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Optical and SCF–Xα–SW Investigations of $M(\pi\text{-}C_2H_4)$, Where M = Cu, Ag, and Au

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Recent matrix spectroscopic studies, focusing attention on group 1B metal atom reactions with ethylene, have provided an avenue to the novel series of highly colored, paramagnetic, mono(ethylene) complexes $Cu(C_2H_4)$, $Ag(C_2H_4)$, and $Au(C_2H_4)$. A distinctive feature of each of these species is a single, intense, visible absorption and a less pronounced ultraviolet band, both displaying a monotonic energy behavior of the form Au > Cu > Ag and Ag > Au > Cu, respectively. In this study, the utility of the SCF–Xα–SW molecular orbital method, for correlating the calculated and observed electronic structures and one-electron excitation energies of $M(C_2H_4)$ (where M = Cu, Ag, Au), is examined. A series of spin-unrestricted and -restricted calculations for both ground- and excited-state electronic configurations have been conducted. In brief, the outcome is an appreciation of group 1B metal atom–olefin bonding interactions, some enlightening comparisons with the M = Ni, Pd, or Pt neighboring triad of mono(ethylene) complexes, and in particular a satisfying accountability of all the aforementioned electronic spectral trends.

Introduction

Known, stable ethylenic complexes of the group 1B elements invariably involve the metals in their oxidized forms. There exist a wide variety of Cu(I), Ag(I), and Au(I) mononuclear complexes,[1] as well as a number of mixed-oxidation-state binuclear complexes containing both Au(I) and Au(III).[2] Zerovalent copper, silver, and gold complexes of ethylene, however, were unknown prior to their synthesis via the metal vapor technique.[3-5] Recently, other investigations of binary metal atom–ethylene systems have been reported for Ni,[6,7] Pd,[8,9] Pt,[10] Co,[11] and Rh[12] on the matrix scale while macroscale metal vapor syntheses have been reported for tris(ethylene) and tris(bicyclo[2.2.1]heptene) complexes of Ni, Pd, and Pt.[13]

Although some of the group 8 metal complexes such as $Ni(C_2H_4)$, $Ni_2(C_2H_4)$, and $Co_2(C_2H_4)$ have been shown to have considerable value as localized chemisorption models for ethylene bonded to the respective metal surfaces, similar attempts to mimic the much more weakly bonded group 1B metal–ethylene surface intermediates[14] have been less rewarding, mainly because of a basic deficiency of vibrational data for the chemisorbed molecules. However, the molecular simplicity of these binary metal–ethylene complexes has attracted the attention of a number of theoreticians who have recognized their importance as fundamental "test cases" for evaluating a variety of vibrational[15] and electronic structure calculational procedures.[16] With the recent development of the SCF–Xα–SW method[17] and its application to some noble metal–ethylene complexes,[18] a direct correlation has been established between accurate electronic structure calculations and the optical properties of matrix-isolated species. In this context, it may be noted that a wide range of semiempirical and ab initio molecular orbital techniques has been applied to a number of metal–ethylene systems.[7,18-26]

The neutral metal–ethylene complexes of the present study have been obtained by direct reaction of the $d^{10}s^1$ group 1B metal atoms with ethylene under matrix cryogenic conditions.[3-5] Unlike their group 8 counterparts, the resulting complexes are open-shell systems bearing one unpaired electron. This difference is most strikingly shown in their electronic spectra, where all of the group 1B metal–ethylene complexes are highly colored, while those of the group 8 metals have no visible absorptions. The purple and green colors of $Ag(C_2H_4)$ and $Au(C_2H_4)$, respectively, have been previously attributed to a charge-transfer band centered in the visible region of the optical spectrum, associated with the excitation of the unpaired electron.[3,5]

The synthesis and infrared isotopic characterization of these complexes has afforded the opportunity for a detailed comparison of the theoretically determined electronic structure and excitation energies with the experimentally determined optical spectra. Furthermore, effects due to an unpaired electron spin

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are also amenable to investigation. The following study therefore focuses exclusively on the electronic structure, bonding, and optical properties of the group 1B mono(ethylene) complexes.

SCF-Xα-SW Method

The electronic structure calculations were performed by using the self-consistent field-Xα-scattered wave method.[17] A molecule, or cluster, is geometrically partitioned into contiguous atomic, interatomic, and extramolecular regions. For each molecular orbital a model, one-electron Schrödinger equation is then solved as a function of an energy parameter, ϵ, within each region by using spherically averaged potentials in the atomic and extramolecular regions and a volume-averaged potential in the interatomic region. These potentials include the Xα statistical approximation to exchange correlation. When ϵ is the appropriate eigenvalue, the wave functions and their first derivatives are joined continuously throughout the various regions of the cluster.

