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Metal Atom Chemistry and Surface Chemistry: (Carbon dioxide)silver, $Ag(CO_2)$. A Localized Bonding Model for Weakly Chemisorbed Carbon Dioxide on Bulk Silver

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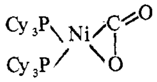
The reaction of silver atoms with $^{12}CO_2$, $^{12}CO_2/Ar$, and $^{12}CO_2/^{13}CO_2/Ar$ mixtures at 10–25 K is shown by infrared, Raman, and UV–visible spectroscopy to lead to a single, highly labile product which is best formulated as a weakly bound binary transition-metal carbon dioxide complex $Ag(CO_2)$. Spectroscopically, (carbon dioxide)silver displays the properties expected for a weakly perturbed CO_2 moiety. In support of this proposal CNINDO geometry optimizations for the chosen model $Na(CO_2)$ favor a side-on bonded π-type complex with a minimum energy configuration corresponding to a O–C–O valence angle of approximately 170°. Under this assumption, extended Hückel molecular orbital calculations proved to be a useful aid for understanding the optical spectrum of $Ag(CO_2)$. The possible relevance of these data to those for CO_2 weakly chemisorbed onto bulk silver and the possible intermediacy of weakly bound surface CO_2 complexes in CO/O_2 and C_2H_4/O_2 heterogeneous oxidations over supported and unsupported silver catalysts are briefly discussed.

Introduction

The catalytic conversion of carbon dioxide to organic compounds is a chemical process that has attracted considerable attention in recent years.[2a] One finds, however, that despite the availability of enormous reserves of CO_2 and CO_2 precursors, surprisingly little is documented about the interactions of transition-metal complexes and CO_2 and CO_2 fixation per se.

It is convenient to divide the reactions of CO_2 with transition-metal complexes into three main types: insertion into M–H, M–C, M–N, and M–O bonds,[2] insertion into activated carbon–hydrogen bonds,[4b] and direct coordination.[2a,3] We also note that ultraviolet irradiation of air-saturated solutions of *trans*-$[RhCl(CO)(PPh_3)_2]$ results in oxidation of CO to CO_2 and PPh_3 to Ph_3PO.[4a] Definitive structural information for complexes containing coordinated CO_2 is presently sparce. One of the two known crystal structures[5,6] is



The local environment around the Ni atom is planar and the CO_2 ligand possesses a bent geometry and is coordinated through the carbon atom and one of the oxygen atoms.[5] The available x-ray, infrared, and UV–visible evidence presently favors nickel oxidation state II in this complex,[5] although this point is open to discussion.

Recently, we have attempted to model some heterogeneous catalytic reaction intermediates and reactions on "naked" metal atoms[7] and small, well-defined "naked" metal clusters.[8] In particular, we have studied the silver atom catalyzed oxidation of ethylene to ethylene oxide and carbon monoxide to carbon dioxide.[7] A number of possible catalytic intermediates have been isolated and some carbon dioxide complexes have been suspected.

In understanding heterogeneous catalysis, a metal surface, for example, can be considered to serve certain functions. First, the activation energies of otherwise thermodynamically accessible chemical reactions are reduced by way of temporary surface-bond formation. Adsorbent bonds may then be broken, and providing surface residence times are sufficiently long, chemical transformations may ensue. Finally, product species must be released so as to reinstate the surface sites to their originally active state.

From the point of view of carbon monoxide and hydrocarbon oxidations, known reaction channels often lead to CO_2. Yet, surprisingly, few experimental surface studies have been reported for CO_2 and little is known about the CO_2 chemisorption bond.[9] This is unfortunate, because in heterogeneous oxidations one aims to avoid catalyst poisoning (overly bound surface intermediates), but, on the other hand, one requires a reasonable interaction energy so as not to adversely affect surface residence times and vital bond cleavage processes, often necessary for complex chemical transformations to take place. It is therefore our contention that for a thorough understanding of heterogeneous oxidations, a detailed knowledge of the surface CO_2 bond is most desirable.

In an effort to characterize products formed in transition metal atom based, matrix oxidation reactions such as $Ag/CO/O_2$,[7] $Ag/CO/N_2O$,[10] $Ag/C_2H_4/O_2$,[7] and $Ag/C_2H_4/N_2O$,[10] we have been stimulated to investigate the possible existence of binary transition-metal carbon dioxide complexes. This paper reports some of our findings for silver atom–carbon dioxide matrix reactions. The results point to the existence of a very labile $Ag(CO_2)$ complex which apart from its inherent chemical interest may serve as a localized bonding model for future studies of $Ag(CO_{2\,ads})$. It certainly provides a uniquely simple model for probing the spectroscopic properties of weakly coordinated CO_2 in a situation which obviates the extraneous effects of interfering ligands.

