O)_{1-4}$ clusters are also anion-molecule complexes with $Au^-$ in the former cases and $Au_2^-$ in the latter cases acting as the chromophores for photodetachment. The electron binding energies of the centers of each of the $Au_2^-(D_2O)_{1-4}$ spectra are interpreted to be their vertical detachment energies, and they are 2.27, 2.56, 2.79, and 2.99 eV, respectively. For the reasons described above, the sequential spectral shifts between adjacent size clusters primarily reflect the energy required to remove a single water molecule from the larger of the two. Thus, for example, the spectral shift between the spectra of $Au_2^-(D_2O)_1$ and $Au_2^-$ is 0.33 eV, and this is approximately the energy required to remove a water molecule from $Au_2^-(D_2O)_1$. Likewise, the spectral shift between $Au_2^-(D_2O)_2$ and $Au_2^-(D_2O)_1$ is 0.29 eV, and this is the approximate energy needed to remove one water molecule from $Au_2^-(D_2O)_2$.

### 3.3. $AuOH^-$

The photoelectron spectrum of $AuOH^-$, measured with 3.49 eV photons, is presented in Fig. 3 along with its Franck–Condon fit. This spectrum reflects transitions from

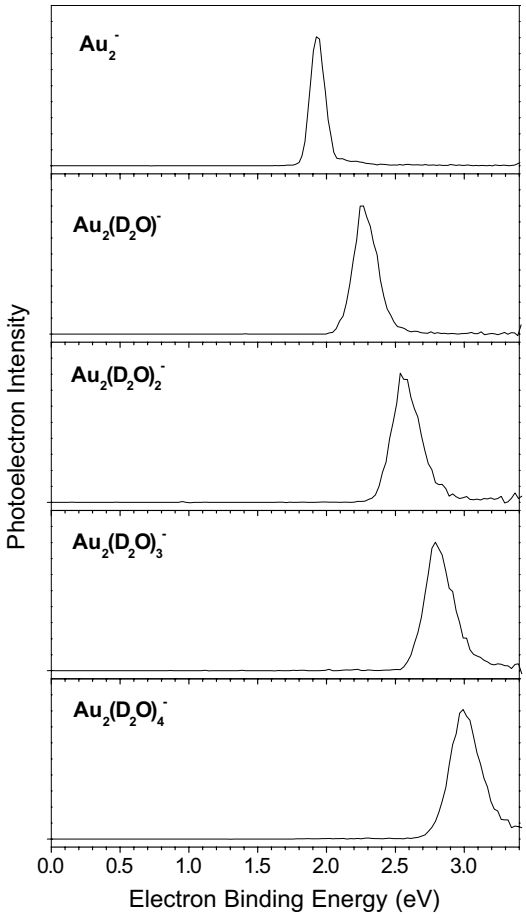


Fig. 2. The photoelectron spectra of $Au_2^-$, $Au_2^-(D_2O)_1$, $Au_2^-(D_2O)_2$, $Au_2^-(D_2O)_3$, and $Au_2^-(D_2O)_4$, all recorded with 355 nm photons.

the lower vibrational levels (v″) of the electronic ground state of $AuOH^-$ to several vibrational levels (v′) of the electronic ground state of neutral AuOH. Given that the photoelectron spectrum of $AuOH^-$ is rich with vibrational features, a thorough Franck–Condon analysis was performed to extract values for the adiabatic electron affinity, as well as the displacement and the vibrational temperature of the anion. The Franck–Condon fitting of the AuOH/$AuOH^-$ system was carried out using the Hutchisson method (independent harmonic oscillators) implemented with FCFGAUS 03 and PESCAL 2004 programs [21,22,24]. UB3LYP/SDD and UMP2/SDD calculations of the geometry and frequency of the anion and neutral species were performed using GAUSSIAN 03 [23]. The resulting data was input into FCFGAUS 03 in order to extract and format the calculated data for subsequent input into PESCAL 2004.

