

# Self-Consistent Field Calculations of Hole States of Carbon Monoxide. Electron Density Functions by Computer Graphics

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**Abstract:** *Ab initio* calculations using a moderately large basis set (double  $\zeta$  plus polarization functions) are reported for various states of  $\text{CO}^+$ , with emphasis on the core hole states, and  $\text{CO}$ . Three-dimensional perspective plots of electron density and difference functions are used to visually study the validity of Koopmans' theorem for core hole states and to probe associated electronic relaxation phenomena. Significant relaxation is associated with specific molecular environment; valence orbital contraction is dependent on proximity to the core hole generated. Calculations were also performed on  $\text{NO}^+$  and  $\text{CF}^+$  in order to provide a qualitative visual evaluation of Jolly's empirical "equivalent cores" method. The results show that electron densities in bonds and at neighboring atoms do respond to a core hole approximately as if the core hole were a nuclear charge.

Carbon monoxide is an extensively studied molecule, both theoretically and experimentally. The spectra of the ground state, many neutral excited states (valence and Rydberg), and several bound states of the positive ion have been tabulated.<sup>2</sup> More recently, uv<sup>3</sup> and X-ray<sup>4</sup> photoelectron spectra have been reported for carbon monoxide. Photoelectron spectroscopy (ultraviolet, UPS,<sup>5</sup> and X-ray, XPS,<sup>6</sup>) has been applied to developing the electronic structures of a wide variety of atoms and molecules. They have become effective probes into the ionization process and the generation of states not readily accessible by other techniques; this is especially true of states generated in XPS by ionization of a core electron leading to unipositive atomic or molecular ions typically hundreds of electron volts above the ground state.

In the past, various quantum mechanical models have been tested against the UPS and XPS results. XPS chemical shifts have been correlated with charge densities calculated using Pauling electronegativities<sup>6</sup> or semiempirical MO methods such as the extended Hückel treatment<sup>7</sup> or the CNDO<sup>7,8</sup> prescription. These relationships generally suffice to give a qualitative picture of the ionized state, but cases have been found where charge densities, even when calculated by a

Mulliken population analysis on *ab initio* wave functions, lead to wrong predictions.<sup>9</sup>

Another approach<sup>10</sup> of utilizing *ab initio* calculations involves the application of Koopmans' theorem (KT)<sup>11</sup> to an SCF model for ionization; that is, the ionization potentials are approximated by the respective one-electron orbital energies of the parent neutral molecule. In this approximation, electronic relaxation and differences in correlation and relativistic energies of molecule and ion are neglected. The difference in correlation and relativistic energies of molecule and ion is expected not to be greater than about 1 eV for light atoms.<sup>10e</sup> Neglect of orbital contraction, however, is a more serious problem. Consequently, KT core ionization potentials are generally 5–8% higher than the experimental values.<sup>10e</sup> Nevertheless, calculations of chemical shifts of core electron ionization potentials as differences of KT binding energies usually agree quite well with XPS measurements.<sup>10</sup> This agreement suggests that, within a series of compounds, reorganization or "relaxation" energies are reasonably similar. A theoretically more rigorous procedure is to carry out *ab initio* calculations on both the molecule and its ionized state. Only a few such applications have been reported,<sup>12</sup> undoubtedly because of problems associated with the calculation of open shell states and of convergence to specific states. Coulson and Gianturco<sup>10c</sup> call the use of KT the "sudden" approximation whereas allowing for electronic relaxation is called the "adia-

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(2) P. H. Krupenie, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 5 (1966); this work contains 278 references.

(3) D. W. Turner and D. P. May, *J. Chem. Phys.*, **45**, 471 (1966).

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(6) (a) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Upsal.*, **20** (1967); (b) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, I. O. Werne, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969.

(7) D. N. Hendrickson, H. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **9**, 612 (1970).

(8) (a) J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968); (b) P. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **10**, 378 (1971).

(9) M. Barker and D. T. Clark, *Chem. Commun.*, **22**, 23, 24 (1970).

(10) (a) D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.*, **52**, 3295 (1970); (b) H. Basch, *Chem. Phys. Lett.*, **5**, 337 (1970); (c) U. Gelius, B. Roos, and P. Siegbahn, *ibid.*, **4**, 471 (1970); (d) J. F. Wyatt, I. M. Hillier, V. R. Saunders, J. A. Conner, and M. Barber, *J. Chem. Phys.*, **54**, 5311 (1971); (e) H. Basch and L. C. Snyder, *Chem. Phys. Lett.*, **3**, 333 (1969); (f) W. G. Richards, *Int. J. Mass. Spectrom. Ion Phys.*, **2**, 419 (1969); (g) C. A. Coulson and F. A. Gianturco, *Mol. Phys.*, **18**, 607 (1970).

(11) T. Koopmans, *Physica*, **1**, 104 (1933). The application of KT to CO has been discussed recently in ref 4 and 10f.

(12) (a) P. S. Bagus, *Phys. Rev.*, **139**, A619 (1965); (b) M. E. Schwartz, *Chem. Phys. Lett.*, **5**, 50 (1970); (c) I. M. Hillier, V. R. Saunders, and M. H. Wood, *ibid.*, **7**, 323 (1970); (d) P. S. Bagus and H. F. Schaefer III, *J. Chem. Phys.*, **55**, 1474 (1971); (e) P. S. Bagus and H. F. Schaefer III, *ibid.*, **56**, 224 (1972); (f) F. A. Gianturco and C. Giudotti, *Chem. Phys. Lett.*, **9**, 539 (1971).

batic" approximation. As normally used, however, the latter is not really an adiabatic energy change as in a  $0 \leftarrow 0$  transition. It is actually an approximation to a vertical transition in which the molecular structure is unchanged but in which the electronic distribution is allowed to "relax" to the energetic minimum of the ionized state. In our use of this term we will use quotation marks, *i.e.*, "adiabatic."

In this paper, we present *ab initio* SCF calculations of several core and valence ionized states of carbon monoxide. For comparison purposes we report SCF calculations of CO itself at a similar basis set level and we interpret the results with three-dimensional perspective diagrams of electron density functions. This technique allows particularly a qualitative evaluation of a thermochemical approach to the prediction of energy shifts.<sup>13</sup>

Such plots also help to identify subtle features unobservable in a Mulliken population analysis; that is, these plots permit analysis based on pattern recognition rather than just analysis based on numbers.

### Method of Calculation

All of our calculations utilized the Roothaan formalism for treating closed and open shells,<sup>14</sup> *i.e.*, a single-configuration HF approach. The basis set chosen was the double  $\zeta$  STO set of Clementi,<sup>15</sup> augmented with two  $3d\sigma$  and two  $3d\pi$  functions (exponents of 2.5 and 3.5, respectively) on both carbon and oxygen. Calculations of  $\text{NO}^+$  and  $\text{CF}^+$ , used in the evaluation of Jolly's "equivalent cores" method,<sup>13</sup> were also done using the appropriate Clementi set with additional  $3d\sigma$  and  $3d\pi$  functions (the exponents used are identical with the C and O polarization functions). All ions are calculated explicitly, but the orbital exponents used are those of the neutral ground state species. The SCF calculations were accomplished with the ALCHEMY program at IBM, San Jose.

### Results

The total electronic energy, dissociation energy, dipole moment, and  $R_e$  calculated for CO with various basis sets and types of calculations are compared in Table I. The purpose of this comparison is to show how the basis set we used for the various states of  $\text{CO}^+$  compares when used for the ground state of CO. The value of McLean and Yoshimine (BA + P) for the total energy is the best single-configuration result to date and is considered to be near the HF limit. This puts our calculation only about 0.02 au from the HF limit; we may therefore expect our calculations for the positive hole states to be comparably close to the single-configuration limit.

The electronic structure of the ground state of CO has been discussed previously and need not be repeated here. Contour diagram representations of the electron density distribution are also available. The three-dimensional perspective diagram of the electron density has been published<sup>16</sup> for the minimum basis set, STO-4G.<sup>17</sup> A similar plot with the present DZ + 3d basis

(13) (a) W. L. Jolly, *J. Amer. Chem. Soc.*, **92**, 3260 (1970); (b) W. L. Jolly and D. N. Hendrickson, *ibid.*, **92**, 1863 (1970).

(14) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); *ibid.*, **32**, 179 (1960).

(15) E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).

(16) A. Streitwieser, Jr., and P. H. Owens, "Orbital and Electron Density Diagrams," Macmillan, New York, N. Y., 1973, p 97.

Table I. Comparison of Basis Sets

Ref	$E_{\text{Total}}$ (at $R = 2.132$ au), hartrees	$R_e$ (calcd), au	$D_e$ , eV at 2.132	$\langle z \rangle$ , $D^0$ at 2.132 au
<i>a</i>	-112.7860	2.081	-2.91	+0.274
<i>b</i>	-113.0179			-0.077
<i>c</i>	-113.14557			-0.331
<i>d</i>	-112.3924	2.132	12.499	
STO-4G <sup>e</sup>	-112.03565			+0.655
(BA + P) <sup>f</sup>	-112.7891		7.93	+0.28
(DZ + 3d) <sup>f</sup>	-112.7700			+0.14
This work	-112.7698	2.103	7.60	+0.165
Exptl	-113.377	2.132 <sup>h</sup>	11.24 <sup>h</sup>	-0.112 <sup>i</sup>

<sup>a</sup> W. M. Huo, *J. Chem. Phys.*, **43**, 624 (1965). <sup>b</sup> F. Grimaldi, A. LeCourt, and C. Moser, *Int. J. Quantum Chem., Symp.*, **1**, 153 (1967). <sup>c</sup> Reference 22. <sup>d</sup> R. C. Sahni, C. D. LaBudde, and B. C. Sawhney, *Trans. Faraday Soc.*, **62**, 1993 (1965). <sup>e</sup> A one-point calculation at  $R = 2.132$  au was performed in order to obtain a wave function of minimum basis quality for comparison pictorially with our extended basis work; see Figure 2. <sup>f</sup> M. Yoshimine and A. D. McLean, *Int. J. Quantum Chem., Symp.*, **1**, 313 (1967). <sup>g</sup> A + implies  $\text{C}^+\text{O}^-$  and a - implies  $\text{C}^-\text{O}^+$ . <sup>h</sup> Reference 2. <sup>i</sup> C. A. Burrus, *J. Chem. Phys.*, **28**, 427 (1958); B. