BF obtain 1.31 for the ratio of the AEs of Cu₄ and Au₄. This also strongly suggests that their computed AE value, at least for Cu₄, is in error.

The vertical IPs of Cu₄, Ag₄, and Au₄ shown in Figure 7 of BF follow the trend Cu > Au > Ag. Considering that the IP of Ag atom is only 0.15 eV less than Cu atom, it is particularly surprising that their vertical IP of Ag₂ is about 2 eV less than for Cu₄. Our MCSCF vertical IPs (eV) are Cu₄ (6.16), Ag₂ (5.86), and Au₄ (7.32). These are expected to be 85–90% of the true values based on the computed atomic IPs. In contrast to BF, our tetramer IPs follow the same trend (Au > Cu > Ag) as the atomic IPs.

The MRCl + Q AEs reported in the reply by Balasubramanian and Das, which are 3.6, 1.0, and 0.7 eV smaller than his previous results for Cu₄, Ag₂, and Au₄, respectively, support the MCSCF values reported in this Comment. While our MCSCF AEs are smaller than their MRCl + Q values, our scaled MCSCF AEs are slightly larger, which is consistent with the fact that our values are scaled based on experiment, while the MRCl + Q results are expected to be too small due to limitations in both the one- and n-particle treatments. We feel that it is valid to scale the MCSCF results, because they are size extensive and the nature of the bonding is very similar in the different sized clusters. The fact that the MCSCF IPs are larger than the SDCI + Q values can probably be attributed to the lack of size extensivity in the SDCI + Q method. Our scaled AE value of 5.9 eV for Cu₄ is consistent with the upper bound of 6.3 eV given by Jarrold and Creegan, and we feel that the scaled MCSCF AE values should be the most accurate and consistent set available. Thus we conclude that the MRCl + Q calculations reported in the reply by Balasubramanian and Das fully support our MCSCF calculations, which show that the bonding in the group IB tetramers is completely consistent with that for the dimers, trimers, and bulk.

Registry No. Ag₄, 64475-45-2; Au₄, 124236-18-6; Cu₄, 65357-62-2.

(8) Attributed to M. F. Jarrold and K. M. Creegan in ref 7.

Reply to Comments on "Binding Energies and Ionization Potentials of the Tetramers of Cu, Ag, and Au"  

Sir: In response to the previous Comment by Bauschlicher et al. (BLP), we point out that the focus of the previous article is the geometries and energy separations of low-lying electronic states of Ag₄ and Cu₄. We computed the ionization potentials (IP) and atomicization energies (AE) mainly for qualitative comparison with the corresponding values of Au. Nevertheless, the results of 44-electron multireference singles + doubles CI (MRSDCI) containing 1.4 million configurations after complete active space treatment are reported below.

We start with a CASSCF method which distributed the four outermost electrons in all possible ways among the metal valence s orbitals. Although excitations of the 40 d electrons were not allowed at the CASSCF stage, the final MRSDCI calculations included excitations of all 44 electrons. BLP use a single-configuration SCF method to obtain orbitals for their MCSCF study. The basis set is comparable in the two methods, and note that indeed in a previous CASSCF/CI study on Au₄, 10-component 4f functions were included and the effects of these functions were found to be insignificant. In the previous study, Balasubramanian and Feng (BF) used a CASSCF/32e CI approximation for Cu₄ and Au₄ mainly because of technical limitations with an earlier version of ALCHEMY II codes that runs with 8 megabytes of memory. However, with an improved version (on an IBM 3090/300) provides 32 megabytes. The 32e MRSDCI was satisfactory for the computation of geometries and energy separations of Ag₄ and Cu₄, the focus of the previous study, although we were aware that it is less satisfactory for the computation of IP and AE. Nonetheless, this approximation provided reasonable AE and IP for Au₄ in a previous study. The AE reported for Cu₄ was in error. For the dissociated supermolecule, the reference occupations had to be permuted for the MRSDCI since the POLCI natural orbitals which were used for the MRSDCI computations are ordered while the CASSCF orbitals are randomly arranged. In doing so, the occupancy of one reference configuration was incorrectly permuted. The IP of Cu₄ in the previous study was also larger due to an orbital space inconsistency.