Gold hydroxide has three vibrational modes. In the course of fitting the photoelectron spectrum of $AuOH^-$, we found its Au–O stretch ($\nu_3$) to have the dominant effect on the spectrum, while its bending mode ($\nu_2$) and its O–H stretching mode ($\nu_1$) to each have a negligible effect. These impacts were evaluated by varying both the displacement and frequency for each mode, while monitoring the resulting spectral fit. Thus, the best fit was obtained by using a

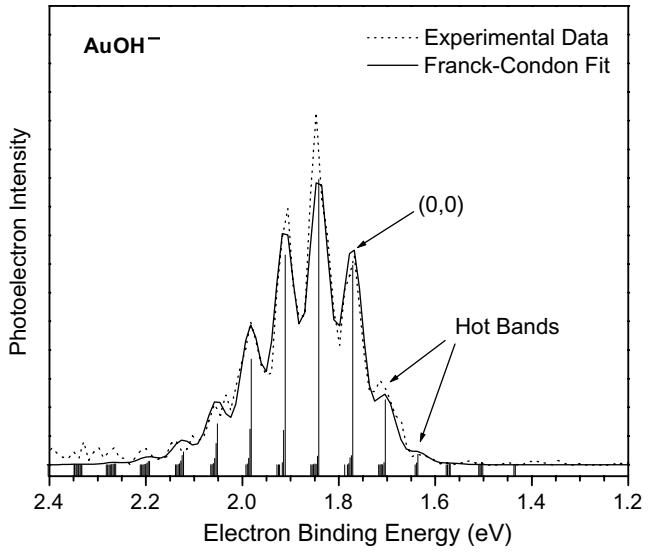


Fig. 3. The photoelectron spectrum of $AuOH^-$ and its Franck–Condon analysis fit. The vertical lines denote the PESCAL 2004-generated stick spectrum. This spectrum was recorded with 355 nm photons.

single mode simulation. The five parameters, i.e. $\nu_3$, $\Delta k_3$, T, FWHM, and EA, were treated as live variables and optimized to obtain the best fit to the experimental spectrum. The fitted $\Delta k$ value for the Au–O stretch indicates a bond length displacement of 0.118 Å for the Au–O bond upon detachment of the excess electron, in good agreement with the value obtained from UMP2/SDD calculations (0.103 Å). [To compute this value, we used the reduced mass of the $\nu_3$ mode in the optimized AuOH structure obtained from GAUSSIAN03.] The adiabatic electron affinity (EA) was determined to be $1.771 \pm 0.015$ eV. All of the optimized parameters are displayed in Table 1. The experimental spectrum and the fitted spectrum are presented together in Fig. 3.

Hirao and coworkers have conducted theoretical calculations on neutral AuOH and have discussed its anomalous properties from a relativistic viewpoint [13]. At the DK3-CCSD(T) level of theory, they found $\nu_3$ to be 569 $cm^{-1}$, while our Franck–Condon analysis determined $\nu_3$ to be 566 $cm^{-1}$. Using the value that we determined for the adiabatic electron affinity of AuOH and the literature value for the electron affinity of the gold atom in the following thermochemical cycle,

$$EA[Au] - EA[AuOH] = D_0[Au \cdot OH] - D_0[Au \cdot OH]^-, \quad (2)$$

Table 1
Optimized parameters obtained from our Franck–Condon fit of the $AuOH^-$ photoelectron spectrum

| | |
|---|---|
| $\nu_{(0-0)}$ position (eV) | 1.771 |
| $T$ (K) | 515 |
| FWHM (eV) | 0.057 |
| $\Delta k_3$ (Å$(\mu)^{1/2}$) | −0.421 |
| $\omega_e$(anion $\nu_3$) ($cm^{-1}$) | 544 |
| $\omega_e$(neutral $\nu_3$) ($cm^{-1}$) | 566 |

where $D_0$[Au·OH] is the dissociation energy for neutral AuOH breaking into Au and OH and where $D_0[Au{\cdot}OH]^-$ is the dissociation energy for the $AuOH^-$ anion breaking into $Au^-$ and OH, one can see that $D_0$[Au·OH] must be larger than $D_0[Au^-{\cdot}OH]$ by 0.54 eV. Hirao's BSSE-corrected value of $D_e$[Au·OH] at the DK3-CCSD(T) level of theory is 2.02 eV. This suggests an approximate value for $D_0[Au^-{\cdot}OH]$ of less than ~1.5 eV.

