

## INTERACTION OF GOLD ATOM WITH CLUSTERS OF WATER: FEW COMPUTATIONAL MISE-EN-SCÈNES WITH HYDROGEN BONDING MOTIF

Eugene S. KRYACHKO

*Bogolyubov Institute for Theoretical Physics, Kiev-143, 03680 Ukraine and  
Department of Chemistry, Bat. B6c, University of Liege, Sart-Tilman, B-4000 Liege 1, Belgium;  
e-mail: eugene.kryachko@ulg.ac.be*

Received May 23, 2008

Accepted August 26, 2008

Published online December 1, 2008

*Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday.*

The present work outlines the fair relationship of the computational model with the experiments on anion photoelectron spectroscopy for the gold–water complexes  $[\text{Au}(\text{H}_2\text{O})_{1 \leq n \leq 2}]^-$  that is established between the auride anion  $\text{Au}^-$  and water monomer and dimer thanks to the nonconventional hydrogen bond where  $\text{Au}^-$  casts as the nonconventional proton acceptor. This work also extends the computational model to the larger complexes  $[\text{Au}(\text{H}_2\text{O})_{3 \leq n \leq 5}]^-$  where gold considerably thwarts the shape of water clusters and even particularly breaks their conventional hydrogen bonding patterns. The fascinating phenomenon of the lavish proton acceptor character of  $\text{Au}^-$  to form at least six hydrogen bonds with molecules of water is computationally unveiled in the present work for the first time.

**Keywords:** H bonds; Au clusters; Second-order perturbation Møller-Plesset; MP2 calculations; DFT calculations.

### NON-COVALENT INTERACTIONS, HYDROGEN BONDING AND NANO-DIMENSIONS

It is true that nano-dimensions made a paradigm shift<sup>1</sup> in the theory of molecular interactions<sup>2</sup>, and, in particular, in that its branch – theory of non-covalent interactions<sup>3–5</sup> – that governs the world of supramolecular chemistry and molecular recognition. The theory of non-covalent interactions covers a broad spectrum of different types of interactions, among which the hydrogen bonding interaction is definitely one of the most important.

The hydrogen bonding interaction is the well recognized and deeply studied phenomenon<sup>6–23</sup>. It manifests in the formation of a so called classical or conventional hydrogen (H) bond. According to Pimentel and McClellan<sup>7</sup> (see also<sup>6,8–23</sup>), “a hydrogen bond is said to exist when (i) there

is evidence of a bond, and (ii) there is evidence that this bond sterically involves a hydrogen atom already bonded to another atom". This definition suggests that a conventional hydrogen bond is at least an attractive interaction of three parties. One is a proton donor atom or molecule X that donates the bonded hydrogen atom H, casting as a second party in the form of the hydron  $H^{\delta+}$  ( $0 < \delta+ \leq 1$ ), to the third party – a proton acceptor group Y. The latter, while interacting with the X–H, yields the X–H...Y hydrogen bond.

An arbitrary X–H...Y H bond is geometrically characterized by the bond length  $R(X-H)$ , the H-bond separation  $r(H...Y)$ , and the bond angle  $\angle XHY$ . By definition, the H bond X–H...Y is formed if the following conditions are satisfied<sup>6-22</sup>:

(i) there exists a clear evidence of the bond formation – this can be, e.g., the appearance of the H-bond stretching mode  $\nu_{\sigma}(X...Y)$ ;

(ii) there exists a clear evidence that this bond specifically involves a hydrogen atom (hydron) bonded or bridged to Y predominantly along the bond direction X–H (see particularly<sup>18,21</sup>);

(iii) the X–H bond elongates relative to that in the monomer, i.e.

$$\Delta R(X-H) := R_{\text{complex}}(X-H) - R_{\text{monomer}}(X-H) > 0;$$

(iv) the H-bond separation  $r(H...Y)$  defined as the distance between the bridging proton and the proton acceptor Y is shorter than the sum of van der Waals radii of H and Y, that is, shorter than the so called van der Waals cutoff (see particularly<sup>14,15,19</sup> and also<sup>21</sup> quoted in<sup>21</sup>)

$$r(H...Y) < w_H + w_Y$$

where  $w_Z$  is the van der Waals radius of Z (Z = H, Y). Note that  $w_H$  varies and is usually taken the value of either  $1.20 \text{ \AA}^{24a}$  or  $1.10 \text{ \AA}^{24b}$ , and  $w_{Au} = 1.66 \text{ \AA}$ . The distance  $r(X...Y)$  between the proton donor X and the proton acceptor Y is often referred to as the H-bond length. The necessary but insufficient condition imposed on  $r(X...Y)$  to indicate that the H bond is formed is that  $r(X...Y) < w_X + w_Y$ ;

(v) the stretching vibrational mode  $\nu(X-H)$  undergoes a red shift with respect to that of the isolated X–H group, that is

$$\Delta \nu(X-H) := \nu_{\text{complex}}(X-H) - \nu_{\text{monomer}}(X-H) < 0$$

and its IR intensity significantly increases;

(vi) the proton nuclear magnetic resonance ( $^1\text{H}$  NMR) chemical shift in the  $\text{X-H}\cdots\text{Y}$  hydrogen bond is shifted downfield compared to the monomer.

It is worth mentioning that the conditions (iii)–(vi) can also be treated as an indirect justification of validity of (ii).

Via the hydrogen or hydron “bridge”, a hydrogen bond establishes the connection between the atoms X and Y. Their electronegativities exceed the electronegativity of the hydrogen atom. Hence, X and Y can be particularly chosen as F (3.98), N (3.04), O (3.44), C (2.55), P (2.19), S (2.58), Cl (3.16), Se (2.55), Br (2.96) and I (2.66), where the corresponding Pauling electronegativity is given in parentheses. The Y atoms possess a lone pair of electrons and therefore play the role of typical conventional proton acceptors in the formation of conventional hydrogen bonds, as though, the existence of the lone-pair electrons in the proton acceptor cannot be ruled out<sup>25</sup>.

The above definition of the hydrogen bond interaction is rather general and allows to unify many types of interaction under the “hydrogen bonding” category, thus considerably broadening its conventional manifold (see in particular<sup>26,27</sup> and references therein), either its X- or Y-submanifolds. Interestingly, the Y-submanifold is largely extended by including the transition-metal “nonconventional” proton acceptors, such as Co, Rh, Ir, Ni, Pd, Pt, Ru, and Os<sup>21b–21d,22</sup>, despite that they do not possess free electron pairs, in contrast to the conventional ones. The specific criteria which additionally characterize such nonconventional hydrogen bonds are the following (refs<sup>26b–26c</sup>: (a) the bridging hydrogen is bonded to a rather electronegative element, (b) the acceptor metal atom is electron-rich (e.g. late transition metals) with filled d shells (recall here<sup>25</sup>), (c) the bonding arrangement is approximately linear (see also<sup>27a</sup>).

What about gold – the “cornerstone” of nanoscience due to the discovery of more than two decades ago that gold nanoparticles supported on metal oxides reveal the exclusively high catalytic activity for CO oxidation<sup>28</sup>? Whether can gold enter the Y-submanifold? Or put in the other words: Whether the gold atom or clusters of gold are prone to play, interacting with conventional proton donors such as the O–H and N–H groups, a role of a proton acceptor and hence to participate in the formation of nonconventional hydrogen bonds?