Experimental Section

Monatomic silver was generated by directly heating a thin tungsten rod (0.025 in.) around the center of which was wound silver wire (0.005 in.). The silver metal (99.99%) was supplied by Imperial Smelting Co., Toronto. Research grade $^{12}C^{16}O_2$ (99.99%) and Ar (99.99%) were supplied by Matheson of Canada, and $^{13}C^{16}O_2$ (99.0%) was supplied by Prochem, N. J. The furnace used for the evaporation of the metals has been described previously.[11] The rate of silver atom deposition was continuously monitored using a quartz crystal microbalance.[12] In the infrared experiments, matrices were deposited on either a NaCl or CsI plate cooled to 10–12 K by means of an Air Products Displex closed-cycle helium refrigerator. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer. UV–visible spectra were recorded on a Varian Techtron instrument in the range 190–900 nm, the sample being deposited on a NaCl optical plate. Raman spectra were recorded on a Spex 1401 double monochromator equipped with a Spectra Physics 164 Ar ion laser and dc amplification and photon counting detection (see ref 24 for details of our matrix Raman setup).

Results and Discussion

Ultraviolet–Visible Experiments. Let us first consider the UV–visible spectral data obtained when Ag atoms are cocondensed with $^{12}CO_2/Ar \simeq 1/10$ matrices at 10–12 K ($Ag/Ar \simeq 1/10^4$). A typical trace is shown in Figure 1A. Aside from the characteristic absorptions of matrix-isolated silver atoms[13,14a] (labeled Ag), a new, weak absorption is observed at about 275 nm. On warming the matrix to 20–25 K, the resonance absorptions of atomic silver gradually decrease in intensity with the concomitant rapid growth of new absorptions at roughly 404, 340, 286, and 248 nm (Table I). These four new absorptions continue to grow in intensity up

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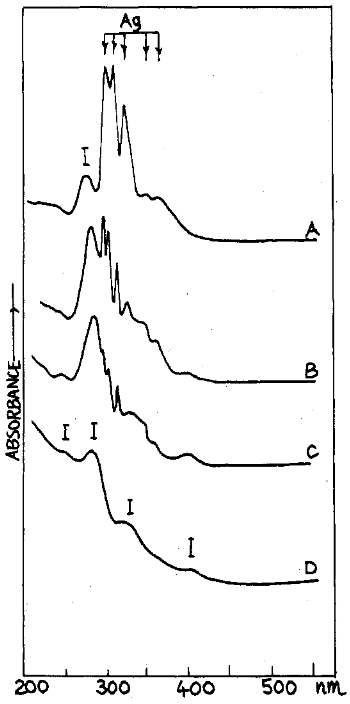


Figure 1. UV-visible spectra of the products formed when Ag atoms are cocondensed with $^{12}C^{16}O_2/Ar \simeq 1/10$ mixtures ($Ag/Ar \simeq 1/10^4$) (A) at 10–12 K. B–D show the effect of matrix annealing at 25, 35, and 40 K. (Atomic silver resonances are indicated and the new complex $Ag(CO_2)$ is labeled I).

Table I. UV-Visible Spectral Data for $Ag(CO_2)$ in Various Matrix Environments (nm)

$Ag/^{12}C^{16}O_2$ ($1/10^4$)	$Ag/^{12}C^{16}O_2/Ar$ (0.001/1/10)	$Ag/^{12}C^{16}O_2/Ar$ (0.01/1/100)
410	404	405 393 }[a]
344 327 }[a]	340	348
291	286	280 270 }[a]
245	248	246

[a] Possible matrix site or multiple trapping effects or resolution of two closely spaced yet different electronic transitions. The former assignment is favored on the grounds that these splittings tend to disappear on matrix annealing.

to about 35 K (Figure 1C) and essentially maintain the same relative intensities throughout the annealing process. On this basis, we ascribe them to a single-absorbing species labeled I. The strongest absorption of I at 286 nm after the 35 K warm-up (Figure 1C) clearly corresponds to the original absorption observed at 275 nm on 10–12 K deposition (Figure 1A), having undergone a small temperature-dependent matrix shift.

