Electronic structure of Cu₆, Ag₆, Au₆, and their positive ions

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The ground state energies of the group IB hexamer (Cu₆, Ag₆, and Au₆) for four possible structural models, namely, A₁ with a capped pentagonal structure (C₅v), A₁ with a tripyramidal structure (C₃v), A₁ with a circular ring structure (D₆h), and T₉ with an octahedral structure, as well as the positive ions, Cu⁺⁺, Ag⁺⁺, and Au⁺⁺ were computed using complete active space multiconfiguration self-consistent-field (CASMCSCF) followed by first, second order configuration interaction and multireference singles + doubles configuration interaction including d correlation methods. We considered excited states of Cu⁺⁺ also. The results indicated that the capped pentagonal structure is the most favorable structure in energy among the four structures for all three hexamers. The computed ionization potentials (IPs) of Cu⁺⁺, Ag⁺⁺, and Au⁺⁺ follow the order IP(Au⁺⁺) > IP(Cu⁺⁺) > IP(Ag⁺⁺).

I. INTRODUCTION

The electronic structure and spectroscopy of clusters of group IA and IB metal atoms have been the topic of several studies. As noted in a recent review by Bonačić-Koutecký et al., while theoretical studies of alkali metal (group IA) clusters of large size are feasible, this is not the case for larger clusters of group IB elements due to the problem of d-electron correlations. Specifically, these authors noted that clusters containing six or more atoms are likely to be formidably difficult. There are several interesting experimental studies on Cu₆, Au₆, and larger clusters. The assignment of the observed spectra is very difficult without the knowledge of geometries and energy levels as noted in these recent papers. Taylor et al. have considered the negative ion photodetachment spectra of Au⁻. We reinterpret these spectra based on theoretical calculations on three possible geometrical structures for Au⁻ and Au⁺.

Stimulated by the experimental studies for Cu₆ by Jarrold and Creegan, Au₆ by Taylor et al., Cu₆-Ag₆ by Hoe et al., we carry out ab initio theoretical studies including d-electron correlation effects on several possible geometries of Cu₆, Ag₆, Au₆ as well as Cu⁺⁺, Ag⁺⁺, and Au⁺⁺. We consider excited electronic states of Cu⁺⁺ also. We employ complete active space multiconfiguration self-consistent-field (CAS-MCSCF) followed by first-order, second-order configuration interaction (FOCI, SOCI) calculations without d-electron correlations and multireference configuration interaction (MRCI) calculations including d-electron correlations. We compute the geometries, energy separations, and ionization potentials (IPs). Our computed IPs mimic the experimental trend for Cu₆-Au₆ observed by Jarrold and Creegan. We also find that the IP trend for Cu₆-Au₆ is consistent with the corresponding trend for smaller clusters. Our scaled IPs of Ag₆ and Au₆ also support the experimental values suggested by Cheng and Duncan for the vertical IPs of these species.

II. METHOD OF CALCULATIONS

Our choice of the possible geometries for Cu₆-Au₆ was motivated by the previous studies of Bonačić-Koutecký et al. on alkali metal clusters as well as our study on Au₆. As noted in the review by Bonačić-Koutecký et al., these authors have considered several possible structures [tripyrimal (C₃v), capped pentagon (C₅v), planar triangular (D₃h), and other structures] and find that the tripyramidal is the lowest although the capped pentagon is only slightly higher.

A previous study on Au₆ (Ref. 16) suggested that the capped pentagon is the lowest for the neutral cluster but the hexagonal ring structure is favored for the anion. Hence in the present study, we considered four possible structures for Cu₆-Ag₆, namely capped pentagon, tripyramidal, hexagonal ring, and octahedron. We considered the triangular (D₃h) structure used by Bonačić-Koutecký et al., for Na₆ (Ref. 3) in our preliminary CASSCF studies and found this to be higher than both the capped pentagon and the tripyramidal structure. Hence this structure was not considered at higher levels of theory.