## GOLD AND HYDROGEN BONDING: A NONCONVENTIONAL PROTON ACCEPTOR

The Pauling electronegativity of the atom of gold is 2.54, that is, it is greater of that of H. Gold, obviously, obeys the foregoing condition (b). Hence, it can be in principle a potential candidate for a nonconventional proton acceptor – this suggestion was computationally proved for the first time in<sup>29</sup>. The latter reported a strong computational evidence of the propensity of a triangular gold cluster to behave as a proton acceptor with the O–H group of formic acid and the N–H one of formamide. Speaking precisely, it was shown that the triangular Au<sub>3</sub> cluster rather strongly binds either formamide or formic acid and forms with them the planar and cyclic complexes. The bonding involves two ingredients: the anchoring bond between the gold atom and the carbonyl oxygen and the N–H...Au or O–H...Au contacts between Au and the amino group of formamide or the hydroxyl group of formic acid. As argued in<sup>29</sup>, these contacts share all the common features (i)–(vi) of the conventional hydrogen bonds and therefore, they can therefore be treated as their nonconventional analogs.

Since this work<sup>29</sup>, the existence of the X–H...Au<sub>n</sub> nonconventional hydrogen bond was computationally demonstrated for a wide variety of molecules in different charge states  $Z = 0, \pm 1$ , ranging from the Au<sub>n</sub>-DNA bases and Au<sub>n</sub>-DNA duplexes<sup>30a–30c</sup>, to Au<sub>n</sub>-(HF)<sub>m</sub><sup>30d</sup>, [Au<sub>n</sub><sup>Z</sup>-(H<sub>2</sub>O)<sub>m</sub>]<sup>Z 30e</sup>, and [Au<sub>n</sub>-(NH<sub>3</sub>)<sub>m</sub>]<sup>Z 30f–30g</sup> complexes. The latter family includes the smallest nano-sized tetrahedral gold cluster Au<sub>20</sub><sup>Z</sup>(T<sub>d</sub>)<sup>31</sup> (see also<sup>32</sup> for current review and references therein). The charge-state specificity of the bonding ingredients of the Au<sub>n</sub><sup>Z</sup>-(NH<sub>3</sub>)<sub>m</sub> complexes unveiled in<sup>30f–30g</sup> has recently been explored to formulate the bonding encoding approach for molecular logic<sup>30h</sup>. On the experimental side, the hydrogen acceptor propensity of the gold atom and some its clusters has been experimentally detected for the complexes [Au(H<sub>2</sub>O)]<sup>-</sup>-Ar<sub>n</sub><sup>33</sup>, [Au(H<sub>2</sub>O)<sub>n=1,2</sub>]<sup>-</sup><sup>34</sup>, and [Au(H<sub>2</sub>O)]<sup>-</sup><sup>35</sup>, the crown compound [Rb([18]crown-6)(NH<sub>3</sub>)<sub>3</sub>]Au-NH<sub>3</sub><sup>36</sup> (see also<sup>37</sup>), for the complexes of small gold clusters with acetone<sup>38a</sup> and with amino acids<sup>38b–38d</sup> (see also the closely related recent work<sup>39</sup>), and for the gold(III) antitumor complex<sup>40</sup>. The latter work reports the synthesis and properties of the Au(III) compound of tridentate ligand 1,4,7-triazacyclononane (TACN) [Au(TACN)Cl<sub>2</sub>][AuCl<sub>4</sub>]. In its cationic state, the Au(III) atom is bound by two N atoms of TACN and two atoms of Cl. The unbound amine group of TACN forms with Au(III) the Au(I)–H(3C) (in the notations of<sup>40</sup>) bond length of 1.91 Å.

The experimental works<sup>33–37</sup> have been focused on the nonconventional X–H...Au<sup>-</sup> hydrogen bonds that involve the auride anion Au<sup>-</sup>. The latter be-

has very similar to the heavier halides  $\text{Br}^-$  and  $\text{I}^-$  which are known as rather good proton acceptors in hydrogen-bonded systems<sup>19,24</sup>. The bonding patterns of the compound  $[\text{Rb}([\text{18}]\text{crown-6})(\text{NH}_3)_3]\text{Au-NH}_3$ <sup>36a-36b</sup> comprise of the hydrogen bonds which are formed between neutral ammonia molecules playing as proton donors, on the one hand, and auride anions as proton acceptors on the other. Four  $\text{NH}_3$  molecules are coordinated to  $\text{Au}^-$  and simultaneously three of them, characterized by the distance  $r(\text{N}\cdots\text{Au}^-) = 3.73 \text{ \AA}$ , are coordinated to Rb centers. The fourth is uncoordinated to the latter and separated from  $\text{Au}^-$  by  $r(\text{N}\cdots\text{Au}^-) = 3.63 \text{ \AA}$ . The corresponding bridged hydrogen atom is distanced from  $\text{Au}^-$  by  $r(\text{H}\cdots\text{Au}^-) = 2.581 \text{ \AA}$  and forms the bonding angle  $\angle\text{NHAu}^- = 158.1^\circ$ . Thus, the geometric criteria (i)–(iv) are obeyed for the  $\text{X-H}\cdots\text{Au}^-$  contact that is then definitely the hydrogen bond. Moreover, the auride anion has the 5d shell filled with the  $5d^{10}6s^2$  valence electrons (see e.g.<sup>30e</sup>) – that is, the condition (b) is also satisfied. Besides, the proton donor N atom is highly electronegative (condition (a)), and the angle  $\angle\text{NHAu}^-$  is within the range determined by the condition (c)<sup>36a</sup>.

The aim of the present work is to offer the number of computational mise-en-scènes behind the experiments on anion photoelectron spectroscopy of gold–water complexes  $[\text{Au}(\text{H}_2\text{O})_{1\leq n\leq 2}]^-$ <sup>34</sup> and their generalization to the larger ones,  $[\text{Au}(\text{H}_2\text{O})_{3\leq n\leq 5}]^-$ . The existence of such complexes is provided the nonconventional  $\text{X-H}\cdots\text{Au}^-$  hydrogen bonds that glue together the auride anion and water clusters (cf. e.g.<sup>41</sup>). Note that the computational methodology of the present work is outlined in Appendix.

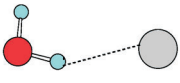
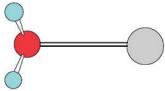
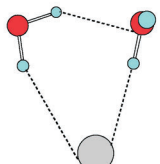
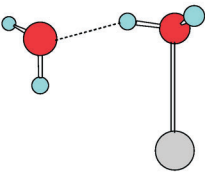
#### HYDROGEN BONDING PATTERNS BETWEEN AURIDE ANION AND CLUSTERS OF WATER

The key computational facts about the most stable anionic complexes  $[\text{Au}(\text{H}_2\text{O})_{1\leq n\leq 5}]^-$  are collected in the left column of Table I. Since the computational electron affinity of the gold atom is high:  $\text{EA}^{\text{theor}}(\text{Au}) = 2.129 \text{ eV}$ <sup>42</sup>, it is therefore the gold atom of  $[\text{Au}(\text{H}_2\text{O})_{1\leq n\leq 5}]^-$  where the most excess electron charge is located on. This is witnessed by the Mulliken charges of gold which are e.g. equal to  $q_M^{n=1}(\text{Au}) = -0.902$  and  $q_M^{n=2}(\text{Au}) = -0.839$ , and therefore, as anticipated, the gold atom mainly exists in  $[\text{Au}(\text{H}_2\text{O})_{1\leq n\leq 5}]^-$  as the auride anion. The latter casts as the strong proton acceptor, even stronger in some cases than the oxygens of the studied water clusters: this can readily be seen by juxtaposing the stretching frequency  $\nu(\text{O-H}(\cdots\text{Au})) = 3279 \text{ cm}^{-1}$  of the hydron  $\text{H}_{\text{bonded}}$ , which belongs to the proton-donor water molecule of the water dimer and H-bonded to  $\text{Au}^-$  in  $[\text{Au}(\text{H}_2\text{O})_2]^-$ , and the

$\nu(\text{O-H}(\cdots\text{O})) = 3727 \text{ cm}^{-1}$  of the H, that bridges the water dimer within  $[\text{Au}(\text{H}_2\text{O})_2]^-$ .<sup>43</sup> It is worth mentioning that the aforementioned stretching vibrational mode  $\nu(\text{O-H}(\cdots\text{Au}))$  of  $[\text{Au}(\text{H}_2\text{O})_2]^-$  is the lowest one among the considered series of complexes. Two direct and significant consequences can be drawn from the fact that the auride anion functions as the strong proton acceptor in the complexes  $[\text{Au}(\text{H}_2\text{O})_{1n\leq 5}]^-$ .

TABLE I

The computational mise-en-scènes of bonding between the auride anion (left column) or the gold atom (right column) and the selected clusters of water molecules  $(\text{H}_2\text{O})_{1n\leq 5}$ . The vertical detachment energies (VDE) and adiabatic detachment energy (ADE) are given in eV. The ZPE-corrected binding energies ( $E_b^{\text{ZPE}}$ ) and energy differences are given in kcal mol<sup>-1</sup>,  $R(\text{O-H})$  and  $r(\text{H}\cdots\text{Y})$  in Å,  $\angle\text{XHY}$  in °, and  $\nu(\text{X-H})$  in cm<sup>-1</sup>. The reference asymptote for the complex  $[\text{Au}(\text{H}_2\text{O})_n]^Z$  is the infinitely separated  $\text{Au}^Z$  and  $(\text{H}_2\text{O})_n$  where  $Z = -1, 0$  and  $(\text{H}_2\text{O})_n$  designates the ground-state cluster of  $n$  molecules of water. The exception is  $n = 4$ , as indicated below by asterisk, when the R-sided conformer  $[\text{Au}(\text{H}_2\text{O})_4]_{\text{R}}^Z$  is treated with respect to  $\text{Au}^Z$  and the corresponding water cluster  $(\text{H}_2\text{O})_4^{3\text{D}}$  which is thoroughly discussed in Appendix. The quantities chosen to characterize the nonconventional hydrogen bonds  $\text{O-H}\cdots\text{Au}^-$  are underlined. The MP2 values are presented in curly brackets

Z = -1	Z = 0
<p><b><u>n = 1</u></b></p>  <p>VDE = 2.71 (VDE<sup>expt</sup> = 2.76 [35]) ADE<sup>ZPE</sup> = 2.61</p> <p><math>q_{\text{M}}(\text{Au}) = -0.902</math>      <math>q_{\text{M}}(\text{H}_2\text{O}) = -0.098</math>  <math>R(\text{O-H}) = \underline{0.9865}</math> {0.9796}; 0.9631 {0.9615}  <math>\Delta R(\text{O-H}_{\text{bonded}}) = 0.0244</math>    <math>r(\text{H}_{\text{bonded}}\cdots\text{Au}) = 2.437</math> {2.464}  <math>\angle\text{OH}_{\text{bonded}}\text{Au} = 157.3</math>  <math>\nu(\text{O-H}) = \underline{3403}</math>; <u>{3556}</u>; 3849 {3849}  <math>\Delta\nu(\text{O-H}_{\text{bonded}}) = -414</math>  <math>-E_b^{\text{ZPE}} = 12.30</math> {12.92} {14.32 [36a]}; 12.43 [34]</p>	 <p><math>q_{\text{M}}(\text{Au}) = -0.053</math>      <math>q_{\text{M}}(\text{H}_2\text{O}) = 0.053</math>  <math>R(\text{Au-O}) = 2.670</math> {2.634}  <math>R(\text{O-H}) = 0.9640</math> {0.9618}  <math>\nu_{\text{sym,asym}}(\text{O-H}) = 3790, 3897</math> {3852, 3973}  <math>-E_b^{\text{ZPE}} = 1.21</math> {1.30} {2.61 [36a]}; 1.11 [44]</p>
<p><b><u>n = 2</u></b></p>  <p>VDE = 3.17 (VDE<sup>expt</sup> = 3.20 [35]) ADE<sup>ZPE</sup> = 2.84</p> <p><math>q_{\text{M}}(\text{Au}) = -0.839</math>      <math>q_{\text{M}}(\text{H}_2\text{O}) = -0.117, -0.044</math>  <math>R(\text{O-H}) = \underline{0.9925}</math> {0.9878}; <u>0.9738</u> {0.9698}; 0.9703  {0.9668}; 0.9635 {0.9616}</p>	 <p><math>q_{\text{M}}(\text{Au}) = -0.097</math>      <math>q_{\text{M}}(\text{H}_2\text{O}) = 0.108, 0.011</math>  <math>R(\text{Au-O}) = 2.520</math> {2.411}  <math>R(\text{O-H}) = 0.9778</math> {0.9733}; 0.9663</p>

## Number 1

This predetermines rather large, by the absolute value, binding energies  $E_b^{ZPE}$ . As demonstrated in Table I, the latter range from 12.3 kcal mol<sup>-1</sup> for  $n = 1$  to ~19.7–22.7 kcal mol<sup>-1</sup> for  $n = 2-4$ , and apparently approaches the saturation threshold of ca. 23.6 kcal mol<sup>-1</sup> for  $n = 5$ . Note that the presented computational  $E_b^{ZPE}$  are consistent with the experimental  $E_b^{ZPE-expt}$ <sup>35</sup>, for instance, with  $E_b^{ZPE-expt}([AuH_2O]^-) = 10.4$  kcal mol<sup>-1</sup> and with the stabilization energy of  $[Au(H_2O)_2]^-$  taken with respect to the asymptote  $[AuH_2O]^- + H_2O$ . The latter, as estimated in<sup>35</sup> as equal to ca. 10.2 kcal mol<sup>-1</sup>, fairly agrees with our value of 10.9 kcal mol<sup>-1</sup>.

Actually, the strength of the nonconventional hydrogen bonds of the studied complexes is underestimated because they mainly involve so called “free” O–H groups of water clusters that do not participate in the water–

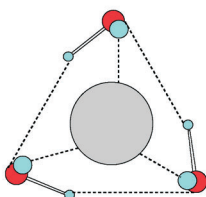
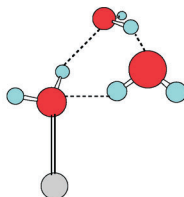
$\Delta R(O-H) = 0.0296, 0.0127, -0.0004$ $r(H_{\text{bonded}} \cdots Au) = 2.346 \{2.322\}, 2.745 \{2.762\}$ $r(H \cdots O) = 2.095 \{2.096\}$ $\angle OH_{\text{bonded}} Au = 161.1 \{161.3\}, 148.8 \{149.8\}$ $\angle OHO = 152.3 \{152.4\}$ $v(O-H) = 3279 \{3369\}, 3643 \{3742\}; 3727 \{3830\}; 3846 \{3916\}$ $\Delta v(O-H) = -535, -171, +21$ $-E_b^{ZPE} = 19.72 \{20.74\}$	$\{0.9622\}; 0.9637 \{0.9616\}, 0.9630 \{0.9609\}$ $r(H \cdots O) = 1.840 \{1.828\}$ $\angle OHO = 160.6 \{164.9\}$ $v(O-H) = 3563 \{3665\}; 3774 \{3862\}; 3855 \{3924\}, 3890 \{3977\}$ $\Delta v(O-H) = -143$ $-E_b^{ZPE} = 3.24 \{3.61\}$
<p><b><math>n = 3</math></b></p>  <p style="text-align: center;"><b>VDE = 3.56</b> <b>ADE<sup>ZPE</sup> = 3.03</b></p> $R(O-H) = 0.9789; 0.9716$ $\Delta R(O-H) = 0.0179; -0.0040$ $r(H_{\text{bonded}} \cdots Au) = 2.577$ $r(H \cdots O) = 2.120$ $\angle OH_{\text{bonded}} Au = 149.8$ $v(O-H) = 3527, 3530, 3555; 3681, 3707, 3709$ $\Delta v(O-H) = -361, -363, -339; +121, +89, +80$ $-E_b^{ZPE} = 22.70$	 $R(Au-O) = 2.602$ $R(O-H) = 0.9845, 0.9756, 0.9717$ $\Delta R(O-H) = 0.0044, 0, -0.0039$ $r(H \cdots O) = 1.792, 1.918, 2.018$ $\angle OHO = 155.1, 145.2, 142.5$ $v(O-H) = 3439, 3620, 3690; 3857, 3888, 3895$ $\Delta v(O-H) = -121, +2, +61$ $-E_b^{ZPE} = 1.93$
<p><b><math>n = 4</math></b></p> <p><i>L</i>-sided isomer:</p>	