Table I shows the IPs, Dₚ, and AEs of the dimers and tetramers together with available experimental results from refs 5–8. We have already discussed the results on trimers but Bauschlicher and co-workers have not recognized this earlier work. There is no major disagreement in the results of BLP and ours on trimers, except that (i) the spin-orbit effects are shown to influence the barrier to pseudorotation by 67% in Au₃ while BLP ignored spin-orbit effects and (ii) BLP's CASSCF AEs for the trimers are much smaller especially for Au₃ than our values and experiment as seen from Table I of ref 1. Theoretical results in Table I for the tetramers were obtained through a CASSCF/MRSDCI treatment that included all 44 electrons, all orbitals, and up to 1.4 million configurations. In addition, we calculated the effects of unlinked quadruples through Davidson's corrections.

As seen from Table I, our dimer MRSDCI-D IP are 91% of the experimental values. The Dₚ of Cu₃, Ag₂, and Au₃ have comparable accuracies. We expect the accuracies for the tetramers to be similar to that of the dimers. The Dₚ obtained in the present study for Au₃ (2.1 eV) is the best theoretical value to date. The effect on f functions has been studied at most 0.05 eV. This corroborates the finding of BLP, although their SCF/MCSCF value of 1.90 eV is 10% smaller than our value.

The MRSDCI-D (44e) AEs of Cu₄, Ag₂, and Au₄ are 5.5, 4.2, and 6.2 eV, respectively, for Au₄ and Au₃. Hence, BLP's SCF/MCSCF AEs for Cu₄, Ag₂, and Au₄ are 0.59, 0.44, and 0.9 eV, respectively, lower than our CAS/MRSDCI results. For the dimers and trimers also our SCF/MCSCF values are approximately 4–10% and 5–11% lower than our values and 16–24% lower than experimental values. We believe this is due to the inadequacy of the SCF/MCSCF method to fully account for electron correlation effects since the basis sets are comparable. Furthermore, BLP used a single-configuration SCF method to generate orbitals while we use a more accurate CASSCF method. Consequently, the CASSCF/MRSDCI-D values for the dimers and trimers are in better agreement with the experiment compared to the SCF/MCSCF method.

(4) The major authors of ALCHEMY II are B. Liu, B. Lengsfield, and M. Yoshimine.
(6) Duncan, M., private communications.
(7) Hopkins, J. B.; Langridge-Smith, P. R. R.; Morse, M. D.; Smalley, R. E., unpublished results.
ADDITIONS AND CORRECTIONS

BLP use a scaling factor of 1.2 since their SCF/MCPF $D_2$ and IP of Cu$_4$ are in 17% error compared to the experiment. Our CAS/MRSDCI and MRSDCI-D values are 8-13% lower than experimental values. The scaling factor of BLP is based on a comparison with experiment on dimers and not on any ab initio procedure to account for the missing electron correlation effects in the SCF/MCPF method. Electron correlation effects are different for the three group IB clusters and in fact vary as a function of size. Hence the use of a single scaling factor for all three clusters of all sizes to represent a complicated missing many-body electron correlation effect is questionable. Consequently, we disagree with their claimed accuracies of scaled results and comparison of their scaled results with our unscaled fully ab initio results. It is more appropriate to compare their unscaled results with our unscaled results. Hence we disagree with BLP’s claim that our values are too small. Our study could be in 10% error for the tetramers compared to experimental values since electron correlation effects from 44 electrons and basis set errors could still not be fully accounted. Although our CAS/MRSDCI-D and BLP’s SCF/MCPF to a large extent still do not fully account for correlation effects from all 44 electrons, we have not seen a better agreement for a 44-electron correlation problem with experiment.


### TABLE I: Vertical Ionization Potentials and Binding Energies (eV) of $M_j$ and $M_4$

<table>
<thead>
<tr>
<th>$M_j$</th>
<th>MRSD CI</th>
<th>MRSD CI-D</th>
<th>SDCI CI</th>
<th>SDCI CI-D</th>
<th>expt</th>
<th>$D_4(M_4)$</th>
<th>MRSD CI</th>
<th>MRSD CI-D</th>
<th>SDCI CI</th>
<th>SDCI CI-D</th>
<th>expt</th>
<th>AE($M_4$)</th>
<th>MRSD CI</th>
<th>MRSD CI-D</th>
<th>SDCI CI</th>
<th>SDCI CI-D</th>
<th>expt</th>
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<tbody>
<tr>
<td>Cu</td>
<td>7.0</td>
<td>7.2</td>
<td>7.9$^a$</td>
<td>1.6</td>
<td>1.8</td>
<td>2.08$^b$</td>
<td>5.6</td>
<td>5.8</td>
<td>7.2 ± 0.8$^b$</td>
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<tr>
<td>Ag</td>
<td>6.7</td>
<td>6.9</td>
<td>7.6$^a$</td>
<td>1.3</td>
<td>1.5</td>
<td>1.66$^d$</td>
<td>5.5</td>
<td>5.7</td>
<td>&lt;7.9$^b$</td>
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<tr>
<td>Au</td>
<td>8.5</td>
<td>8.6</td>
<td></td>
<td>2.0</td>
<td>2.1</td>
<td>2.3$^b$</td>
<td>6.9</td>
<td>7.1</td>
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<tr>
<td>Cu$_4$</td>
<td>5.8</td>
<td>5.6</td>
<td>7.1</td>
<td>5.6</td>
<td>5.8</td>
<td>7.2</td>
<td>5.6</td>
<td>5.8</td>
<td>7.2 ± 0.8</td>
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<tr>
<td>Ag$_4$</td>
<td>6.17</td>
<td>6.16</td>
<td>7.2</td>
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<td>6.16</td>
<td>7.2</td>
<td>6.17</td>
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<td>7.2 ± 0.8</td>
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<tr>
<td>Au$_4$</td>
<td>7.9$^a$</td>
<td>7.9$^b$</td>
<td>8.5$^a$</td>
<td>7.9$^b$</td>
<td>7.9$^a$</td>
<td>8.5$^a$</td>
<td>7.9$^b$</td>
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</table>


Page 3026. Equation I, which contains the normalization correction of Gilbert et al. (Ber. Bunsen-Ges. Phys Chem. 1983, 87, 169, eq 4.7), is incorrectly evaluated at high temperatures. Here the Whitten-Rabinovitch approximation was used for molecular state densities; since this is inaccurate for low $E$, the integrals of the form $\int J_0^E f(E) \, dE$ were evaluated as $1 - \int_0^E J_0 f(E) \, dE$. Although these integrals are always accurate to within a few percent with this approximation, this is inadequate for the evaluation of (I) at very high temperatures where the denominator appears as a small difference of large numbers.

We have replaced the above approximate evaluation with a more accurate procedure using direct-count densities. The results are now in complete agreement with the calculations on cycloheptatriene presented by Gilbert et al. and with cyclohexene calculations using an independent program provided by R. Shandross. With this new evaluation, the calculated rate constants for cyclohexene above 1600 K are substantially altered: a fixed $\alpha = (\Delta E)_{down} = 550 \text{ cm}^{-1}$ now generates a good fit to the dissociation data for all conditions. When the weak-collision formulation of Gilbert et al. is correctly applied to this problem, it is actually a fixed $(\Delta E)_{down}$ rather than a fixed $(\Delta E)_{all}$ which most accurately describes the cyclohexene data.