The one-electron Schrödinger equations for the cluster (in the spin-unrestricted case) can be written as eq 1, where $-\nabla_1^2$

$$[-\nabla_1^2 + V_C(1) + V_{X\alpha}^s(1)](\phi_i^s(1)) = \epsilon_i^s(\phi_i^s(1)) \quad (1)$$

is the kinetic energy operator, $V_C(1)$, which is determined classically, is the electrostatic potential at position 1 due to the total electronic and nuclear charge, and $V_{X\alpha}^s(1)$ is Slater's Xα statistical approximation to the exchange correlation (where s = ↑ or ↓),[27] namely

$$V_{X\alpha}\uparrow(1) = -6\alpha[{}^3\!/_{4\pi}(\rho\uparrow(1))]^{1/3} \quad (2)$$

with a similar formula for the spin-down exchange-correlation operator, $V_{X\alpha}\downarrow(1)$. In a spin-unrestricted calculation, the Coulombic potential depends on the total charge density whereas the exchange potential is dependent only on the electronic charge density of the appropriate spin. The total electronic charge density, which is given by eq 3, clearly can

$$\rho(1) = \sum_{i,s} n_i^s(\phi_i^{s*}(1))(\phi_i^s(1)) \quad (3)$$

be separated into spin-up, $\rho\uparrow(1)$, and spin-down, $\rho\downarrow(1)$, components (n_i^s is the occupation number of the ith spin orbital).

The molecular calculations are carried out by initially performing the SCF-Xα atomic calculations with use of a computer program identical with that of Herman and Skillman[28] except for the inclusion of a variable α parameter in the expression for the exchange-correlation potential term. α parameters are generally taken from the tabulations of Schwarz,[29] except for the hydrogen atom, for which a value of 0.77725 is used.[30] A superposition of the charge densities derived from these numerically determined atomic orbitals is then used as the starting point for the molecular calculation. Boundary conditions (i.e, the magnitudes of the atomic sphere radii) are derived by using Norman's method.[31] The α values for the outer sphere and the intersphere regions are set equal to the valence-electron weighted average of the α values of the constituent atoms.

Because of the statistical methods used in the derivation of the Xα exchange potential, the energies calculated represent weighted averages of the energies of the multiplet states that can be derived from a given electronic configuration (in an open-shell situation). With the appropriate choice of occupation numbers in spin-unrestricted calculations, it is often possible to separate multiplet-state energies from the Xα averaging scheme and, in conjunction with Slater's transition-state concept,[17,27] obtain reasonably accurate values for spin-allowed transition energies.[32,33] The question as to which states are averaged can be answered by determining the molecular term symbols, which arise from the electronic configuration under consideration, by the application of group theoretical techniques.[34]

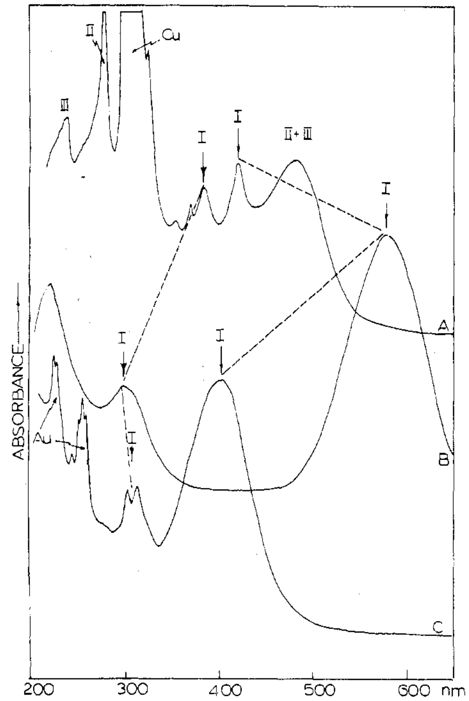

Figure 1. Matrix ultraviolet-visible spectra of the products of the cocondensation reactions of (A) copper atoms with $C_2H_4/Ar = 1/10$, (B) silver atoms with undiluted C_2H_4, and (C) gold atoms with $C_2H_4/Ar = 1/10$ at 10-12 K showing the characteristic ultraviolet and visible absorptions of $Cu(C_2H_4)$ (I), $Cu(C_2H_4)_2$ (II), and $Cu(C_2H_4)_3$ (III) in A, $Ag(C_2H_4)$ in B, and $Au(C_2H_4)$ in C. The presence of some unreacted copper and gold atoms is indicated by "Cu" and "Au".

Energies calculated in the SCF-Xα-SW method are usually expressed in terms of the Rydberg energy unit, and bond distances and coordinates are given in terms of multiples of the Bohr radius of the hydrogen atom. These are easily converted to more familiar units by relationships 4-6.[35]

$$R_\infty = 1.097373177\ (83) \times 10^5\ \text{cm}^{-1} \quad (4)$$

$$R_\infty = 13.605804\ (36)\ \text{eV} \quad (5)$$

$$a_0 = 5.2917706\ (44) \times 10^{-9}\ \text{cm} \quad (6)$$

Ultraviolet-Visible Experiments for Copper, Silver, and Gold Atom Cocondensations with Ethylene

As some of the experimental data have been reported in previous publications from this laboratory,[3,5] we will only

