



Photodetachment velocity map imaging of the $^1A' \leftarrow ^2A'$ transition in the AuOH anion



Bradley R. Visser^{a,1}, Matthew A. Addicoat^{a,2}, Jason R. Gascooke^b, Xinxing Zhang^c, Kit Bowen^c, Warren D. Lawrance^b, Gregory F. Metha^{a,*}

^a Department of Chemistry, University of Adelaide, South Australia 5005, Australia

^b School of Chemical & Physical Sciences, Flinders University, G.P.O. Box 2100, Adelaide, South Australia 5001, Australia

^c Departments of Chemistry and Materials Science, Johns Hopkins University, Baltimore, MD 21218, United States

ARTICLE INFO

Article history:

Received 31 January 2015

In final form 27 February 2015

Available online 6 March 2015

ABSTRACT

A velocity map imaging spectrometer was used to investigate the (\tilde{X}^1A' AuOH + e⁻ ← \tilde{X}^2A' AuOH⁻ + hν) photodetachment transition at 560 nm. The extracted spectrum shows a well-defined vibrational progression, ω_3' , with a frequency of 567(5) cm⁻¹. The adiabatic electron affinity is assigned to 1.695(5) eV and the presence of a vibrational hot band allows the determination of the corresponding anion frequency to 431(20) cm⁻¹. This represents a re-assignment of the photoelectron spectrum previously reported by Zheng et al. [1]. A Franck–Condon simulation based on coupled cluster calculations is in excellent agreement with the observed vibronic progression.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Zheng et al. [1] have reported a photoelectron spectroscopy (PES) study of AuOH⁻ as part of a broader investigation of Au⁻(H₂O)_{1,2} and Au₂⁻(D₂O)_{1–4}. This study revealed an extensive vibrational progression of the Au–OH stretch in the ground state and the authors were able to assign spectroscopic constants with the aid of Franck–Condon simulations. Here, we report a re-investigation of the AuOH⁻ spectrum using the VMI technique. This technique has been used recently to study small gold containing species such as AuH [2], AuC₂ [3,4] and AuI₂ [5] at high resolution, often resulting in the observation and assignment of vibronic transitions to the neutral ground states.

The experimental resolution of the current study exceeds that of the previous work and allows the direct measurement of the adiabatic electron affinity as well as the vibrational frequencies of both the neutral and anionic ground states that are excited in the transition. This has led to a re-assignment of the $X^1A' + e^- \leftarrow X^2A' + h\nu$ spectrum. Experimental data for the anisotropy of the observed

vibronic transitions are reported for the first time. The experimental results are supported by CCSD calculations and Franck–Condon (FC) simulations.

2. Experimental method

Details of the experiment have been published previously and are briefly recapped here [3]. Gold containing anions were produced within a Smalley-type laser ablation source based on our previous design [6] and expanded into high vacuum within a two chamber, differentially pumped system. AuOH⁻ was produced by seeding water into the carrier gas. Following expansion the clusters were pulse extracted orthogonally by a two stage Wiley–McLaren type time of flight, with space focus adjusted to provide sharp temporal distributions of the anions at the point of photodetachment. Mass selection was achieved by varying the photodetachment timing. The photodetachment laser power was varied in order to keep the number of detected electrons at a rate of ~1 per laser pulse, but was typically on the order of a few microjoules at the point of entry into the chamber. Velocity mapping was performed by a homebuilt, two stage imaging lens that was based upon the original design of Eppink and Parker [7].

A position sensitive detector consisting of dual MCPs in a chevron configuration and a phosphor screen was located 250 mm from the final electrode of the VMI electrode assembly. In order to minimize background noise the MCP was gated for 50 ns around the arrival time of the signal electrons. Images were collected using a

* Corresponding author at: Department of Chemistry, The University of Adelaide, South Australia 5005, Australia.

E-mail address: greg.metha@adelaide.edu.au (G.F. Metha).

¹ Current address: Paul Scherrer Institute, General Energy Department, CH-5232 Villigen, Switzerland.

² Current address: Engineering and Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany.

home built camera containing a charge-coupled device (CCD) sensor. After collection, the circularity of the images was corrected using the circularization method designed by Lawrance and Gascooke [8] that has been used in previous VMI studies [3,9,10].

Energy calibration was performed using the Au^- anion photodetachment signal, due to the large signal to noise ratio and accurately determined electron affinity (EA) [11]. Conversion of the final experimental image into a 3-dimensional representation of the photodetachment event was achieved through the application of the inverse Abel transform [12].

The binding energy spectrum was extracted from the radial data of the image and the anisotropy values were determined by masking individual vibronic transitions and fitting to the angular distributions within these ranges. Experimental spectroscopic constants were determined by performing a least squares fit to the experimental spectrum.

3. Computational details

The ground electronic states of anionic and neutral AuOH were calculated using DFT and CCSD methods based upon the structures previously reported for the neutral [13]. All DFT calculations were undertaken using the GAUSSIAN 09 suite of programs [14] employing the B3P86 hybrid functional and the Stuttgart Relativistic Small Core (SRSC) basis set. For Au, the MWB60 ECP was used, leaving the remaining 19 electrons to be calculated as valence. For the oxygen and hydrogen atoms, the Dunning/Huzinaga full double zeta (D95) basis set was used. Subsequently, the ground electronic states were re-optimized and frequency calculations were undertaken using coupled cluster including single and double excitations with relativistic corrections (RCCSD for neutral AuOH, ROCCSD for the anion). In these calculations, oxygen and hydrogen atoms were described using Dunning's aug-cc-pVTZ basis set [15] and the Au atom was described using aug-cc-pVTZ-PP and associated ECP [16,17]. Harmonic frequency calculations were performed on all optimized geometries.

In the study of Ikeda et al. [13] it was reported that the results of the molecular geometry calculations for AuOH were highly dependent on the inclusion of the treatment of relativistic effects. For instance the Au–OH bond length decreased from 2.145 to 1.963 Å following the inclusion of relativistic effects, which was associated with the relativistic contraction of the valence *s* orbital of Au. The latter value is consistent with our DFT and CCSD calculations, both of which incorporate relativistic corrections.

The CCSD-calculated structural and vibrational data were used as starting parameters for the simulation of Franck–Condon transition intensities for the prediction of the photodetachment spectra. FC simulations were performed with the ezSpectrum software suite [18] using the parallel approximation. The energy of the 0_0^0 transition (1.695(5) eV), the applied convolution resolution (typically 15 meV), and the temperature (~250 K), were adjusted to obtain the best match to the experimental spectra.

4. Results and discussion

The inverse Abel transformed experimental image of AuOH^- obtained at an exciting wavelength of 560 nm is shown in Figure 1. The corresponding experimental spectrum is presented with the best fit Franck–Condon simulated spectrum in Figure 2. The spectrum is dominated by transitions spaced by $567(5) \text{ cm}^{-1}$, with a reduced spacing observed between the peaks labelled A and 0 of $431(20) \text{ cm}^{-1}$. The anisotropy parameter was determined for each vibronic transition and is plotted against electron kinetic energy in Figure 3. The calculated lowest energy molecular geometries can be found in Figure 4 and important data are summarized in Table 1.

