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## A Theoretical Study of the Excited States of Ag<sub>3</sub>

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Recently there has been considerable interest in the properties and reactivities of small metal clusters. However, for the transition metal trimers, gas phase spectroscopy exists only for Cu<sub>3</sub>[1]. The Cu<sub>3</sub> optical spectrum was obtained using resonant two photon ionization(R2PI) spectroscopy. Application of R2PI to other transition metal clusters has been hindered by difficulty in finding non-predissociating intermediate states for these molecules. In the case of Cu<sub>3</sub> the upper state in the strong optical transition has been assigned as a 3s Rydberg state [2,3] arising from excitation of one electron from a 4s<sup>e'</sup> orbital to a 3s Rydberg orbital. Analogous low-lying Rydberg states are expected for other transition metal trimers. In this paper calculations are reported for the excited states of the Ag<sub>3</sub> molecule. In an earlier paper[4] the excitation energy to the 3s Rydberg state of Ni<sub>3</sub> was reported.

Calculations have been carried out for the ground state of Ag<sub>3</sub> by Walch et al.[5] using a relativistic effective core potential (ECP) and correlating the 5s and 4d electrons (33 electrons for Ag<sub>3</sub>). These authors found a <sup>2</sup>B<sub>2</sub> ground state with a bond angle of 69°, but there is an excited state of <sup>2</sup>A<sub>1</sub> symmetry only 100 cm<sup>-1</sup> higher (See Table I.). As discussed in detail elsewhere[5], the global potential surface for Ag<sub>3</sub> describes a fluxional molecule with a pseudorotation barrier given by the <sup>2</sup>B<sub>2</sub> → <sup>2</sup>A<sub>1</sub> separation. Basch[6] also studied the ground state and some of the low-lying excited states of Ag<sub>3</sub> using a relativistic ECP, but only the 5s electrons were correlated. Since 4d shell correlation is expected to be important in Ag<sub>3</sub> and since the basis set used by Basch did not contain sufficiently diffuse functions to describe the Rydberg states studied here, it was worthwhile to reexamine the excited states

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EXCITED STATES OF Ag<sub>3</sub> (Eloret Corp.) 5 P  
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of  $\text{Ag}_3$ .

The calculations for the excited states use the same relativistic ECP and the same valence basis set as in Ref. 5. In order to describe the Rydberg orbitals, the valence basis set was augmented by a set of hydrogenic-like 3s, 3p, and 3d functions located at the molecular center of mass. These basis functions consisted of a (21) contraction of three term GTO fits[7] to STO type functions with  $\zeta = 1/3$ . The calculations consisted of single configuration SCF followed by singles and doubles CI(SDCI) using both the direct CI and the externally contracted CI(CCI) of Siegbahn[8]. In all cases the 5s and 4d electrons were correlated ( 33 electrons). The effect of higher excitations was estimated by Davidson's correction [9]. The CI calculations were carried out with the MOLECULE[10]- SWEDEN[11] system of programs. In addition, coupled pair functional[12] calculations were carried for the  $\text{Ag}_3$  ground state and for  $\text{Ag}_3^+$  in order to more accurately determine the ionization potential of  $\text{Ag}_3$ . The latter calculations were carried out using the Karlsruhe[13] adaptation of the COLUMBUS[14] codes. The ground state energy was obtained for the  $^2\text{B}_2$  state at the geometry determined in Ref. 5. The geometries of  $\text{Ag}_3^+$ , of the  $^2\text{A}'_1$  (3s Rydberg state), and of the  $4d \rightarrow 5s$  state were optimized at the CCI plus Davidson's correction level with the constraint of  $\text{D}_{3h}$  symmetry. The geometries for the remaining states were not optimized but were taken as equilateral triangle with a Ag-Ag distance of  $5.30 a_0$ , which is close to the  $\text{Ag}_3^+$  equilibrium geometry.

The ground state of  $\text{Ag}_3^+$  is a  $^1\text{A}'_1$  state with the configuration  $5s a_1'^2$  in  $\text{D}_{3h}$  symmetry. At the CCI level the ionization potential (I.P.) of  $\text{Ag}_3$  is 4.64 eV. Applying Davidson's correction increases the I.P. to 4.81 eV., while the uncontracted CI plus Davidson's correction gives 4.82 eV. Given the relatively large Davidson's correction, CPF calculations were also carried out leading to 4.93 eV. The CPF I.P. is expected to be the most reliable, since the CPF method is size consistent and the neutral molecule has one more electron than the positive ion. The I.P. of  $\text{Ag}_3$  has not been measured experimentally. The symmetric stretch frequency in  $\text{Ag}_3^+$  is slightly larger than in  $\text{Ag}_3$ , but the Ag-Ag distance is about the same as the average of the Ag-Ag distance in the  $^2\text{A}_1$  and  $^2\text{B}_2$  states of  $\text{Ag}_3$ .