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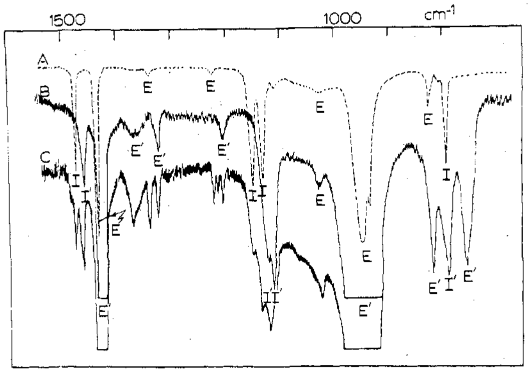

Figure 2. Matrix infrared spectra of the products of the cocondensation reaction of atomic silver with (A) $^{12}C_2H_4/Ar = 1/10$, (B) $^{13}C_2H_4/Ar = 1/10$, and (C) $^{12}C_2H_4/^{13}C_2H_4/Ar = 1/2/10$ at 10–12 K showing the characteristic $^{12}C/^{13}C$ isotope patterns in the $\nu(C{=}C)$ stretching and $\delta(CH_2)$ deformational regions for Ag(C$_2$H$_4$). E and E′ refer to uncomplexed $^{12}C_2H_4$ and $^{13}C_2H_4$ and I and I′ refer to Ag($^{12}C_2H_4$) and Ag($^{13}C_2H_4$), respectively.

Table I. Observed and Predicted Electronic Excitation Energies

complex	transitn	exptl[a]	spin restricted[a]	spin unrestricted[a]
Cu(C$_2$H$_4$)	$5a_1 \rightarrow 6a_1$	26 200	25 400	25 900
	$6a_1 \rightarrow 3b_2$	23 800	14 600	14 600
Ag(C$_2$H$_4$)	$5a_1 \rightarrow 6a_1$	33 600	30 000	31 000
	$6a_1 \rightarrow 3b_2$	18 200	12 300	12 300
Au(C$_2$H$_4$)	$5a_1 \rightarrow 6a_1$	32 300	28 900	29 800
	$6a_1 \rightarrow 3b_2$	24 900	11 900	12 000

[a] Energies quoted in cm^{-1}.

briefly describe our new experiments and mention the salient features of the earlier experiments that are pertinent to the theoretical aspects of the present study.

Recall that the copper atom–ethylene cocondensation reaction leads to three binary complexes of the form Cu(C$_2$H$_4$)$_n$, where $n = 1, 2,$ or 3.[3] A typical optical spectroscopic trace under $C_2H_4/Ar = 1/10$ conditions is depicted in Figure 1A, from which it is possible to discern three sets of absorptions, labeled I, II, and III, characteristic of the three mononuclear complexes Cu(C$_2$H$_4$), Cu(C$_2$H$_4$)$_2$, and Cu(C$_2$H$_4$)$_3$, respectively (see original papers for the experimental details[3,5]). Of particular note in this study is the identification of two bands at 420 and 382 nm associated with (ethylene)copper.

The silver– and gold–ethylene systems differed markedly from that of copper in that only a single complex could be identified for the two heavier metals under a wide range of concentration conditions. Infrared isotopic substitution experiments (see, for example, the Ag/$^{12}C_2H_4/^{13}C_2H_4$ "isotopic doublets" for the $\nu(C{=}C)$ mode in the 1500–1400-cm^{-1} region of Figure 2) established mono(ethylene) stoichiometries for both Ag(C$_2$H$_4$) and Au(C$_2$H$_4$).

(Ethylene)silver in solid ethylene displayed one observable ultraviolet band at about 300 nm (obscured by Ag and Ag$_2$ absorptions in the original study[5,36]) and a single intense visible absorption centered around 580 nm. The ultraviolet absorption of (ethylene)gold was centered at about 310 nm, slightly red shifted with respect to Ag(C$_2$H$_4$) but blue shifted compared with Cu(C$_2$H$_4$). The visible absorption of Au(C$_2$H$_4$) peaked around 410 nm. Hence, the origin of the purple and green hues of the silver–, gold–, and copper–mono(ethylene) complexes can be understood in terms of the relative positions of the visible absorption bands. These data are summarized in Figure 1 and Table I.

For the purposes of aiding the optical spectral assignments, it is pertinent to note that cocondensation of Ag atoms with $C_2H_4/O_2 = 1/1$ mixtures at 10–12 K yields the complex (C$_2$H$_4$)Ag$^+$O$_2^-$ ($^{12}C_2H_4/^{13}C_2H_4$ and $^{16}O_2/^{16}O^{18}O/^{18}O_2$ infrared isotopic stoichiometric confirmation[36]). Of significance here is the *absence* of any visible absorption and a noticeable *blue* shift of the ultraviolet absorption relative to the zerovalent Ag(C$_2$H$_4$) complex in Ar (Figure 3), supporting the idea of oxidation state (I) in (C$_2$H$_4$)Ag$^+$O$_2^-$ (with a d^{10} closed-shell configuration for silver in the cation) and the association of color in the three mono(ethylene) complexes with the excitation of the unpaired electron.