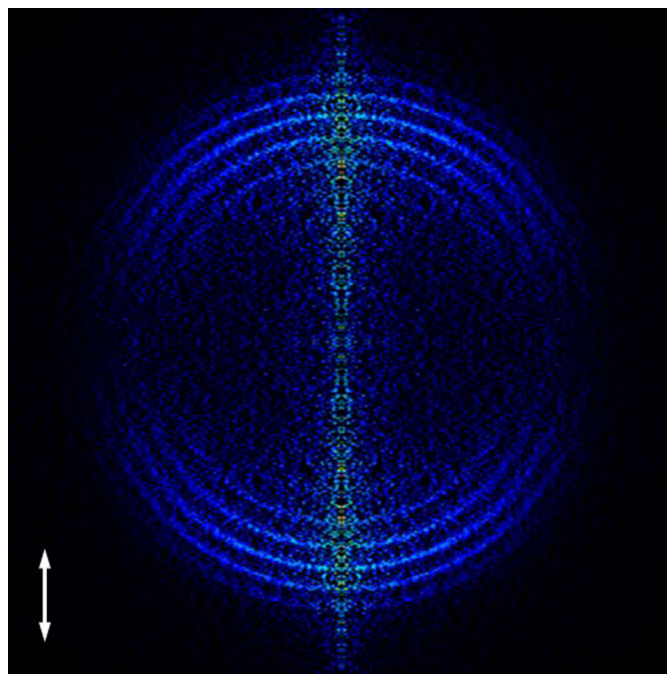


Figure 1. Inverse Abel transformed image of AuOH^- at a photodetachment wavelength of 560 nm (2.214 eV). Photon polarization is along the vertical axis of the image (vertical arrow).

Energies are reported with respect to the energy of the ground state of neutral AuOH.

As shown in Figure 2, the spectrum consists of five evenly spaced transitions, labelled 0–5, beginning at 1.695 eV with separation $567(5) \text{ cm}^{-1}$. The vibrational spacing agrees very well with that reported by Zheng et al. [1]. Very good agreement is also achieved with the calculated Au–OH (ω_3') vibrational wavenumber from this work (583 cm^{-1}) and that of Ikeda et al. (569 cm^{-1}) [13]. Therefore, peaks 0–5 are assigned as a progression of the Au–OH stretching vibration in neutral AuOH, 3_0^n ($n=0-5$) emanating from the origin band 0_0^0 at 1.695(5) eV (*i.e.* peak 0). The vibrational spacing between peaks A and 0 of $431(20) \text{ cm}^{-1}$ agrees well with the Au–OH $^-$ stretching frequency calculated in this work of 435 cm^{-1} and thus leads to the assignment of peak A to the 3_1^0 transition.

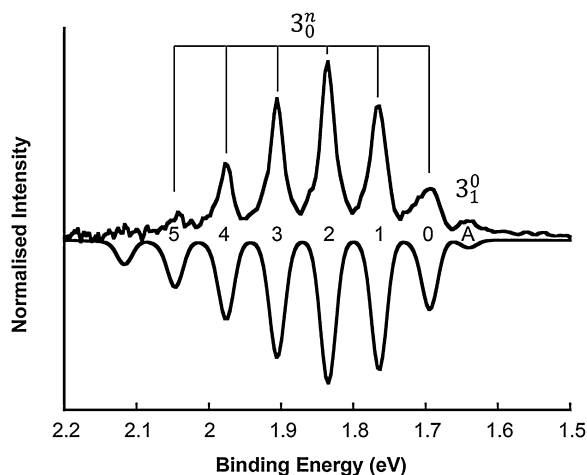


Figure 2. The photodetachment binding energy spectrum of AuOH^- collected at 560 nm excitation is shown in the upper trace. The lower trace is the Franck–Condon simulated spectrum of the $^1A' \leftarrow ^2A'$ transition that best fits the experimental data (see text for details).

Table 1
Harmonic vibrational frequencies (cm^{-1}) and relative energies (eV) for the $^2A'$ state (anion, top two rows) and $^1A'$ state (neutral, bottom two rows) calculated at R(O)CCSD/aug-cc-pVTZ (see text for further details).