TABLE I  
(Continued)

water hydrogen bonds. Consider for instance the complex  $[\text{Au}(\text{H}_2\text{O})_3]^-$ . Its water trimer is considerably enlarged in comparison to the equilibrium one in the neutral charge state in order to accommodate the auride anion. The difference in energy between these two forms of water trimer, equal to  $10.78 \text{ kcal mol}^{-1}$ , is the additional contribution that, together with  $E_b^{\text{ZPE}}([\text{Au}(\text{H}_2\text{O})_3]^-)$ , determines the strength of the three nonconventional  $\text{O}-\text{H}\cdots\text{Au}^-$  hydrogen bonds of  $[\text{Au}(\text{H}_2\text{O})_3]^-$ .

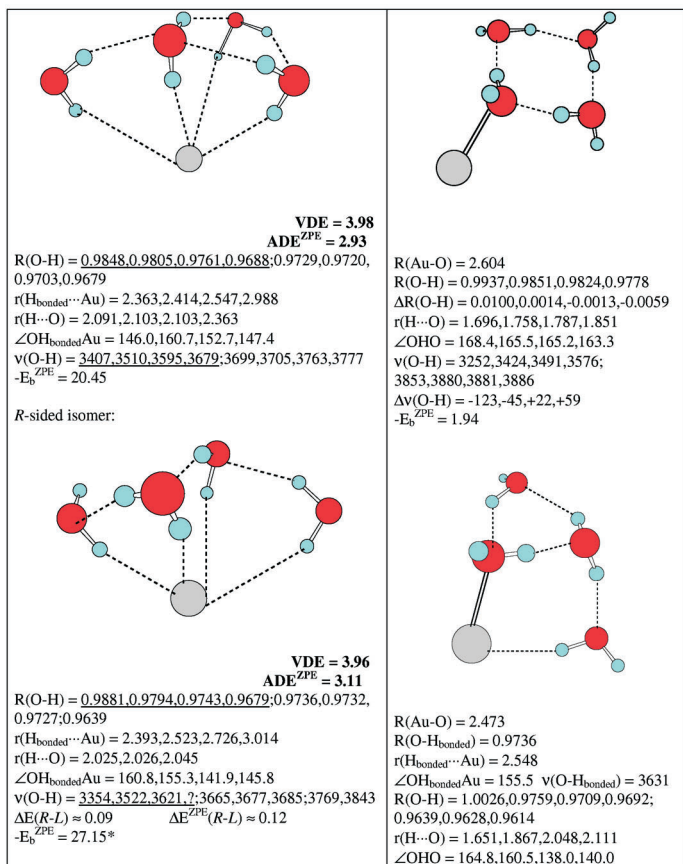


TABLE I  
(Continued)



## Number 2

The auride anion is a strong proton acceptor that, while interacting with a water cluster, significantly perturbs it. This perturbation manifests in a number of ways.

One of them is spectroscopic – it is the formation of a wide infrared window  $\Delta\nu_w(\text{O-H})$  of ca.  $450\text{ cm}^{-1}$  in  $[\text{Au}(\text{H}_2\text{O})]^-$  between the most red-shifted O-H stretching mode(s) and the next one(s). This window narrows to  $\sim 80\text{ cm}^{-1}$  in  $[\text{Au}(\text{H}_2\text{O})_2]^-$  and to  $\sim 130\text{ cm}^{-1}$  in  $[\text{Au}(\text{H}_2\text{O})_3]^-$  and is superimposed with the stretches of the conventional O-H...O hydrogen bonds in larger complexes.

The other is that the auride anion can also be a “breaker” of the water-water hydrogen bonds as e.g. occurs under the formation of the complexes  $[\text{Au}(\text{H}_2\text{O})_{4,5}]^-$ .

## APPROACHING THE EXPERIMENT: ELECTRON DETACHMENT

Let us now turn to the computational mise-en-scènes gathered in the right column of Table I and served to deeper understand the experiments on anion photoelectron spectroscopy of gold-water complexes<sup>35</sup>. Since gold is the key carrier of the excess electron charge of the complexes

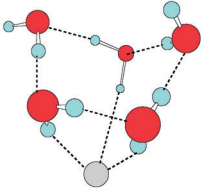
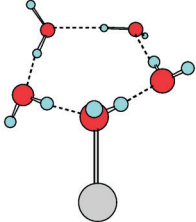
	$\Delta E^{\text{ZPE}}(\text{R-L}) = 4.08$ $-E_b^{\text{ZPE}} = 4.44^*$
<p><b>n = 5</b></p>  <p>VDE = 3.71 ADE<sup>ZPE</sup> = 3.07</p> <p>R(O-H) = 0.9848,0.9842,0.9780;0.9926,0.9903,0.9792,0.9768,0.9760; r(H<sub>bonded</sub>...Au) = 2.451,2.462,2.606 r(H...O) = 1.732,1.755,1.910,1.930,1.933 <math>\angle\text{OH}_{\text{bonded}}\text{Au} = 156.2,166.1,155.2</math> v(O-H) = 3269,3316;<u>3431,3446,3528</u>;3581,3599,3624; 3874,3877 <math>-E_b^{\text{ZPE}} = 23.63</math></p>	 <p>R(Au-O) = 2.624 R(O-H) = 0.9936,0.9878,0.9858,0.9841,0.9796 r(H...O) = 1.685,1.720,1.737,1.751,1.807 <math>\angle\text{OHO} = 173.3,175.5,174.3,174.2,174.8</math> v(O-H) = 3250,3362,3418,3465,3542; 3856,3878,3881,3886,3893 <math>-E_b^{\text{ZPE}} = 1.82</math></p>

TABLE I  
(Continued)

$[\text{Au}(\text{H}_2\text{O})_{1 \leq n \leq 5}]^-$ , a removal of this charge, formally implying the alternation  $Z = -1 \Rightarrow Z = 0$  of the charge states, converts the auride anion into the neutral gold atom. Despite the high electron affinity of the latter, Au may only induce a small charge transfer from the adjacent oxygen atom and, as a result, forms with the latter the so called Au–O anchoring bond (see<sup>30c</sup> for more detailed discussion and for references). This anchoring bond is very weak, as reflected in the corresponding binding energies. For  $n = 1-5$ , the shortest Au–O anchoring bond of 2.520 Å is formed in  $[\text{Au}(\text{H}_2\text{O})_2]^-$  – naturally, its formation is characterized by the large binding energy  $E_b^{\text{ZPE}}([\text{Au}(\text{H}_2\text{O})_2]) = 3.2 \text{ kcal mol}^{-1}$ .