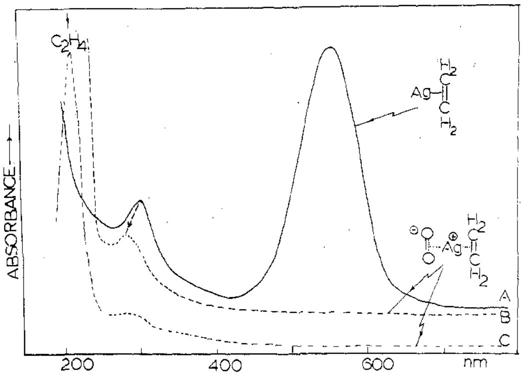

Figure 3. Matrix ultraviolet–visible spectra of the products of the cocondensation reactions of silver atoms with (A) $C_2H_4/Ar = 1/10$ and (B) $C_2H_4/O_2 = 1/1$ at 10–12 K where B is a scale-expanded trace of C.

Table II. Geometry, Radii, and α Values for the Xα Calculations of M(C$_2$H$_4$) (M = Cu, Ag, Au)

atom	x[a]	y[a]	z[a]	radius[a]	α
OUT	0.00	0.00	0.00	6.088 40	*b*
M[c]	0.00	0.00	0.00	2.526 00	*c*
C	0.00	1.265 00	−3.836 00	1.710 00	0.759 28
ES1	0.00	0.00	4.066 00	1.540 00	*b*
ES2	4.066 00	0.00	0.00	1.540 00	*b*
H	1.755 40	2.328 30	−3.836 00	1.270 00	0.777 25
C	0.00	−1.265 00	−3.836 00	1.710 00	0.759 28
ES2	−4.066 00	0.00	0.00	1.540 00	*b*
H	−1.755 40	2.328 30	−3.836 00	1.270 00	0.777 25
H	−1.755 40	−2.328 30	−3.836 00	1.270 00	0.777 25
H	1.755 40	−2.328 30	−3.836 00	1.270 00	0.777 25

[a] All positions and radii reported in multiples of the Bohr radius (a_0) of the hydrogen atom. [b] α = 0.737 39, 0.734 75, 0.730 71 for Cu(C$_2$H$_4$), Ag(C$_2$H$_4$), and Au(C$_2$H$_4$), respectively. [c] M = Cu, α = 0.706 97; M = Ag, α = 0.701 45; M = Au, α = 0.693 01.

SCF–Xα–SW Calculations for Cu(C$_2$H$_4$), Ag(C$_2$H$_4$), and Au(C$_2$H$_4$)

For a probe of the basic electronic structure, bonding characteristics, and optical excitation energies of the group 1B mono(ethylene) complexes, SCF–Xα–SW molecular orbital calculations have been performed. For the purposes of comparison of the three mono(ethylene) complexes among themselves as well as with other Xα calculations of metal–olefin compounds[18] (and in the absence of molecular geometry details for M(C$_2$H$_4$)), the calculations were performed by using the same geometry for all three complexes. Furthermore, interstitial or "empty" spheres were also used in constructing the muffin-tin potential so as to be consistent with previous work.[18] Partial wave expansions were included for values of *L* up to 4 for the outer sphere ("OUT"), 2 for the metal atoms, 1 for the carbon atoms, and 0 for the hydrogen atoms and the empty spheres ("ES1" and "ES2"). The complete structural parameters are listed in Table II.

Both spin-restricted and spin-unrestricted calculations were performed for all three compounds. The complete partial wave

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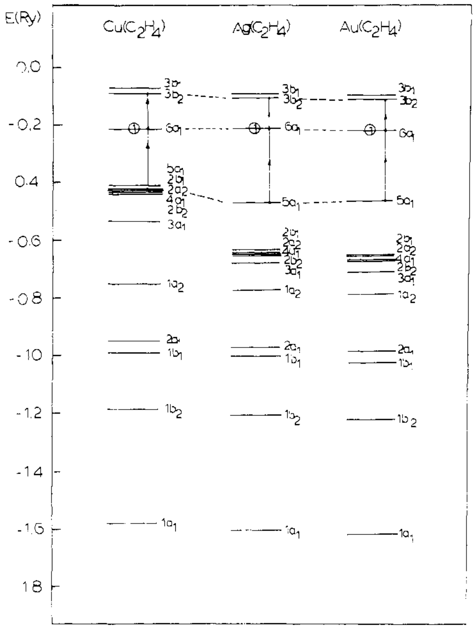

Figure 4. SCF–$X\alpha$–SW spin-restricted energy level schemes for $Cu(C_2H_4)$, $Ag(C_2H_4)$, and $Au(C_2H_4)$. Energies are quoted in Rydberg units. The highest occupied molecular orbital is indicated by the position of the spin-up electron.

analyses for the ground-state spin-restricted calculations are available as supplementary material. For the sake of simplicity, the partial wave contributions from the empty spheres have been omitted. They are involved only in the a_1 and b_1 symmetry blocks and generally contain only a very small percentage of the total charge distribution in any given orbital. In any event, their partial wave breakdown is 100% s character since their partial wave expansions were restricted to $L = 0$.