	State	ΔE	ω_1 O—H stretch	ω_2 Au—O—H bend	ω_3 Au—O stretch
Theory	$^2A'$	-1.6015	3832	741	434
Experimental	"	-1.695			431(20)
Theory	$^1A'$	0	3831	965	583
Experimental	"				567(5)

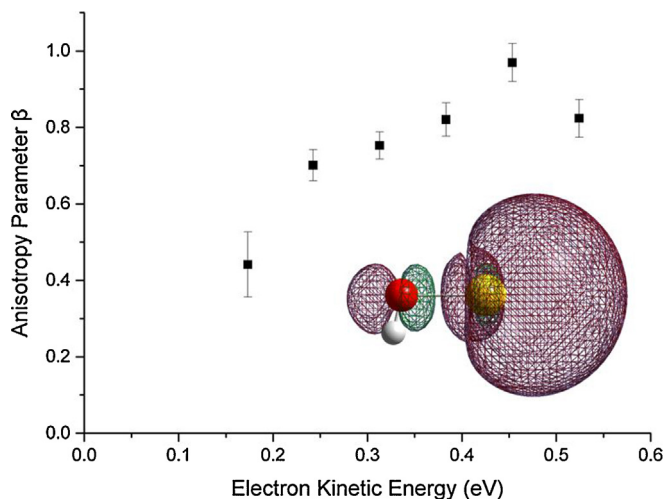


Figure 3. Values of the anisotropy parameter β determined for the respective vibronic transitions plotted against (excess) electron kinetic energy. The SOMO for the anion is shown in the inset.

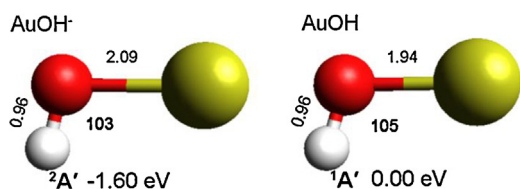


Figure 4. Lowest anion and neutral geometries obtained for the R(O)CCSD calculations. Electronic energies are given relative to the global minimum neutral structure. The units for bond length are Angstroms and degrees for bond angle.

This assignment is in contrast with the work of Zheng et al. [1], who reported the Au—OH⁻ stretching frequency to a value of 544cm^{-1} by placing the origin at 1.771 eV and fitting a Franck–Condon simulation to the experimental spectrum. The difference in assignment is essentially a shift of one vibrational quantum, which we are able to correctly re-assign due to the higher resolving measurements afforded by the VMI technique. The difference in the vibronic assignment leads to a re-determination of the adiabatic electron affinity of AuOH⁻ to 1.695(5) eV, which is in good agreement to the value of 1.6015 eV calculated in this study with the CCSD method.

The calculated ground state geometries of both AuOH and AuOH⁻ are of C_s symmetry and differ primarily in the Au—O bond distance, which is 15 pm longer in the anion. Franck–Condon simulations performed with the calculated molecular geometries and vibrational frequencies lead to a spectrum that is in very good agreement with the experimental spectrum. The simulated spectrum is shown as the mirror image (lower) trace in Figure 2. The best match to the relative intensities of the hot and main transitions is achieved by fitting with an initial (anion) vibrational temperature of 250(50) K. This value is consistent with measurements of the

temperature of other species investigated with the current experimental setup [3].

Figure 3 shows the anisotropy parameter, β , determined for each of the transitions plotted as a function of electron kinetic energy ($\nu_3' = 0$ is at 0.52 eV, $\nu_3' = 5$ is at 0.17 eV). The parameter is observed to scale linearly with electron kinetic energy within this energy range and is distributed around a mean value of +0.7. Wu et al. have recently measured a value of 1.9 for the Au ($^2S, d^{10}s^1$) \leftarrow Au⁻ ($^1S, d^{10}s^2$) transition [2]. This transition is $^2S (d^{10}s^1) \leftarrow ^1S (d^{10}s^2)$ and thus electrons are ejected in the form of a P wave, which corresponds to a β value of 2 [19]. Based on our spectral assignment the excess electron of AuOH⁻ is ejected from a singly occupied molecular orbital (SOMO) that has a significant (66%) Au 6s-orbital character, which is shown as an inset in Figure 3. The positive β values measured here are consistent with this assignment. The error bars in Figure 3 indicate an uncertainty of 3σ in the least squares fit to the angular intensity distributions. Noise from the inverse Abel transform is found to significantly degrade the confidence of the fit.