Nevertheless, the anchoring bond enables to re-polarize the adjacent O–H bond of the neighboring water molecule and substantially activates it within the O–H...O hydrogen bond if  $n \geq 2$ . For  $n = 2$ ,  $\Delta R(\text{O–H}) = 0.008 \text{ \AA}$ ,  $\Delta r(\text{H...O}) = -0.093 \text{ \AA}$ , and  $\Delta \nu(\text{O–H}) = -143 \text{ cm}^{-1}$ , relative to the gas-phase water dimer. Since the anchoring interaction is weak, the relaxation of the water cluster within  $[\text{Au}(\text{H}_2\text{O})_{1 \leq n \leq 5}]^-$  is not significant, in contrast to the anionic charge state. For example, the energy difference between the equilibrium water trimer and that of  $[\text{Au}(\text{H}_2\text{O})_3]$  amounts only to 0.4 kcal mol<sup>-1</sup>.

The experiments on anion photoelectron spectroscopy of  $[\text{Au}(\text{H}_2\text{O})]^-$  and  $[\text{Au}(\text{H}_2\text{O})_2]^-$  that are conducted in<sup>35</sup> measure the vertical detachment energies,  $\text{VDE}_1^{\text{expt}} = 2.76 \text{ eV}$  and  $\text{VDE}_2^{\text{expt}} = 3.20 \text{ eV}$  which correspondingly agree with the computational ones,  $\text{VDE}_1^{\text{theory}} = 2.708 \text{ eV}$  and  $\text{VDE}_1^{\text{theory}} = 3.187 \text{ eV}$ . From the viewpoint of the chemical bonding patterns that are formed in the studied gold–water complexes, the charge state alternation  $Z = -1 \Rightarrow Z = 0$ , which can be achieved either by using different metallic supporters or/and applied voltage, the NeNePo (“A Negative ion-to Neutral-to Positive ion”) experimental technique (see<sup>45</sup> and references therein), the resonant photoionization<sup>46</sup>, or by varying pH in different solvents<sup>47</sup>, executes a simple switch-type operation. In the most studied cases, the latter transforms the nonconventional O–H...Au hydrogen bonding interaction to the Au–X anchoring one, except the cyclic R-sided conformer  $[\text{Au}(\text{H}_2\text{O})_4]_{\text{R}}^{Z=0}$  which is stabilized by both the anchoring and nonconventional hydrogen bonding interactions.

The total relaxation of the studied systems under the charge state alternation  $Z = -1 \Rightarrow Z = 0$  is rationalized in terms of the adiabatic detachment energy or shortly ADE. As follows from Table I, the VDE-ADE difference amounts to 0.15 eV for  $n = 1$ , 0.36 eV for  $n = 2$ , 0.53 eV for  $n = 3$ , then rises to 1.05 eV for  $n = 4$  and falls to 0.62 eV for  $n = 5$ . On the one hand, this difference can be interpreted as the effect of solvent on the electron detachment that causes the significant relaxation of the solvent molecules. On the

other, it implies that the concept of VDE is not generally true, as far as larger solvent clusters are on the stage. The latter solvation, as is remarkably seen from the case of  $n = 4$ , results in that the bottom of the solvent potential energy surface is quite dense, accommodating many conformers with nearly equal energies. Nevertheless, their VDEs and ADEs can be essentially different as in the present case of  $n = 4$  when the  $\Delta\text{VDE(L-R)}$  is only 0.02 eV, whereas  $\Delta\text{ADE(L-R)} = -0.18$  eV.

As was noticed above, the key source of that VDE drastically distinguishes from the ADE is the considerable solvent relaxation that is actually a breakage of the hydrogen bonding patterns of water clusters by the auride anion. This is transparently observed for the L-sided isomer of  $[\text{Au}(\text{H}_2\text{O})_4]_{\text{L}}^-$  when the water tetrameric ring is broken to accommodate the auride anion. The number of nonconventional hydrogen bonds is equal to 4. And remarkably, all hydrogen are involved in the hydrogen bonds of  $[\text{Au}(\text{H}_2\text{O})_4]_{\text{L}}^-$  and  $[\text{Au}(\text{H}_2\text{O})_4]_{\text{R}}^-$ , either conventional or nonconventional.

#### SUMMARY: "GOLD-WATER BIRTHDAY CAKE"

*Hamlet: Do you see yonder cloud that's almost in shape of a camel?*

*Polonius: By the mass, and 'tis like a camel indeed.*

*Hamlet: Methinks it is like a weasel.*

*Polonius: It is backed like a weasel.*

*Hamlet: Or like a whale.*

*Polonius: Very like a whale.*

*Scene II. – A Hall in the Castle.*

*William Shakespeare "Hamlet, Prince of Denmark"*

It is pretty obvious indeed that writing on the special occasion is a fair work that allows to explore such writing mode or style which might not be so precisely appropriate for a scientific paper – it can however be perfectly suitable for the Festschrift paper. Regarding this particular Festschrift occasion (see the dedication), we have intended to partially take this advantage of the aforementioned author's freedom that any Festschrift may generously offer, and to touch the extremely broad topic of what the entire spectrum of physico-chemical consequences of the charge-state alternations stands for by exposing some computational "thought" mise-en-scènes that lie behind the concrete experiments on anion photoelectron spectroscopy of gold-water complexes  $[\text{Au}(\text{H}_2\text{O})_n]^Z$  ( $Z = -1, 0$ ), actually referred to the "Negative ion-to Neutral" experiments.

In the present work, we have demonstrated what matters and relevant to the experiments on anion photoelectron spectroscopy for the gold–water complexes and, especially, the computational evidence of interesting synergetic effect between the nonconventional O–H...Au hydrogen bonding interaction and the Au–X anchoring one that both govern the gold–water complexes in the different charge states. If we are unable to determine their charge state,  $Z = -1$  or  $Z = 0$ , these complexes look like, in Shakespeare's terms, “camels” or “whales”. What about  $Z = +1$ ? It was not initially been thought to discuss this charge state because of many earlier studies on the interaction of  $\text{Au}^+$  with, for example, water molecules<sup>48</sup> and the DNA bases and base pairs<sup>49</sup> and, in particular, the recent work<sup>50</sup> which reveals a rather surprising dumbbell-type structure around  $\text{Au}^+$  exhibiting two Au–O anchoring bonds, each ended by rigid tetrameric rings of water. It has however initiated our study, without which, we believe, the present Festschrift work would be quite incomplete, of how many nonconventional hydrogen bonds with water the auride anion enables to form simultaneously? Comparing with maximum two anchoring Au–O bonds that the gold atom can form at once<sup>48</sup>, Fig. 1 unveils the fascinating phenomenon that the cluster  $[\text{Au}(\text{H}_2\text{O})_{12}]^-$  is bound by six nonconventional O–H...Au<sup>-</sup> hydrogen bonds which basic characteristics are summarized in Table II. Regarding the fair occasion of writing this Festschrift paper, this complex surprisingly resembles, in a quantum-chemical sense, an enchanting “birthday cake” where the auride anion looks like a candle!