The four structures considered in the present study are shown in Fig. 1. The first model is a capped pentagon (CP) with an overall C₅v symmetry. There are two kinds of bond lengths in the CP structure. In this structure, the cap to origin distance is independent of the metal–metal distance in the pentagon (Fig. 1). The second model is tripyramidal (TP) with C₃v symmetry and \( r_{1,2} = r_{1,3} = r_{1,6} = r_{5,1} = r_{5,3} = r_{5,6} = r_{5,4} = r_{2,6} = r_{2,3} = r_{6,4} = r_{3,4} \). The third model is a ring (R) with D₆h symmetry which looks like benzene with \( r_{1,2} = r_{2,3} = r_{3,4} = r_{4,5} = r_{5,6} = r_{6,1} \). The fourth model is an octahedron (O) with \( O_h \) symmetry and \( r_{1,2} = r_{1,3} = r_{1,4} = r_{1,5} = r_{6,2} = r_{6,3} = r_{6,4} = r_{6,5} = r_{6,1} = r_{6,3} = r_{6,5} = r_{6,2} \). We used the relativistic effective core potentials (RECPs) from Ref. (30) which included the outer \((n-1)\) \( d^{10}n^8\) shells in the valence space uniformly for Cu, Ag, and Au, where \( n \) is the principal quantum number. Valence Gaussian basis sets of \((3\sigma p^3d)\) quality published in Ref.

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The calculations for all three clusters and their positive ions. The CASSCF calculations included the six valence $s$ electrons in the active space. All valence $s$ orbitals (six of them) of the group IB atoms were included in the active space. The cored electrons were kept inactive in the sense that excitations made in the C, group. The computations of the octahedral, CASSCF and CI computations of the CP structure were made in the C, space, and ring structures were made in the C, space. Hence all distances were slightly longer at all levels of theories in the previous study.16

As seen from Table I, at the CASSCF, FOCI, SOCI, and MRCI levels which included $d$ correlation effects the capped pentagon ($C_{5v}$) is the lowest for Cu$_6$. It is somewhat interesting that the TP structure is favored at the SOCI level but note that the SOCI does not include electron correlation effects from the 3$d$ shells of the Cu atoms. Without inclusion of $d$ correlation effects Cu$_6$ behaves similar to Li$_6$ and Na$_6$ for which Bonacic-Koutecky et al.3 found the tripymadial structure to be slightly lower than the capped pentagon. However, upon inclusion of the 3$d$-electron correlation effects through the MRCI method which correlated 48 electrons of Cu$_6$, the capped pentagon is favored.

As seen from Table I, the lowest states of CP, TP, and ring structures are singlets while the lowest state of the octahedron is a $3T_{2g}$ state. Of course, the octahedral structure will undergo Jahn–Teller distortion. The effects of electron correlations on both geometries and energy separations are quite interesting. The geometries are somewhat less sensitive to electron correlations for Cu$_6$. Only the MRCI which includes 3$d$-correlation effects introduces non-negligible changes in bond lengths. The energy separations are more sensitive to electron correlations as seen from Table I. For example, the TP structure is 1 eV higher than CP at the CASSCF level, 0.5 eV higher at the...
### TABLE I. Geometries and energy separations of the electronic states of Cu₆ and Cu⁺. *ab

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Structure</th>
<th>Symmetry</th>
<th>State</th>
<th>CASSCF</th>
<th>FOCI</th>
<th>SOCI</th>
<th>MRCI</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R₁(Å)</td>
<td>E(eV)</td>
<td>R₁(Å)</td>
<td>E(eV)</td>
</tr>
<tr>
<td>Cu₆</td>
<td>CP</td>
<td>C₃v</td>
<td>1'A₁</td>
<td>2.55</td>
<td>2.55</td>
<td>2.53</td>
<td>0.91</td>
</tr>
<tr>
<td>TP</td>
<td>C₃s</td>
<td>1'A₁</td>
<td>2.61</td>
<td>1.05</td>
<td>2.52</td>
<td>0.51</td>
<td>2.63</td>
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<td>R</td>
<td>D₆h</td>
<td>1'A₁g</td>
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<td>0.91</td>
<td>2.49</td>
</tr>
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<td>3'Tₕg</td>
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<td>2.65</td>
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<td>D₆h</td>
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<td>2.50</td>
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<td>4'E₁g</td>
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<td>2.98</td>
<td>8.51</td>
<td>2.92</td>
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</table>