The energy level diagrams for the spin-restricted calculations are illustrated in Figure 4. The assignment of the ground state is totally unambiguous as the lone electron resides in the $6a_1$ orbital in each case, which is well separated from any neighboring levels. Thus, the three complexes are each described by a $^2A_1$ ground-state electronic term symbol.

From the partial wave analyses (available as supplementary material), one can easily see that the C–C bond is well represented by the $1a_1$ orbital while the four symmetry combinations of the C–H bonds are best described by the $1b_2$, $1b_1$, $2a_1$, and $1a_2$ molecular orbitals. All five of these energy levels are essentially intraligand localized bonds. Interaction with a metal atom produces a very slight upward shift of these levels on passing from Au to Ag to Cu, as has been noted for the binary ethylene complexes of nickel, palladium, and platinum.[18]

The $4a_1$, $2a_2$, and $2b_1$ orbitals are, in each of the complexes, nonbonding in character and are almost exclusively metal d orbitals. The $4a_1$ orbital is illustrated in Figures 5 and 6, along with the wave function contour diagrams for the $3a_1$, $5a_1$, $6a_1$, $2b_2$, and $3b_2$ orbitals of $Cu(C_2H_4)$ and $Ag(C_2H_4)$, respectively. The $4a_1$ figure represents the $d_{x^2-y^2}$ orbital of Cu and Ag but appears with only two lobes due to the fact that the *yz* plane is being plotted and the other two lobes of this d orbital, which are above and below this plane, have zero amplitude in the plane. (Similar figures have been obtained for the $Au(C_2H_4)$ complex, but they are virtually identical with those of $Ag(C_2H_4)$ and have thus been omitted.)

Figure 4 clearly shows that, while the σ framework orbitals and the upper three molecular orbitals ($6a_1$, $3b_2$, $3b_1$) are relatively unaffected by the change in metal to which the ethylene ligand is attached, there is a dramatic stabilization of the middle group of molecular orbitals ($3a_1$ to $5a_1$) on passing from Cu to Ag. This effect is much less pronounced on passing from Ag to Au, and, in fact, the calculations indicate that $Ag(C_2H_4)$ and $Au(C_2H_4)$ have virtually identical electronic structures (for identical geometries). This is due largely to the stabilization of the Ag and Au d orbitals with respect to the Cu d orbitals (similar effects have been noted in $X\alpha$ studies of Cu_2 and Ag_2[37] as well as $Cu(CO)_n$ and $Ag(CO)_n$[38] where $n = 1, 2,$ or 3).

Previous calculations on $Ni(C_2H_4)$, $Pd(C_2H_4)$, and $Pt(C_2H_4)$[18b] indicated that the major metal–ethylene bonding interactions in the mono(ethylene) complexes involved the $3a_1$ and the $2b_2$ orbitals. Within the framework of the Dewar–Chatt–Duncanson description of bonding in metal–olefin complexes,[22,39] the $3a_1$ orbital corresponds to the one in which the ethylene π-bond charge density is donated to the empty metal d orbital while the $2b_2$ orbital represents the back-donation of charge density from a filled metal d orbital to the π^* orbital of ethylene. In the case of the group 8 metal–mono(ethylene) complexes, the $X\alpha$ calculations[18b] predicted appreciable charge density centered between the metal and the ligand in both orbitals and thus, supported the Dewar–Chatt–Duncanson model. Examination of the partial wave analyses (available as supplementary material) and the contour diagrams for the $3a_1$ and $2b_2$ orbitals (Figures 5 and 6) of the group 1B mono(ethylene) complexes clearly reveals that, while an appreciable amount of charge density is located between the metal and the ligand in the $3a_1$ orbital, the amount of back-donation of charge density from the metal d orbital to the ethylene ligand in the $2b_2$ orbital is virtually zero. In fact, the $2b_2$ orbital is essentially metal d in character. This is due largely to the increased stabilization of the group 1B metal d levels relative to those of the group 8 metals. The completely filled d orbitals of the coinage metals are acting more like filled atomic core levels than like bonding valence orbitals. Hence, the group 1B metal–ethylene complexes can be visualized mainly as σ-bonded molecules.

It was previously concluded that the $5a_1$ orbital, in the calculations of the mono(ethylene) complexes of nickel, palladium, and platinum, was essentially nonbonding (or weakly antibonding) in character and that the variations in the appearance of the orbitals was due largely to the differences in the polarizabilities of the three metals. The same appears to be true in the case of the group 1B metal–ethylene calculations. The $5a_1$ orbital is largely composed of metal d character in the case of copper (d_{z^2}) while there appears to be a greater degree of mixing of metal and ligand orbitals in the case of silver and gold. It must be remembered, though, that the atomic orbitals of silver and gold are more diffuse than those of copper. As a result, the differences between the net bonding energy of the three cases is rather minimal, although one might be tempted to attribute a greater metal–ligand bonding interaction to the silver and gold species on the basis of either the partial wave analyses or the contour diagrams.