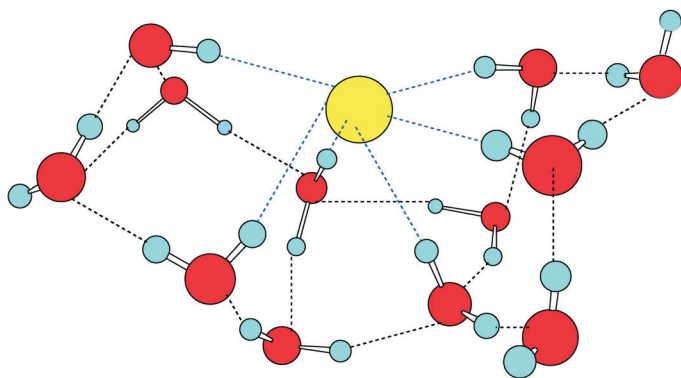


FIG. 1

The “birthday-cake” cluster  $[\text{Au}(\text{H}_2\text{O})_{12}]^-$  with six blue nonconventional O–H...Au<sup>-</sup> hydrogen bonds. Its electronic energy is equal to  $-1053.751779$  hartree and  $\text{ZPE} = 190.04$  kcal mol<sup>-1</sup>. The nonconventional hydrogen bonding patterns of this cluster are summarized in Table II. Yellow ball is gold, oxygen atoms are indicated by red and the hydrogens by light blue balls

## APPENDIX: COMPUTATIONAL METHODOLOGY AND NOTES

All calculations reported in the present work were performed by means of the Gaussian 03 package of quantum chemical programs<sup>51</sup>. The Kohn–Sham self-consistent field formalism with the hybrid density functional B3LYP potential was used in conjunction with the basis set comprised of the standard Pople basis set 6-311±G(d,p) for non-gold atoms and the energy-consistent 19-(5s<sup>2</sup>5p<sup>6</sup>5d<sup>10</sup>6s<sup>1</sup>) valence electron relativistic effective core potential developed by Ermler, Christiansen and co-workers with the primitive basis set (5s5p4d)<sup>52</sup> for the gold ones. In addition, the second-order perturbation Møller–Plesset (MP2) calculations within the frozen-core approximation were performed for small gold–water clusters  $[\text{Au}(\text{H}_2\text{O})_{n=1,2}]^{\text{Z}=0,-1}$ .

All geometrical optimizations were performed with the keywords ‘Tight’ and ‘Int = UltraFine’. The harmonic vibrational frequencies and unscaled zero-point energies (ZPE) were also calculated, for the latter being used to correct the binding energies. Enthalpies and entropies, which are also reported in the present work, were obtained from the partition functions calculated at room temperature (298 K) using Boltzmann thermostatics and the rigid-rotor harmonic-oscillator approximation<sup>53</sup>.

The present work exploits two isoenergetic isomers,  $[\text{Au}(\text{H}_2\text{O})_4]_{\text{L}}^-$  and  $[\text{Au}(\text{H}_2\text{O})_4]_{\text{R}}^-$  which however take different pathways under the electron detachment. If the former proceeds to the conformer  $[\text{Au}(\text{H}_2\text{O})_4]_{\text{L}}$  where water molecules arrange in the well-known tetrameric ring structure  $(\text{H}_2\text{O})_4^{\text{ring}}$  with the planar oxygen frame<sup>54</sup>, the latter adapts the 3D shape  $(\text{H}_2\text{O})_4^{3\text{D}}$ , as demonstrated in Fig. 2. In the gas phase, the water cluster  $(\text{H}_2\text{O})_4^{3\text{D}}$

TABLE II

The hydrogen bonding patterns of the cluster  $[\text{Au}(\text{H}_2\text{O})_{12}]^-$  which are displayed in Fig. 1 and characterized by the bond distances (in Å), bond angles (in °), and concomitant stretching frequencies (in  $\text{cm}^{-1}$ )

R(O–H)	$r(\text{H}_{\text{bonded}}\cdots\text{Au})$	$\angle\text{OH}_{\text{bonded}}\text{Au}$	$\nu(\text{O–H})$
0.9819	2.469	170.2	3465, 3476
0.9752	2.572	162.7	3604
0.9740	2.610	163.1	3500, 3582, 3635, 3656
0.9739	2.644	164.1	3635, 3637, 3656
0.9738	2.632	165.1	3635, 3637, 3656
0.9732	2.539	174.1	3476, 3550, 3519, 3550

lies naturally higher the  $(\text{H}_2\text{O})_4^{\text{ring}}$  by  $\Delta E^{\text{ZPE}} = 6.58 \text{ kcal mol}^{-1}$ . Their enthalpy difference  $\Delta H = 7.45 \text{ kcal mol}^{-1}$ . Due to the large entropy difference,  $\Delta S = 9.88 \text{ cal K}^{-1} \text{ mol}^{-1}$ , the Gibbs free energy difference is lowered to  $\Delta G = 4.51 \text{ kcal mol}^{-1}$ . Furthermore: the total dipole moment of  $(\text{H}_2\text{O})_4^{3\text{D}}$  is rather large, i.e., 3.63 D, compared to that  $(\text{H}_2\text{O})_4^{\text{ring}}$  is non-polar. This implies that the 3D cluster  $(\text{H}_2\text{O})_4^{3\text{D}}$  can be energetically favorable in polar environment.

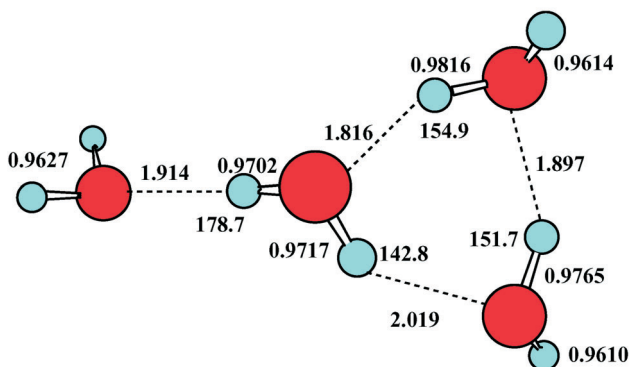


FIG. 2

The lower-energy 3D water tetrameric cluster  $(\text{H}_2\text{O})_4^{3\text{D}}$ . The selected bond distances are given in Å and bond angles in  $^\circ$ . Its stretching frequencies  $\nu(\text{O-H})$  are the following: 3483, 3595, 3671, 3744, 3816, 3885, 3893, and 3918  $\text{cm}^{-1}$ . For comparison, the corresponding frequencies of  $(\text{H}_2\text{O})_4^{\text{ring}}$ : 3375, 3469 (doublet), 3507, 3884 (quartet). Interestingly, the latter spectrum possesses a large window of  $\sim 380 \text{ cm}^{-1}$  between 3507 and 3884  $\text{cm}^{-1}$ .

The author gratefully thanks Françoise Remacle, Kit Bowen, Alfred Karpfen, Pekka Pyykkö, Camille Sandorfy<sup>†</sup>, Lucjan Sobczyk, George V. Yukhnovich, and Georg Zundel<sup>†</sup> for encouraging discussions, useful suggestions, and valuable comments. He also would like to thank Prof. Jiří Pittner for the kind invitation and the reviewer for the valuable comments and suggestions. This work was partially supported by the IAP P6/42 "Clusters and Nanowires".

## REFERENCES AND NOTES

1. Kuhn T. S.: *The Structure of Scientific Revolutions*, p. 168. University of Chicago, Chicago 1962.
2. See e.g. for current literature: a) Pyykkö P.: *Angew. Chem. Int. Ed.* **2004**, 43, 4412; b) Pyykkö P.: *Inorg. Chim. Acta* **2005**, 358, 4113; c) Pyykkö P.: *Chem. Soc. Rev.* **2008**, in press; d) Yang P. (Ed.): *The Chemistry of Nanostructured Materials*. World Scientific, Singapore 2003; e) Kaplan I. G.: *Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials*. Wiley, Chichester 2006; f) Kryachko E. S.: *Int. J. Quantum Chem.* **2008**, 108, 198; and references therein.