During these annealing processes, the resonance absorptions of atomic silver gradually decay and have virtually disappeared at 35 K (Figure 1C). At 40 K, the absorptions of I also begin to decay as the argon matrix begins to sublime from the low-temperature window. Carbon dioxide and silver concentration studies[14] demonstrate that compound I is the *sole mononuclear* product of the $Ag/CO_2/(Ar)$ matrix cocondensation reaction. For example, ultraviolet–visible experiments performed under mononuclear conditions, but in *pure* carbon dioxide matrices ($Ag/^{12}CO_2 \simeq 1/10^4$), produce intense spectra on deposition at 10–12 K (Figure 2A and Table I). Note in particular the very low intensity of the atomic resonance absorptions of Ag (implying that the reaction goes almost to completion in pure CO_2) which tend to decay with

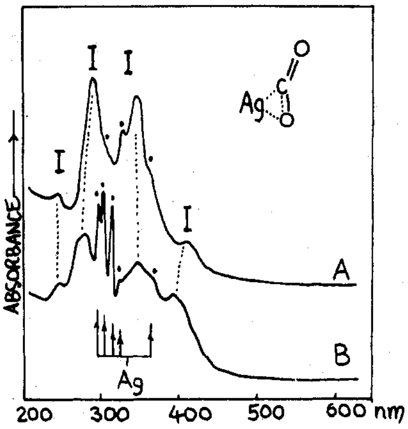


Figure 2. Same as Figure 1A except showing the effect of using (A) pure $^{12}C^{16}O_2$ and (B) $^{12}C^{16}O_2/Ar \simeq 1/100$ deposited at 10–12 K (where $Ag/^{12}C^{16}O_2 \simeq 1/10^4$ and $Ag/Ar \simeq 1/10^4$).

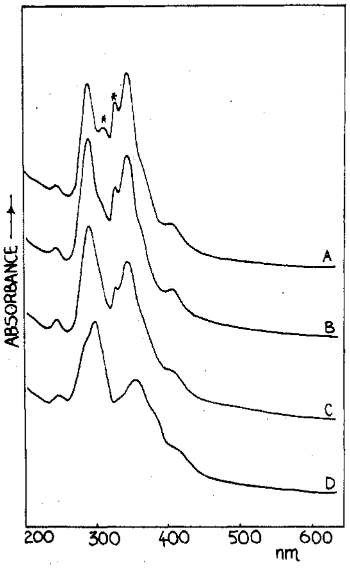
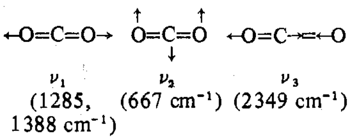


Figure 3. (A) Same as Figure 2A. (B–D) Effect of matrix annealing at 40, 60, and 80 K (where absorptions associated with trace amounts of atomic silver are indicated with an asterisk).

matrix annealing (Figure 3A to 3D) and the obvious resemblance of the $Ag/^{12}CO_2$ optical spectra to those obtained under dilute conditions $Ag/^{12}CO_2/Ar \simeq 0.01/1/100$ to $0.001/1/10$ (Figures 2B and 1A, and Table I).

It is also pertinent to note that one and the same compound can be generated in $Ag/^{12}CO_2$ depositions conducted at 25 K (Figure 4). Particularly significant, from the standpoint of the thermal stability of I, is the observation that the complex can be retained in solid $^{12}CO_2$, essentially unchanged up to about 100 K at which point it appears to fall apart, presumably to $^{12}CO_2$ and silver clusters (Figure 4B to 4E).

Infrared and Raman Experiments. Recall that gaseous $^{12}CO_2$ is a linear $D_{\infty h}$ triatomic molecule with three fundamental modes of vibration[15]



By convention ν_1 and ν_3 are referred to as the symmetric and asymmetric CO stretching modes whereas ν_2 is the degenerate CO deformational mode. By simple symmetry arguments one can immediately deduce that the centrosymmetrical nature of the free CO_2 molecule imposes mutual exclusion restrictions

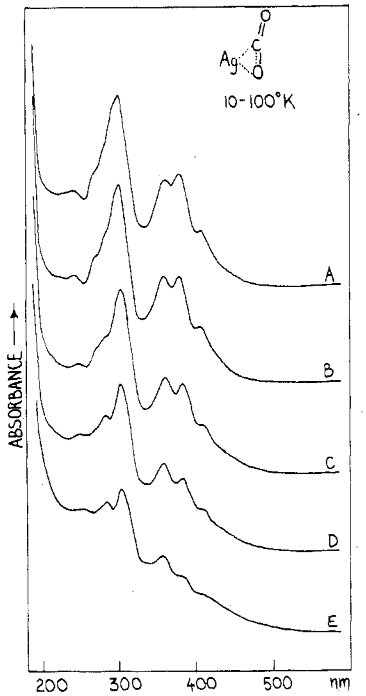


Figure 4. (A) Same as Figure 2A but deposited at 25 K. (B–E) Effect of matrix annealing at 40, 60, 80, and 100 K.

on the vibrational activities, and as a result, ν_1 is Raman active while ν_2 and ν_3 are infrared active. Apart from weak bands due to natural abundance $^{13}CO_2$, and overtone–combination bands, the presence of a classic Fermi-resonance between ν_1 and $2\nu_2$ at 1285/1388 cm^{-1} in the Raman spectrum of $^{12}CO_2$ must be borne in mind.[15,19]

Other points of interest concerning the vibrational properties of $^{12}CO_2$ relate to its bonding in transition-metal complexes[1-6] and to its adsorption on various oxide and zeolitic supports.[9] For adsorbed CO_2 on these supports, it is generally recognized that bands occurring in the region of 2370–2320 cm^{-1} are due to the physical adsorption of molecular carbon dioxide whereas bands occurring in the region of 1700–1200 cm^{-1} may reasonably be ascribed to chemisorbed carbon dioxide, possibly in the form of a bidentate ion.[9] Exposure to higher CO_2 pressures and heating can convert this form of chemisorbed CO_2 to a more strongly bound surface carbonate ion similar to that present in bulk carbonates.[9] In the case of the handful of known transition-metal carbon dioxide complexes, characteristic absorptions occur in the regions of 1750–1550 and 1350–1150 cm^{-1}. The positions and numbers of absorption bands attributable to the vibrations of bound CO_2 in these complexes indicate a marked decrease in both the carbon–oxygen bond order and the symmetry of the triatomic species upon complexation.[1-6] These frequency shifts are similar to those reported for chemisorbed CO_2 on Ni (1640, 1390 cm^{-1})[9b] and on NiO (1620, 1360 cm^{-1})[9b] and suggest a bent structure for the CO_2 groups as found crystallographically for $[(Cy)_3P]_2Ni(CO_2)$.[5] We also note that the infrared spectrum of the carbon dioxide anion free radical (generated by exposing alkali halide disks containing the formate ion to γ rays from a cobalt source) shows a carbon–oxygen stretching band in the range of 1665–1625 cm^{-1} depending on the support.[16] ESR,[17] ultraviolet,[18] and infrared isotopic data[16] have also been reported for this radical anion and lead to a valence angle of 134°. Significantly, the B_2 first excited state for free CO_2 ($1\pi_g \rightarrow 2\pi_u$)[19] bends to 122°.

In the context of the present investigation, the matrix infrared data for $Ag/^{12}CO_2$ and $Ag/^{12}CO_2/Ar$ cocondensation reactions yielded evidence of an essentially unperturbed CO_2 moiety. Apart from the characteristic absorptions of unreacted $^{12}CO_2$ in the matrix (which could easily obscure weak compound lines of I in the proximity of ν_2 and ν_3 of free $^{12}CO_2$) no evidence was found for bands in the 1800–1500- and 1500–1000-cm^{-1} spectral regions which would be indicative of a strongly bound form of $^{12}CO_2$.[1-6] With these results in mind, the corresponding matrix-isolation laser-Raman experiments were undertaken using Ar ion 4880- and 5140-Å excitations, and a typical trace is displayed in Figure 5B. Knowing that ν_2 and ν_3 are Raman inactive for $^{12}CO_2$ and $^{12}CO_2/Ar$ matrices (Figure 5A), we note particularly the growth of Raman lines at 2360/653 cm^{-1} when silver atoms are deposited with these matrices. The Raman line at 653 cm^{-1}, being more intense and more well defined than the line at 2360 cm^{-1}, was subjected to a $^{12}C^{16}O_2/^{13}C^{16}O_2$ isotopic study and yielded a doublet structure at 653/636 cm^{-1} consistent with the (carbon dioxide)silver formulation $Ag(^{12}C^{16}O_2)/Ag(^{13}C^{16}O_2)$ proposed earlier. Of special note in these experiments is the Raman activity of two vibrational modes in *close proximity* to the normally Raman-inactive ν_2 and ν_3 modes of free $^{12}CO_2$. From these vibrational data, one is forced to the inescapable conclusion that small but significant frequency shifts and Raman activity of "ν_2 and ν_3 infrared-type modes" support the contention of weakly bonded carbon dioxide in $Ag(CO_2)$, a comparable state of affairs to that found for CO_2 physically adsorbed on oxide and zeolite surfaces.[9]

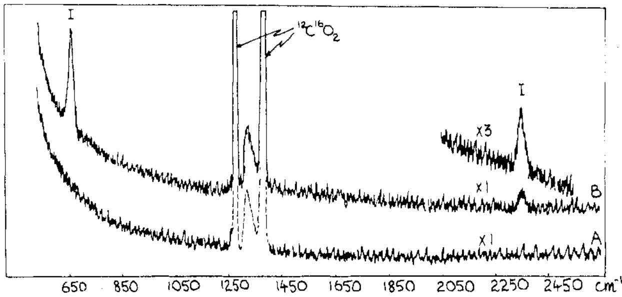
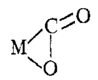


Figure 5. Matrix Raman spectra of (A) pure $^{12}C^{16}O_2$ and (B) Ag atoms cocondensed with $^{12}C^{16}O_2$ at 10–12 K ($Ag/^{12}C^{16}O_2 \simeq 1/10^4$) showing the lines associated with unreacted $^{12}C^{16}O_2$ and $Ag(^{12}C^{16}O_2)$ labeled I.

Molecular Orbital Calculations. In an attempt to better understand the dramatic ultraviolet frequency shifts on passing from free CO_2 to CO_2 complexed to Ag in $Ag(CO_2)$, we have performed a number of different molecular orbital calculations. Initial studies focused on the determination of molecular geometry. For example, within the framework and limitations of extended Hückel molecular orbital techniques we find that extremely distorted structures are favored, the basic geometry being that of an asymmetrical CO_2 moiety, side-on bonded to the metal:



Bond lengths were assumed to be the sum of the single-bond covalent radii, and for C=O a normal carbon–oxygen double bond length was employed. Variation of bond angle with energy is illustrated in Figure 6 for $Ag(CO_2)$, the minimum-energy geometry occurring for θ = 125°. We note in passing that similar calculations for $Cu(CO_2)$ yielded an angle θ = 115°, which is in line with the recent theoretical findings of Anderson[20] for CO_2 chemisorbed on model Cu surfaces. However, the degree of bending indicated in these calculations is far too exaggerated to be consistent with the $Ag(CO_2)$ infrared and Raman results and would imply a far greater charge transfer from the silver to the CO_2 than appears likely.

A second molecular orbital study was initiated for $M(CO_2)$ using the CNINDO program of Dobosh[21] in an attempt to obtain a more reasonable predicted geometry. A number of

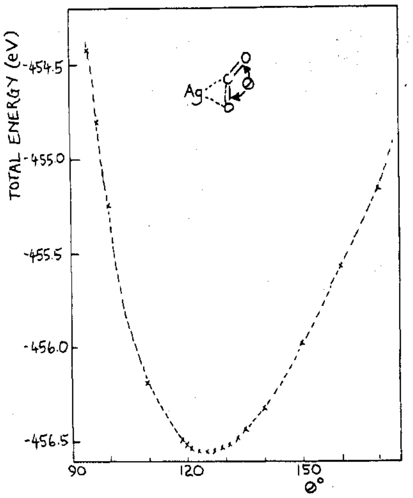


Figure 6. Graphical representation of the variation of the total energy (eV) of $Ag(CO_2)$ with changes in the valence angle θ within the framework and approximations of EH theory.