## Acknowledgments

This material is based upon work supported by the National Science Foundation under Grant No. 0517337. We thank D. Leopold and her group for helpful discussions.

## References

[1] M. Haruta, N. Yamada, T. Kobayashi, S.J. Iijima, J. Catal. 115 (1989) 301.
[2] A. Sanchez, S. Abbet, U. Heiz, W.D. Schneider, H. Hakkinen, R.N. Barnett, U. Landman, J. Phys. Chem. A 103 (1999) 9573.
[3] J. Ho, K.M. Ervin, W.C. Lineberger, J. Chem. Phys. 93 (1990) 6987.
[4] D.M. Cox, R. Brickman, K. Creegan, A. Kaldor, Z. Phys. D: Atom. Mol. Clust. 19 (1991) 353.
[5] B.E. Salisbury, W.T. Wallace, R.L. Whetton, Chem. Phys. 262 (2000) 131.
[6] T.H. Lee, K.M. Ervin, J. Phys. Chem. 98 (1994) 10023.
[7] M.L. Kimble, A.W. Castleman, R. Mitric, C. Burgel, V. Bonacic-Koutecky, J. Am. Chem. Soc. 126 (2004) 2526.
[8] L.D. Socaciu, J. Hagen, T.M. Bernhardt, L. Woeste, U. Heiz, H. Hakkinen, U. Landman, J. Am. Chem. Soc. 125 (2003) 10437.
[9] T. Ichino, A.J. Gianola, D.H. Andrews, W.C. Lineberger, J. Phys. Chem. A 108 (2004) 11307.
[10] Q. Sun, P. Jena, Y.D. Kim, M. Fischer, G. Gantefoer, J. Chem. Phys. 120 (2004) 6510.
[11] W.-J. Zheng, Ph.D. Dissertation, Johns Hopkins University, 2004.
[12] A. Antusek, M. Urban, A.J. Sadlej, J. Chem. Phys. 119 (2003) 7247.
[13] S. Ikeda, T. Nakajima, K. Hirao, Mol. Phys. 101 (2003) 105.
[14] C.-G. Zhan, S. Iwata, Chem. Phys. Lett. 232 (1995) 72.
[15] F. Muntean, M.S. Taylor, A.B. McCoy, W.C. Lineberger, J. Chem. Phys. 121 (2004) 5676.
[16] M.S. Taylor, F. Muntean, W.C. Lineberger, A.B. McCoy, J. Chem. Phys. 121 (2004) 5688.
[17] M.S. Taylor, J. Barbera, C.-P. Schultz, F. Muntean, A.B. McCoy, W.C. Lineberger, J. Chem. Phys. 122 (2005) 054310.
[18] G.J. Rathbone, T. Sanford, D. Andrews, W.C. Lineberger, Chem. Phys. Lett. 401 (2005) 570.
[19] F. Misaizu, K. Tsukamoto, M. Sanekata, K. Fuke, Surf. Rev. Lett. 3 (1996) 405.
[20] M. Gerhards, O.C. Thomas, J.M. Nilles, W.-J. Zheng, K.H. Bowen, J. Chem. Phys. 116 (2002) 10247.
[21] K.M. Ervin, PESCAL, Fortran program, 2004.
[22] K.M. Ervin, FCFGAUS 03, Fortran program, 2004.
[23] M.J. Frisch et al., GAUSSIAN 03, Revision D.01, Gaussian, Inc., Wallingford, CT, 2004.
[24] K.M. Ervin, T.M. Ramond, G.E. Davico, R.L. Schwartz, S.M. Casey, W.C. Lineberger, J. Phys. Chem. A 105 (2001) 10822.