3. Hobza P., Zahradník R.: *Weak Intermolecular Interactions in Chemistry and Biology. Studies in Physical and Theoretical Chemistry*, Vol. 3. Elsevier, Amsterdam 1980.
4. Hobza P., Zahradník R.: *Intermolecular Complexes*. Elsevier, Amsterdam 1988.
5. a) Hobza P., Zahradník R.: *Int. J. Quantum Chem.* **1992**, *42*, 581; b) Zahradník R.: *Acc. Chem. Res.* **1995**, *28*, 306; c) Müller-Dethlefs K., Hobza P.: *Chem. Rev.* **2000**, *100*, 143; d) Hobza P., Zahradník R., Müller-Dethlefs K.: *Collect. Czech. Chem. Commun.* **2006**, *71*, 443.
6. Hadži D., Thompson H. W. (Eds): *Hydrogen Bonding*. Pergamon Press, London 1959.
7. Pimentel C. G., McClellan A. L.: *The Hydrogen Bond*. Freeman, San Francisco 1960.
8. Hamilton W. C., Ibers J. A.: *Hydrogen Bonding in Solids*. Benjamin, New York 1968.
9. Vinogradov S. N., Linell R. H.: *Hydrogen Bonding*. Van Nostrand-Reinhold, New York 1971.
10. Joesten M. D., Schaad L. J.: *Hydrogen Bonding*. Dekker, New York 1974.
11. Schuster P., Zundel G., Sandorfy C. (Eds): *The Hydrogen Bond. Recent Developments in Theory and Experiments*. North-Holland, Amsterdam 1976.
12. Schuster P. in: *Intermolecular Interactions: From Diatomics to Biopolymers* (B. Pullman, Ed.), p. 363. Wiley, Chichester 1978.
13. Schuster P. (Guest Ed.): *Top. Curr. Chem.* **1984**, *120*.
14. Jeffrey G. A., Saenger W.: *Hydrogen Bonding in Biological Structures*. Springer, Berlin 1991.
15. Jeffrey G. A.: *An Introduction to Hydrogen Bonding*. Oxford University Press, Oxford 1997.
16. Scheiner S.: *Hydrogen Bonding. A Theoretical Perspective*. Oxford University Press, Oxford 1997.
17. Hadži D. (Ed.): *Theoretical Treatment of Hydrogen Bonding*. Wiley, New York 1997.
18. Steiner T., Desiraju G. R.: *Chem. Commun.* **1998**, 891.
19. Desiraju G. R., Steiner T.: *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford University Press, Oxford 1999.
20. Steiner T.: *Angew. Chem. Int. Ed.* **2002**, *41*, 48.
21. Karpfen A.: *Adv. Chem. Phys.* **2002**, *123*, 469.
22. Grabowski S. (Ed.): *Hydrogen Bonding – New Insights*, Vol. 3 of *Challenges and Advances in Computational Chemistry and Physics* (J. Leszczynski, Ed.). Springer, Dordrecht 2006.
23. For the recent IUPAC categorization of the hydrogen bond see <http://www.iupac.org/projects/2004/2004-026-2-100.html>
24. a) Bondi A.: *J. Phys. Chem.* **1964**, *68*, 441; b) Rowland R. S., Taylor T.: *J. Phys. Chem.* **1996**, *100*, 7384.
25. Olovsson I.: *Z. Phys. Chem.* **2006**, *220*, 963.
26. a) Crabtree R. H., Siegbahn P. E. M., Wisenstein O., Rheingold A. L., Koetzle T. F.: *Acc. Chem. Res.* **1996**, *29*, 348; b) Brammer L., Zhao D., Ladipo F. T., Braddock-Wilking J.: *Acta Crystallogr., Sect. B: Struct. Sci.* **1995**, *51*, 632; c) Brammer L.: *Dalton Trans.* **2003**, 3145; d) Brammer L., McCann M. C., Bullock R. M., McMullan R. K., Sherwood P.: *Organometallics* **1992**, *11*, 2339; e) Brammer L., Charnock J. M., Goggin P. L., Goodfellow R. J., Koetzle T. F., Orpen A. G.: *J. Chem. Soc., Dalton Trans.* **1991**, 1789.
27. a) Braga D., Grepioni F., Tedesco E., Biradha K., Desiraju G. R.: *Organometallics* **1997**, *16*, 1846; b) Orlova G., Scheiner S.: *Organometallics* **1998**, *17*, 4362; c) Martin A.: *J. Chem. Educ.* **1999**, *76*, 578; d) Epstein L. M., Shubina E. S.: *Coord. Chem. Rev.* **2002**, *231*, 165; e) Jacobsen, H.: *Chem. Phys.* **2008**, *345*, 95.
28. a) Haruta M., Kobayashi T., Sano H., Yamada N.: *Chem. Lett.* **1987**, 405; b) Haruta M., Yamada N., Kobayashi T., Iijima S.: *J. Catal.* **1989**, *115*, 301.

29. Kryachko E. S., Remacle F.: *Chem. Phys. Lett.* **2005**, 404, 142.
30. a) Kryachko E. S., Remacle F. in: *Recent Advances in the Theory of Chemical and Physical Systems* (J.-P. Julien, J. Maruani, D. Mayou, S. Wilson and G. Delgado-Barrio, Eds), Vol. 15, p. 433. Springer, Dordrecht 2006; b) Kryachko E. S., Remacle F.: *Nano Lett.* **2005**, 5, 735; c) Kryachko E. S., Remacle F.: *J. Phys. Chem. B* **2005**, 109, 22746; d) Kryachko E. S., Karpfen A., Remacle F.: *J. Phys. Chem. A* **2005**, 109, 7309; e) Kryachko E. S., Remacle F. in: *Theoretical Aspects of Chemical Reactivity* (A. Torro-Labbe, Ed.), Vol. 16 of *Theoretical and Computational Chemistry* (P. Politzer, Ed.), p. 219. Elsevier, Amsterdam 2006; f) Kryachko E. S., Remacle F. in: *Topics in the Theory of Chemical and Physical Systems* (S. Lahmar, J. Maruani, S. Wilson and G. Delgado-Barrio, Eds), Vol. 16 of *Progress in Theoretical Chemistry and Physics*, p. 161. Springer, Dordrecht 2007; g) Kryachko E. S., Remacle F.: *J. Chem. Phys.* **2007**, 127, 194305; h) Kryachko E. S., Remacle F.: *Mol. Phys.* **2008**, 106, 521; i) Kryachko E. S.: *J. Mol. Struct.* **2008**, 880, 23.
31. Li J., Li X., Zhai H.-J., Wang L.-S.: *Science* **2003**, 299, 864.
32. Kryachko E. S., Remacle F.: *Int. J. Quantum Chem.* **2007**, 107, 2922.
33. Schneider H., Boese A. D., Weber J. M.: *J. Chem. Phys.* **2005**, 123, 084307.
34. Zheng W., Li X., Eustis S., Grubisic A., Thomas O., de Clercq H., Bowen K.: *Chem. Phys. Lett.* **2007**, 444, 232.
35. a) Wu D.-Y., Duan S., Liu X.-M., Xu Y.-C., Jiang Y.-X., Ren B., Xu X., Lin S. H., Tian Z.-Q.: *J. Phys. Chem. A* **2008**, 112, 1313; b) see also Chen Y. X., Zou S. Z., Huang K. Q., Tian Z. Q.: *J. Raman Spectrosc.* **1998**, 29, 749.
36. a) Nuss H., Jansen M.: *Angew. Chem. Int. Ed.* **2006**, 45, 4369; b) Nuss H., Jansen M.: *Z. Naturforsch., B: Chem. Sci.* **2006**, 61, 1205; c) Dietzel P. D. C., Jansen M.: *Chem. Commun.* **2001**, 2208.
37. It is worth mentioning that in the  $[(\text{NMe}_4)\text{Au}]$  compound synthesized in<sup>36c</sup>, the hydrogen atoms of the methyl groups and the auride anion are separated by 2.921(0) Å, with  $r_{\text{min}}(\text{C}\cdots\text{Au}^-) = 3.663(1)$  Å. Such contact separation obeys the van der Waals cutoff condition (iv). However, as the authors of<sup>36c</sup> pointed out, “whether this contact is a true hydrogen bond or not has not yet been proven”, since a short separation  $\text{N}^+-\text{C}-\text{H}\cdots\text{Y}^-$  can be originated from the attractive  $\text{N}^+ - \text{C}\delta^-\text{ulomb}$  interaction where, in addition, the  $\text{H}\cdots\text{Y}^-$  contact prevents a further approach of  $\text{Y}^-$  simply due to steric effects<sup>19</sup>.
38. a) Shafai G. S., Shetty S., Krishnamurty S., Kanhere D. G.: *J. Chem. Phys.* **2007**, 126, 014704; b) Pakiari A. H., Jamshidi Z.: *J. Phys. Chem. A* **2007**, 111, 4391; c) Aqil A., Qiu H., Greisch J.-F., Jérôme R., De Pauw E., Jérôme C.: *Polymer* **2008**, 49, 1145; d) A bit of pedantry: the reference “Remacle et al.” on p. 1151 of<sup>38c</sup> to the works<sup>25,29b,29c</sup> is grammatically inconsistent since: 1) “et al.” (precisely “et alii” or “et alia”) means “and others” (the plural number) and is used for a list of names of more than two authors (e.g., the American Psychological Association style), more than three authors (e.g., the Modern Language Association of America style), or four and more authors (e.g., the American Physical Society style), or even 16 and more authors (according to the American Chemical Society style), and 2) the order of the authors of the cited works<sup>25,29b,29c</sup> is actually opposite.
39. See also Vázquez M.-V., Martínez A.: *J. Phys. Chem. A* **2008**, 112, 1033.
40. Shi P., Jiang Q., Lin J., Zhao Y., Lin L., Guo Z.: *J. Inorg. Biochem.* **2006**, 100, 939.
41. It is interesting to notice in this regard that – as recently shown by Ončák M., Cao Y., Beyer M. K., Zahradník R., Schwarz H.: *Chem. Phys. Lett.* **2008**, 450, 268 – the anionic dimer  $\text{Pt}_2^-$  does not form any hydrogen bond with  $\text{NH}_3$ .