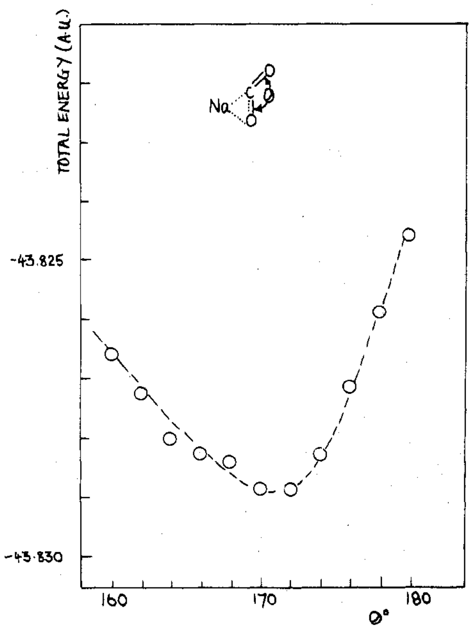


Figure 7. Graphical representations of the variation of the total energy (au) of $Na(CO_2)$ with changes in the valence angle θ within the framework and approximations of CNINDO theory.

different geometry optimizations were attempted including end-on linear M···O=C=O and symmetrical and asymmetrical side-on configurations. The metal chosen for study was the one closest to our coinage metal silver, yet available in Dobosh's program,[21] namely, sodium.

The geometries of lowest energy again corresponded to asymmetrically side-on bonded CO_2. Although a complete geometry optimization was not attempted, the results obtained for only angle variation indicated an energy minimum around θ = 171° as illustrated in Figure 7. Presumably sodium would contribute to a far larger charge transfer than any of the coinage metals; moreover, it is well-known that charge-transfer effects tend to be overemphasized by CNDO (and EH) computational techniques. Thus, the assumption of side-on bonded CO_2 in $Ag(CO_2)$ with an essentially unperturbed CO_2 moiety is a reasonable one and certainly consistent with our infrared and Raman findings.

Table II. Parameters Used in the EHMO Calculations of (Carbon dioxide)silver, $Ag(CO_2)$

Orbital	Orbital exponent	H_{ii}, eV
	Silver	
4d	3.691	−11.58
5s	1.351	−7.56
5p	1.351	−3.83
	Carbon	
2s	1.608	−19.42
2p	1.568	−10.64
	Oxygen	
2s	2.246	−32.33
2p	2.227	−15.80

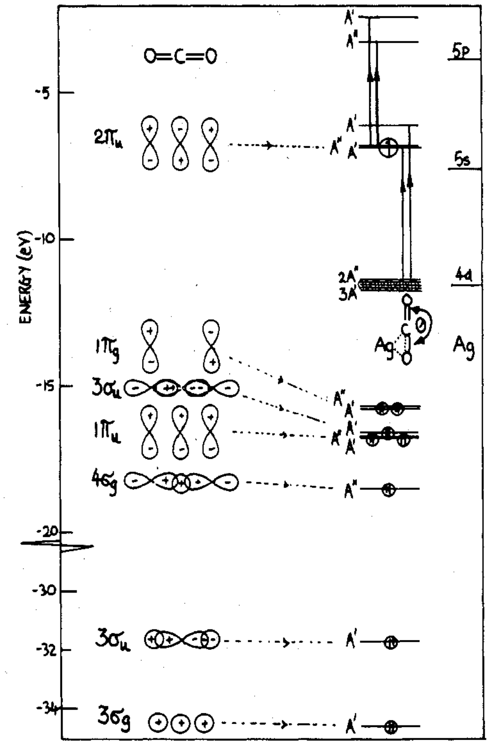


Figure 8. EHMO eigenvalue plots for side-on bonded CO_2 in $Ag(CO_2)$ with C_s symmetry. Positive eigenvalues have been omitted from this diagram. The relationship of some of the levels of complexed CO_2 in $Ag(CO_2)$ to those of uncomplexed $D_{\infty h}$ CO_2 is also indicated in this diagram for reference purposes.

With these geometry optimizations in mind, we reexamined the extended Hückel output for $Ag(CO_2)$ in an effort to gain an insight into the origin of the observed optical transitions of $Ag(CO_2)$. The parameters used in these EHMO calculations are listed in Table II and the calculated eigenvalues are plotted in Figure 8. As anticipated, the side-on bonded conformation with θ close to 180° gives rise to a number of electric dipole, spin-allowed transitions in the spectral range 200–400 nm, in line with our experimental observations.