The differences between the highest occupied molecular orbital, $6a_1$, in the three systems is interesting. If one uses Norman's method of partitioning the outer-sphere, interstitial-sphere, and intersphere charge densities among the major constituent atoms[18d] for the $6a_1$ orbital, one concludes that the percentage charge density localized on the three metals will be 73% on Cu (60% s character) in $Cu(C_2H_4)$, 70% on Ag (62% s character) in $Ag(C_2H_4)$, and 67% on Au (56% s character) in $Au(C_2H_4)$. (While this is not strictly in keeping with Norman's original method, it does emphasize the relatively large contribution to the $6a_1$ level from the metal s

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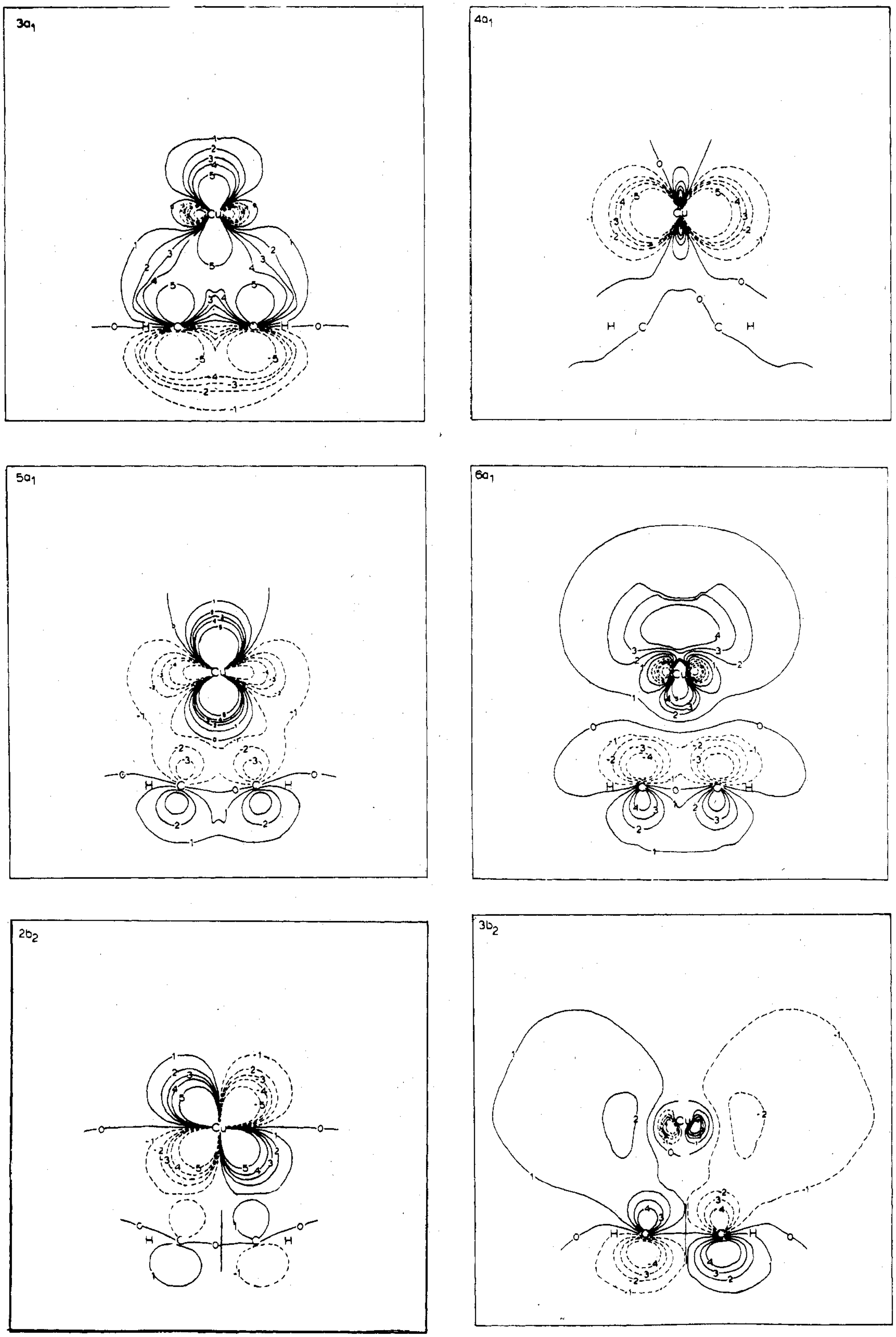

Figure 5. Wave function contour diagrams for selected molecular orbitals of Cu(C_2H_4): (A) $3a_1$, (B) $4a_1$, (C) $5a_1$, (D) $6a_1$, (E) $2b_2$, (F) $3b_2$. Note that positive wave function contours are indicated by a solid line while negative wave function contours are given by dashed lines. Contour specifications: (1) 0.03, (2) 0.06, (3) 0.08, (4) 0.10, and (5) 0.15 in units of (electrons/a_0^3)$^{1/2}$. The "0" contours represent nodal surfaces.

orbital.) It should be pointed out that this molecular orbital is more diffuse than indicated by these values (cf. the percentage charge contributions from the outer sphere and intersphere regions in the supplementary material).

Since the $6a_1$ orbital is essentially nonbonding, or even slightly antibonding, occupation of this orbital might be expected to either add nothing to the overall stability of the complex or, perhaps, weaken the net bonding interaction of

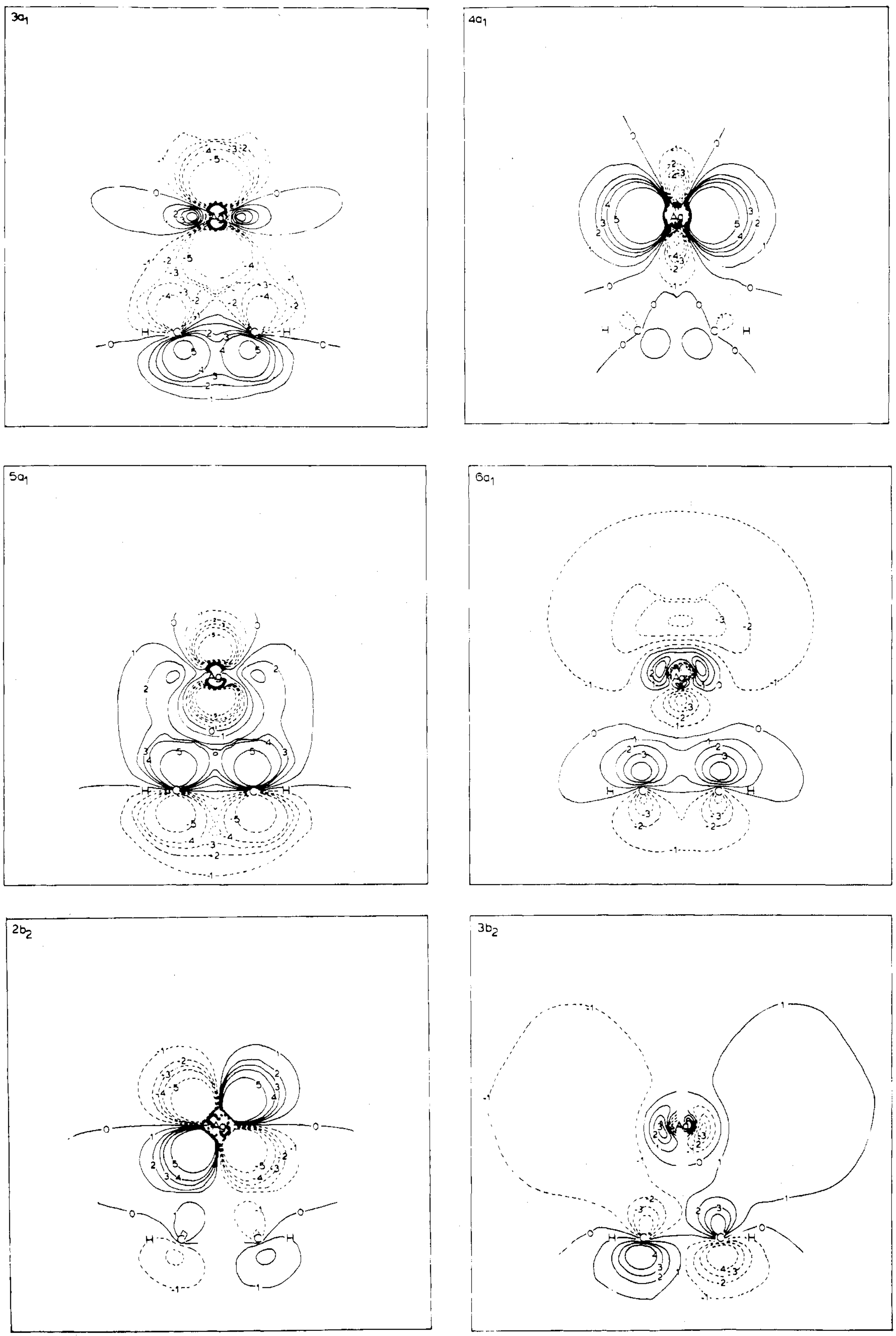

Figure 6. Same as Figure 5 but for selected wave functions of $Ag(C_2H_4)$. See the caption for Figure 5 for orbital and contour specifications.

the group 1B metals with ethylene. Taking into account, as well, the relative ineffectiveness of the $2b_2$ orbital to act as a back-bonding orbital, it is hardly surprising to find that the relative stability of group 1B olefin complexes, obtained via metal-atom synthetic techniques, is less than the corresponding ethylenic complexes of nickel, palladium, and platinum. With only the bonding interaction provided by the $3a_1$ orbital, it would not be expected that any of the mono(ethylene) complexes of copper, silver, and gold would achieve a very high thermal stability.