42. The experimental value of  $EA^{\text{expt}}(\text{Au}) = 2.30 \pm 0.10$  eV according to: a) Ganteför G., Krauss S., Eberhardt W.: *J. Electron Spectrosc. Relat. Phenom.* **1998**, *88*, 35;  $2.308664 \pm 0.000044$  eV according to: b) Jotop H., Lineberger W. C.: *J. Phys. Chem. Ref. Data* **1985**, *14*, 731; and  $2.927 \pm 0.050$  eV according to: c) Taylor K. J., Pettiettehall C. L., Cheshnovsky O., Smalley R. E.: *J. Chem. Phys.* **1992**, *96*, 3319; d)  $EA^{\text{theor}}(\text{Au}) = 2.33$  eV: Buckart S., Ganteför G., Kim Y. D., Jena P.: *J. Am. Chem. Soc.* **2003**, *125*, 14205; e)  $EA^{\text{theor}}(\text{Au}) = 2.166$  eV: Joshi A. M., Delgass W. N., Thomson K. T.: *J. Phys. Chem. B* **2005**, *109*, 22392; f) with the used basis set, MP2 yields 1.536 eV; g)  $EA^{\text{theor}}(\text{Au}) = 1.86$  eV was calculated at the MCPDF computational level in: Bauschlicher C. W., Jr., Langhoff S. R., Partridge H. J.: *J. Chem. Phys.* **1990**, *93*, 8133; g) the PW91PW91 DFT level in conjunction with the basis set used in the present work yields 2.25 eV and 2.31 eV with the LANL2DZ basis set, as reported in: Walker A. V.: *J. Chem. Phys.* **2005**, *122*, 094310.
43. Comparing with the ground-state water dimer, this stretching mode  $\nu(\text{O-H})$  is red-shifted by only  $21 \text{ cm}^{-1}$ .
44. Antušek A., Urban M., Sadlej A. J.: *J. Chem. Phys.* **2003**, *119*, 7247.
45. a) Wolf S., Sommerer G., Rutz S., Schreiber E., Leisner T., Wöste L., Berry R. S.: *Phys. Rev. Lett.* **1995**, *74*, 4177; b) Socaciu-Siebert L. D., Hagen J., Le Roux J., Popolan D., Vaida M., Vajda S., Bernhardt T. M., Wöste L.: *Phys. Chem. Chem. Phys.* **2005**, *7*, 2706; c) Mitrić R., Hartmann M., Stanca B., Bonačić-Koutecký V., Fantucci P.: *J. Phys. Chem. A* **2001**, *105*, 8892; d) Bernhardt T. M., Hagen J., Socaciu-Siebert L. D., Mitrić R., Heidenreich A., Le Roux J., Popolan D., Vaida M., Wöste L., Bonačić-Koutecký V., Jortner J.: *ChemPhysChem* **2005**, *6*, 243.
46. Ishiuchi S.-I., Sakai M., Tsuchida Y., Takeda A., Kawashima Y., Fujii M., Dopfer O., Müller-Dethlefs K.: *Angew. Chem. Int. Ed.* **2005**, *44*, 6149.
47. See e.g. Margulies D., Melman G., Shanzer A.: *J. Am. Chem. Soc.* **2006**, *128*, 4865.
48. a) Hrušák J., Schröder D., Schwarz H.: *Chem. Phys. Lett.* **1994**, *225*, 416; b) Hertwig H., Hrušák J., Schröder D., Koch W., Schwarz H.: *Chem. Phys. Lett.* **1995**, *236*, 194; c) Feller D., Glendening E. D., de Jong W. A.: *J. Chem. Phys.* **1999**, *110*, 1475; d) Lee H. M., Min S. K., Lee E. C., Min J.-H., Odde S., Kim K. S.: *J. Chem. Phys.* **2005**, *122*, 064314; e) Lee H. M., Diefenbach M., Suh S. B., Tarakeshwar P., Kim K. S.: *J. Chem. Phys.* **2005**, *123*, 074328; f) Poisson L., Lepetit F., Mestdagh J.-M., Visticot J.-P.: *J. Phys. Chem. A* **2002**, *106*, 5455; g) Karttunen A. J., Pakkanen T. A.: *J. Phys. Chem. B* **2006**, *110*, 25926.
49. a) Burda J. V., Šponer J., Hobza P.: *J. Phys. Chem.* **1996**, *100*, 7250; b) Šponer J., Sabat M., Burda J. V., Leszczynski J., Hobza P., Lippert B.: *J. Biol. Inorg. Chem.* **1999**, *4*, 537.
50. Reveles J. U., Calaminici P., Beltrán M. R., Köster A. M., Khanna S. N.: *J. Am. Chem. Soc.* **2007**, *129*, 15565.
51. Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Montgomery J. A., Jr., Vreven T., Kudin K. N., Burant J. C., Millam J. M., Iyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G. A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J. E., Hratchian H. P., Cross J. B., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Ayala P. Y., Morokuma K., Voth G. A., Salvador P., Dannenberg J. J., Zakrzewski V. G., Dapprich S., Daniels A. D., Strain M. C., Farkas O., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Ortiz J. V., Cui Q., Baboul A. G., Clifford S., Cioslowski J., Stefanov B. B., Liu G., Liashenko A.,

- Piskorz P., Komaromi I., Martin R. L., Fox D. J., Keith T., Al-Laham M. A., Peng C. Y., Nanayakkara A., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Gonzalez C., Pople J. A.: *Gaussian 03*, Revision C.02. Gaussian, Inc., Wallington (CT) 2004.
52. Ross R. B., Powers J. M., Atashroo T., Ermler W. C., LaJohn L. A., Christiansen P. A.: *J. Chem. Phys.* **1990**, *93*, 6654.
53. McQuarrie D. A.: *Statistical Mechanics*. Harper and Row, New York 1976.
54. See e.g. Kim K. S., Dupuis M., Lie G. C., Clementi E.: *Chem. Phys. Lett.* **1986**, *131*, 451.