In essence, the EHMO analysis yields a group of closely spaced, silver 4d-like levels around −11.50 eV. The *unpaired electron*, originally from the silver, appears to reside in an orbital comprised of an antibonding combination of the original $CO_2(2\pi_u)$ orbital with the $Ag(d_{xz})$ centered around −6.86 eV. This level is in close proximity to the other component of the originally degenerate $CO_2(2\pi_u)$ and Ag(5s) orbitals around −6.82 and −6.13 eV, respectively. Higher levels around −3.25 and −2.38 eV are silver $5p_y$- and $5p_x$-like in character but with some ligand CO_2 mixing. The low-lying levels between −35.0 and −15.0 eV are mainly CO_2-like with small amounts of mixing with symmetry-allowed silver atomic orbitals. The relationship of these molecular orbitals of complexed CO_2 in C_s $Ag(CO_2)$ to those of $D_{\infty h}$ CO_2 is similar to Anderson's scheme shown in ref 20.

Hence, electronic transitions, corresponding to excitations *out of* the closely spaced Ag(4d)-like levels *into* the mixed

Table III. UV-Visible Spectral Data (nm) for $Ag(CO_2)$ and $(Cy_3P)_2Ni(CO_2)$

$(Cy_3P)_2Ni(CO_2)^5$	$Ag(CO_2)$
440	404
350	340
270	286
	248

$CO_2(2\pi_u)$ + $Ag(3d_{xz})$ π-type metal–ligand combination, can be anticipated in the 4.6-eV energy range. Furthermore, electronic transitions *out of* the partially occupied $CO_2(2\pi_u)$ + $Ag(3d_{xz})$ π-type metal–ligand combination (or Ag(5s), depending on the choice of electronic ground state) *into* empty, upper Ag(5p)-like orbitals can be expected to occur in the 4.5–3.6-eV energy range. Although we are hesitant to propose definite assignments for the observed optical transitions of $Ag(CO_2)$ in the energy range 5.06–3.02 eV (Table III), we are gratified to note that our theoretical model for weakly complexed CO_2 in side-on bonded $Ag(CO_2)$ yields transitions of approximately the right number and energy to those observed in practice.

Conclusion

The experimental and theoretical studies of the present investigation lead us to believe that the first example of a binary transition-metal–carbon dioxide complex has been isolated and can be formulated as weakly bound $Ag(CO_2)$ for the following reasons:

1. A single compound I is formed in both dilute and concentrated CO_2/Ar matrices as well as in pure CO_2, suggesting the a priori assignment $Ag(CO_2)$.

2. The Raman data for I together with $^{12}CO_2/^{13}CO_2$ isotopic substitution also support the idea of a weakly coordinated CO_2 moiety in a (carbon dioxide)silver complex.

3. The absence of the UV–visible absorptions and infrared absorptions of monomeric AgO and free or complexed CO provides convincing evidence that the oxidation reaction Ag + CO_2 → AgO + CO has not occurred to any measurable extent under the conditions of our experiments.

4. The UV–visible spectrum calculated for $Ag(CO_2)$, with the C_s side-on configuration and a valence angle close to 180°, is consistent with the observed optical transitions.

5. The remarkably close resemblance of the UV–visible spectra of $Ag(CO_2)$ and $[(Cy)_3P]_2Ni(CO_2)^5$ strongly suggests a similar metal to metal–ligand charge–transfer assignment for bands in the 440–270-nm wavelength region (Table III).

6. The vibrational, electronic, and thermal properties of $Ag(CO_2)$ are *all* consistent with the idea of a very weakly bound CO_2 moiety and, as such, may be considered to throw some illumination on the adsorption properties of CO_2 on bulk silver.

From a localized bonding point of view[7c,8,22] the high thermal lability of $Ag(CO_2)$ implies that CO_2 will adsorb on bulk silver surfaces *only* at appropriately low temperatures. This is an intriguing prediction and one that we hope will be subjected to experimental scrutiny in the near future. Certainly our results imply that CO_2 adsorbed onto bulk silver will probably be bound in a "physisorbed sense" and will almost certainly desorb at room or higher temperatures. Therefore, the chances of active-site poisoning[23] by CO_2 formed as an intermediate and/or product in heterogeneous oxidations based on supported or unsupported silver catalysts are probably slight, although we cannot be sure that an oxidized silver surface, or one covered with hydrocarbon or carbon adsorbed layers, will behave in a similar manner. It will be interesting, therefore, to examine the interaction of silver atoms with CO_2 under cryogenic conditions in the presence of, for example, CO, O_2, or C_2H_4. Furthermore, an extension of this methodology to silver cluster complexes of the type $Ag_n(CO_2)^8$ should provide some insight into the validity of our localized bonding description of $Ag(CO_{2\,ads})$.

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