The excitation energies, geometries, derived harmonic frequencies and transition moments are given in Table I. Given the small I.P. of  $\text{Ag}_3$  one expects a number of

low-lying Rydberg-like states. The electronic structure of these states is very similar to the analogous states of  $\text{Cu}_3$  discussed in detail in Ref. 2. In addition to the CCI calculations, valence CI (VCI) calculations, which included full-CI among the three 5s electrons, were also carried out. From the VCI wave functions transition moments were calculated between each of the Rydberg excited states and the ground state for an equilateral triangle geometry with  $R_{\text{Ag-Ag}} = 5.3 a_0$ . From Table I it is seen that the strongest transition is  $^2A'_1 \rightarrow X^2E'$ . The  $^2A'_1$  state is computed to be at 2.17 eV at the CCI level. The best estimate of this excitation energy is 2.28 eV, based on the CPF ionization potential. A transition observed in matrix studies near 2.55 eV [15] has been assigned to  $\text{Ag}_3$ . Given the large effect of higher excitations on the  $\text{Ag}_3$  I.P., this value is in fair agreement with the computed value.

One state was computed for the configuration  $4d^{29}5s a_1'^2 5s e_x'^1 5s e_y'^1$ . This configuration was considered since the corresponding configuration for  $\text{Cu}_3$  is low-lying. Calculations were carried out for a quartet wavefunction in which the 4d hole was localized on the central Ag atom. For  $\text{Ag}_3$  the excitation energy to this state is 4.94 eV, considerably higher than for  $\text{Cu}_3$  owing to the larger excitation energy to the  $5s^2 4d^9$  state in Ag as compared to the excitation energy to the  $4s^2 3d^9$  state in Cu [16]. Thus, the spectrum for  $\text{Ag}_3$  is expected to be simpler than for  $\text{Cu}_3$  since the  $5s^2 4d^9$  states are shifted to higher energy.

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Table I. Potential Surface Parameters for  $\text{Ag}_3$  and  $\text{Ag}_3^+$ .

state	Geometry		$\omega_e, \text{cm}^{-1}$		$T_e, \text{eV}$		
	$R_1=R_2, a_0$	$\theta, ^\circ$	sym. <sup>a</sup>	bend	VCI	CCI	$f_{ab}^b$
$\text{Ag}_3^+ \ ^1\text{A}'_1$	5.323	60.0	173			4.81	
$\text{Ag}_3 \ 4\text{d} \rightarrow 5\text{s}$	5.475	60.0	123			4.94	
$\text{Ag}_3 \ ^2\text{E}'(3\text{pe}')$	5.3 <sup>c</sup>	60.0			2.77	(3.23) <sup>e</sup>	0.003(1)
$\text{Ag}_3 \ ^2\text{A}'_1(3\text{da}'_1)$	5.3 <sup>c</sup>	60.0			2.73	(3.19) <sup>e</sup>	0.0002(2)
$\text{Ag}_3 \ ^2\text{E}''(3\text{de}'')$	5.3 <sup>c</sup>	60.0			2.62	3.26	0.17(1/2)
$\text{Ag}_3 \ ^2\text{E}'(3\text{de}')$	5.3 <sup>c</sup>	60.0			1.94	(2.40) <sup>e</sup>	0.093(1)
$\text{Ag}_3 \ ^2\text{A}'_1(3\text{sa}'_1)$	5.296	60.0	144		1.71	2.17	0.31(2)
$\text{Ag}_3 \ ^2\text{A}''_2(2\text{pa}''_2)$	5.3 <sup>c</sup>	60.0			1.16	1.42	0.0(2)
$\text{Ag}_3 \ ^2\text{A}_1(2\text{pe}')^d$	5.452	55.2	161	99		0.01	
$\text{Ag}_3 \ \text{X}^2\text{B}_2(2\text{pe}')^d$	5.119	69.2	134	68		0.00	

<sup>a</sup> symmetric stretch frequency.

<sup>b</sup> oscillator strength to the ground  $^2\text{E}'$  state. For degenerate states this is the oscillator strength from one component of the upper state to one component of the lower state. The factors in parentheses are degeneracy factors by which the oscillator strengths should be weighted to give the relative emission intensities. The factor of 1/2 for the  $3\text{de}''$  state arises because half the matrix elements are zero for an  $\text{E}'' \rightarrow \text{E}'$  transition.

<sup>c</sup> computed at the approximate  $\text{Ag}_3^+$  geometry.

<sup>d</sup> results quoted from Ref. 5.

<sup>e</sup> estimated by shifting the VCI energies by the difference between VCI and CCI for the  $^2\text{A}'_1(3\text{sa}'_1)$  state.