*For the CP structure the first distance is r₁₂ = r₂₃ = r₃₄ = r₄₅ = r₅₆ = r₆₇; the second distance is origin to the atom distance (see Fig. 1).

### TABLE II. Geometries and energy separations of Ag₆ and Ag⁺. *

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Structure</th>
<th>Symmetry</th>
<th>State</th>
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<td>E(eV)</td>
<td>R₁(Å)</td>
<td>E(eV)</td>
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<td>CP</td>
<td>C₃v</td>
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<td>2.71</td>
<td>2.71</td>
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<td>C₃s</td>
<td>1'A₁</td>
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<td>0.35</td>
<td>2.82</td>
<td>0.43</td>
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<td>D₆h</td>
<td>1'A₁g</td>
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<td>2.65</td>
<td>1.36</td>
<td>2.65</td>
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<td>D₆h</td>
<td>3'Tₕg</td>
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<td>1.22</td>
<td>2.84</td>
<td>1.00</td>
<td>2.84</td>
</tr>
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<td>D₆h</td>
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<td>4.98</td>
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<td>5.14</td>
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<td>4.98</td>
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<td>5.14</td>
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<td>1.35</td>
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*See footnotes a and b for Table I.
TABLE III. Geometries and energy separations of \( \text{Au}_6 \) and \( \text{Au}_{6+} \). 

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Structure</th>
<th>Symmetry</th>
<th>State</th>
<th>CASSCF</th>
<th>FOCI</th>
<th>SOCI</th>
<th>MRCI</th>
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<td>( \text{Au}_6 )</td>
<td>CP</td>
<td>( \text{C}_{6v} )</td>
<td>( ^1A_1 )</td>
<td>2.72</td>
<td>0.0</td>
<td>2.76</td>
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<td>1.31</td>
<td>1.40</td>
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<td>1.30</td>
</tr>
<tr>
<td>TP</td>
<td>( \text{C}_{2v} )</td>
<td>( ^1A_1 )</td>
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<td>1.00</td>
<td>2.83</td>
<td>0.87</td>
<td>2.84</td>
</tr>
<tr>
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<td>( \text{D}_{6h} )</td>
<td>( ^1A_{1g} )</td>
<td>2.70</td>
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<td>0.88</td>
<td>2.72</td>
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<td>O</td>
<td>( \text{O}_h )</td>
<td>( ^3T_{2g} )</td>
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<td>1.77</td>
<td>2.87</td>
<td>1.50</td>
<td>2.87</td>
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<tr>
<td>( \text{Au}_{6+} )</td>
<td>CP</td>
<td>( \text{C}_{6v} )</td>
<td>( ^2E_1 )</td>
<td>2.76</td>
<td>1.39</td>
<td>2.76</td>
<td>1.40</td>
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<tr>
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<td></td>
<td>6.75</td>
<td>1.40</td>
<td>6.77</td>
<td>1.41</td>
</tr>
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</table>

*See footnotes a and b of Table I.

dedly lowered for \( \text{Ag}_{6+} \), our computed IP is likely to be at most 0.5 eV in error due to geometry which is much smaller than the error in IP due to electron correlations.