The problem of assigning the optical transitions observed experimentally was resolved by considering the energy level schemes of Ag(C_2H_4) and Au(C_2H_4). In both of these complexes, one must consider excitations that can result in the two intense bands centered in the ultraviolet and visible regions of the spectrum. Examination of the energy level schemes for Ag(C_2H_4) and Au(C_2H_4) in Figure 4 reveals that the only likely transition that could account for the ultraviolet band and its persistence in Ag(C_2H_4)$^+$ (with a small blue shift) must involve excitation of an electron from the fully occupied 5a$_1$ orbital to the partially occupied (or empty, in the case of Ag(C_2H_4)$^+$) 6a$_1$ level. In the case of Cu(C_2H_4) there are at least three possibilities that could be considered, but they would all likely be about equal in energy since they all involve excitation of an electron from a Cu d orbital to the 6a$_1$ level. Thus the excitation of an electron from the 5a$_1$ level was chosen for the sake of consistency. The visible transition (absent in Ag(C_2H_4)$^+$) could be accounted for by the excitation of the unpaired electron from the 6a$_1$ orbital to either of the two empty orbitals above it (3b$_2$ or 3b$_1$). Of the latter two energy levels, the 3b$_2$ orbital was considered to be the most likely candidate since it was oriented in the plane of the molecule and transition integrals would be expected to be larger for it than for the 3b$_1$ orbital.

Accordingly, transition-state calculations were carried out in both spin-restricted and spin-unrestricted formats for the 5a$_1$ to 6a$_1$ ultraviolet transition and the 6a$_1$ to 3b$_2$ visible transition for each of the three mono(ethylene) complexes. The results are summarized in Table I. The predicted excitation energies tend to underestimate the observed spectral energies, although the agreement between the ultraviolet band energies and the spin-unrestricted transition-state energies is quite good. Clearly, the visible transitions have not been estimated as accurately as the ultraviolet transitions, and agreement between observed and calculated energies becomes poorer, generally speaking, as one goes from Cu to Au. Part of this problem stems from the limitations of the muffin-tin potential in the scattered wave procedure. When orbitals have a large percentage of the charge in the intersphere and outer-sphere regions, the orbital energies found are invariably too low (i.e., too large in absolute value, $|\epsilon_{\mathrm{calcd}}| > |\epsilon_{\mathrm{cor}}|$). The following denotes the total percentage charge found in the intersphere and outer-sphere regions for the 5a$_1$, 6a$_1$, and 3b$_2$ orbitals for each of the three ethylene complexes:

	Cu(C_2H_4)	Ag(C_2H_4)	Au(C_2H_4)
5a$_1$	14	28	29
6a$_1$	58	71	72
3b$_2$	80	85	86

Note that for the 5a$_1$ → 6a$_1$ transition, the best results, in terms of agreement with the experiment (Table I), are for Cu(C_2H_4). For the Ag(C_2H_4) and Au(C_2H_4) cases, these two orbitals each have a much higher percentage charge density in the intersphere and outer-sphere regions and, thus, one would expect the agreement between calculated and observed values to become progressively worse. In all cases, the 3b$_2$ orbital is very diffuse, and hence its energy should be considerably higher than what is calculated. This is the reason for the somewhat poorer agreement with experimental results for the 6a$_1$ → 3b$_2$ transitions in all cases.

It is interesting to note, though, that the observed trend of decreasing excitation energy for the ultraviolet band, in the order Ag(C_2H_4) > Au(C_2H_4) > Cu(C_2H_4), is well reproduced by the calculations. In the case of the visible excitation energy trend, it is only the Au(C_2H_4) calculation which is out of line with the observed trend (Au(C_2H_4) > Cu(C_2H_4) > Ag(C_2H_4)). Relativistic corrections might prove to be critical to a proper estimate of the excitation energies.[40]

There can be little doubt, however, that the observed optical transitions have been properly accounted for by these SCF–Xα–SW calculations. Arguments based on intensity considerations also support these assignments. Although the 6a$_1$ and 3b$_2$ orbitals have large contributions from the outer-sphere and intersphere regions, they can be crudely described as being metal s and ethylenic π^* in character, respectively. A transition from 6a$_1$ to 3b$_2$ would thus be best described as being charge transfer in nature and, as such, would be expected to be very intense. This is the case experimentally. On the other hand, the transition involving the excitation of an electron from 5a$_1$ to 6a$_1$, where both orbitals have a high degree of metal d and s character, respectively, would not be expected to be as intense. The contributions from the ligand basis functions, especially in the 6a$_1$ orbital, would prevent a drastic reduction of the intensity of the predicted band. Once again, this is borne out by the experimental findings.

Conclusions

Generally speaking, the Xα calculations for group 1B mono(ethylene) complexes have provided a satisfactory description of the metal–olefin bonding which is consistent with their thermal stabilities, relative to their group 8 analogues, and which generally duplicates the optical spectroscopic trends. The agreement between observed and calculated transition energies for all the bands could probably be further improved by geometry optimizations and the inclusion of relativistic corrections. Nevertheless, the impressive degree of correspondence between predicted and measured properties attests to the value of the Xα method for elucidating the electronic architecture and bonding properties of these rather unusual organometallic complexes.

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Registry No. Cu(C_2H_4), 60203-82-9; Ag(C_2H_4), 74411-06-6; Au(C_2H_4), 61943-23-5.

Supplementary Material Available: Partial wave analyses and atomic core levels for spin-restricted SCF–Xα–SW calculations of M(C_2H_4), where M = Cu, Ag, and Au (12 pages). Ordering information is given on any current masthead page.

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