5. Conclusions

Gold hydroxide anions were successfully produced within a laser vaporization cluster source and investigated using the velocity map imaging technique. Analysis of the experimental spectrum led to an alternative assignment of the spectrum and the values of the EA, ω_3' and ω_3'' to 1.695(5) eV, 567(5) cm^{-1} and 431(20) cm^{-1} , respectively. The geometric structures and energies of both neutral and anionic AuOH/AuOH⁻ were calculated at the coupled cluster level. The results of the calculations were found to be in very good agreement with the experimentally assigned values.

Acknowledgements

Financial support from Flinders University and the University of Adelaide is gratefully acknowledged. Support from the Australian Research Council for the purchase and maintenance of the lasers is also acknowledged. Computing resources provided by the National Computational Infrastructure (NCI) Facility and eResearch SA is also gratefully acknowledged. This material is based in part on work supported by the (US) National Science Foundation under Grant No. CHE-1360692 (KHB).

References

- [1] W. Zheng, X. Li, S. Eustis, A. Grubisic, O. Thomas, H. de Clercq, K. Bowen, *Chem. Phys. Lett.* 4440 (2007) 232.
- [2] X. Wu, Z. Qin, H. Xie, R. Cong, X. Wu, Z. Tang, H. Fan, *J. Chem. Phys.* 133 (2010) 44303.
- [3] B.R. Visser, M.A. Addicoat, J.R. Gascooke, W.D. Lawrance, G.F. Metha, *J. Chem. Phys.* 138 (2013) 174310.
- [4] I. León, Z. Yang, L.-S. Wang, *J. Chem. Phys.* 140 (2014) 084303.
- [5] Y.-L. Wang, X.-B. Wang, X.-P. Xing, F. Wei, J. Li, L.-S. Wang, *J. Phys. Chem. A* 114 (2010) 11244.
- [6] M.W. Heaven, G.M. Stewart, M.A. Buntine, G.F. Metha, *J. Phys. Chem. A* 104 (2000) 3308.
- [7] A.T.J.B. Eppink, D.H. Parker, *Rev. Sci. Instrum.* 68 (1997) 3477.
- [8] J.R. Gascooke, *Energy Transfer in Polyatomic-Rare Gas Collisions and van Der Waals Molecule Dissociation* (PhD thesis), Flinders University of South Australia, 2000.

- [9] S. Cavanagh, S. Gibson, M. Gale, C. Dedman, E. Roberts, B. Lewis, *Phys. Rev. A* 76 (2007) 052708.
- [10] M. Van Duzor, F. Mbaïwa, J. Wei, T. Singh, R. Mabbs, A. Sanov, S.J. Cavanagh, S.T. Gibson, B.R. Lewis, J.R. Gascooke, *J. Chem. Phys.* 133 (2010) 174311.
- [11] J. Ho, K.M. Ervin, W.C. Lineberger, *J. Chem. Phys.* 93 (1990) 6987.
- [12] E.W. Hansen, P.-L. Law, *J. Opt. Soc. Am. A* 2 (1985) 510.
- [13] S. Ikeda, T. Nakajima, K. Hirao, *Mol. Phys.* 101 (2003) 105.
- [14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J.A.J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N.J. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, GAUSSIAN 09, Gaussian, Inc., Wallingford, CT, 2009.
- [15] R.A. Kendall, T.H. Dunning, R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6796.
- [16] D. Figgen, G. Rauhut, M. Dolg, H. Stoll, *Chem. Phys.* 311 (2005) 227.
- [17] K.A. Peterson, C. Puzzarini, *Theor. Chem. Acc.* 114 (2005) 283.
- [18] V.A. Mozhaykiy, A.I. Krylov, *ezSpectrum*, <http://iopshell.usc.edu/downloads>
- [19] N.D. Gibson, B.J. Davies, D.J. Larson, *Phys. Rev. A* 48 (1993) 310.