As evidenced from Table I, for \( \text{Ag}_{6} \) too, the CP structure is favored over other structures except that at the highest MRCI level of theory the TP structure is only 0.3 eV higher than the CP structure. This trend is somewhat different from that for \( \text{Cu}_6 \) for which the TP structure is 0.8 eV higher at the MRCI level. The ring structure is at least 1 eV higher than the CP structure at all levels of theory, eliminating this structure as a possible candidate for the ground state of \( \text{Ag}_6 \).

The computed MRCI IP of \( \text{Ag}_6 \) is 4.88 eV. Our previous works on smaller clusters reveal that a scaling factor of 1.11 is required for IPs of all \( \text{Ag}_n \) clusters. Hence our scaled IP of 5.43 eV should be off by only \( \pm 0.3 \) eV compared to the experiment. Cheng and Duncan have suggested that the vertical IP of \( \text{Ag}_6 \) to be lower than 5.6 eV. Our computed IP of \( \text{Ag}_6 \) is 7.2 eV and this value is 6.48 eV. However, as seen from our previous studies on \( \text{Cu}_6 - \text{Au}_{6+} \), the unscaled IP values of 5.5, 4.9, and 6.5 eV follow the order \( \text{IP} (\text{Cu}_6) > \text{IP} (\text{Ag}_6) > \text{IP} (\text{Au}_{6+}) \). The scaled IPs of \( \text{Cu}_6, \text{Ag}_6, \text{Au}_{6+} \) follow this order but the unscaled IP of \( \text{Au}_{6+} \) is only 0.3 eV higher than the IP (\( \text{Cu}_6 \)) while the scaled values differ by 1 eV. Hence the scaled IP of \( \text{Au}_{6+} \) obtained here is only a lower bound and we expect the IP of \( \text{Au}_{6+} \) to be near \( 7.5 \) eV. Cheng and Duncan have suggested that the vertical IP of \( \text{Au}_{6+} \) to be lower than \( 7.9 \) eV. This supports our recommended adiabatic value of \( 7.5 \) eV.

Table IV shows the weights of the leading configurations contributing to the various states and geometries of the

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Structure</th>
<th>Symmetry</th>
<th>State</th>
<th>Configuration</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}_6 )</td>
<td>CP</td>
<td>( \text{C}_{6v} )</td>
<td>( ^1A_1 )</td>
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<td>1.0</td>
</tr>
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<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>TP</td>
<td>( \text{C}_{2v} )</td>
<td>( ^1A_1 )</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>R</td>
<td>( \text{D}_{6h} )</td>
<td>( ^1A_{1g} )</td>
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<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
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<td>( \text{O}_h )</td>
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<td>1.0</td>
<td>1.0</td>
</tr>
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<td>( \text{Ag}_6 )</td>
<td>CP</td>
<td>( \text{C}_{6v} )</td>
<td>( ^2E_1 )</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
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<td></td>
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<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>TP</td>
<td>( \text{C}_{2v} )</td>
<td>( ^1A_1 )</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>R</td>
<td>( \text{D}_{6h} )</td>
<td>( ^1A_{1g} )</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>O</td>
<td>( \text{O}_h )</td>
<td>( ^3T_{2g} )</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{Ag}_{6+} )</td>
<td>CP</td>
<td>( \text{C}_{6v} )</td>
<td>( ^2E_1 )</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
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<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>TP</td>
<td>( \text{C}_{2v} )</td>
<td>( ^1A_1 )</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>R</td>
<td>( \text{D}_{6h} )</td>
<td>( ^1A_{1g} )</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>O</td>
<td>( \text{O}_h )</td>
<td>( ^3T_{2g} )</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{Au}_{6+} )</td>
<td>CP</td>
<td>( \text{C}_{6v} )</td>
<td>( ^2E_1 )</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
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<td>1.0</td>
</tr>
</tbody>
</table>
species considered in this study. As seen from Table IV, the leading configuration of the CP structure is \( 1\alpha_1^2 1\epsilon_1^4 \). This is very similar to the configuration and orbital energy diagram given by Bonačič-Koutecký et al.\(^3\) for \( \text{Na}_6 \) (CP structure). It is easy to show that the same configuration correlates into \( \alpha_1^2 2\alpha_2^2 \alpha_1^2 \) in the \( C_5 \) group, \( \alpha_1^2 \alpha_2^2 \alpha_1^4 \) for the ring structure \( (D_{6h}) \), \( \alpha_1^4 \alpha_2^2 \) (or \( \alpha_1^2 \alpha_2^2 \alpha_1^2 \alpha_2^2 \)) depending on the orientation of the TP structure) for the TP structure, and \( \alpha_1^4 \) \( \epsilon_1^4 \) for the octahedral structure. Bonačič-Koutecký et al. have already done this for \( \text{Na}_6 \) (\( D_{3h}, C_{5v} \), and \( C_{2v} \)) [see Fig. 24 of Ref. 3]. As seen from Table IV of the present work in all cases, the weights of the leading configurations are > 81%.

The positive ion is formed by the removal of an electron from the highest occupied molecular orbital (HOMO). This, of course, leads to different electronic states of different spin multiplicities for the various geometries considered here. For the CP structure, this leads to the \( 2E_1 \) state. For the ring structure, the lowest state is \( 2E_1 \). Interestingly, the octahedral geometry of the positive ion with \( \alpha_1^2 \) \( \epsilon_1^4 \) results in a \( 4A_1^4 \) state. Among the structures we considered this is the only structure with a quartet state as the lowest state.

As evidenced from Table IV, the lowest states of \( \text{Cu}_6^+ \), \( \text{Ag}_6^+ \), and \( \text{Au}_6^+ \) are all \( 2E_1 \) states. Consequently, they will undergo Jahn–Teller distortions from the ideal CP structures. If the distortion is large, the photoelectron spectrum of hexamers is likely to show considerable vibrational progression. We hope that our work will stimulate the possibility of obtaining such spectra for these species.

**IV. CONCLUSION**

We considered \textit{ab initio} investigation of \( \text{Cu}_6^+ \), \( \text{Ag}_6^+ \), \( \text{Au}_6^+ \), and their positive ions which included the effect of \( d \) correlations using CAS-MCSCF, FOCI, SOCI, and MRCI methods. We considered four feasible structures as candidates for the ground state [capped pentagon \( (C_{2v}) \), tripyramidal \( (C_{2v}) \), ring \( (D_{6h}) \), octahedron \( (O_h) \)]. We find that the CP structure with a \( 4A_1 \) state is the lowest among these structures at the highest level of theory. The lowest state of the positive ions was found to be a \( 2E_1 \) state with the capped pentagonal structure and hence this state is predicted to undergo Jahn–Teller distortion. The IPs of hexamers follow the pattern \( \text{IP} (\text{Au}_6) > \text{IP} (\text{Cu}_6) > \text{IP} (\text{Ag}_6) \). Our scaled IP (Cu\(_6^+\)) was found to be in very good agreement with the experiment value obtained by Jarrold and Creagan.\(^{24}\) All states of Cu\(_6^+\) considered here have doublet spin multiplicities with the exception of the octahedral geometry for which \( 4A_1 \) was found to be lowest. Our computations reveal the existence of an excited valence state with an approximate \( \tau \approx 0.9 \) eV. Our computed adiabatic IPs of Ag\(_6^+\) and Au\(_6^+\) support the experimental estimates for vertical IPs provided by Chang and Duncan.\(^{29}\)

**ACKNOWLEDGMENTS**

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\(^{11}\)V. Bonačič-Koutecký, J. Pittner, C. Scheuch, P. Fantucci, and J. Koutecký (to be published) (as referred in Ref. 3).


\(^{29}\)P. Y. Cheng and M. Duncan (private communication); P. Y. Cheng, Ph.D. thesis, University of Georgia, Athens, GA.


\(^{32}\)The major authors of \textit{ALCHEMY} II are B. Lengsfield, B. Liu, and M. Yoshimine.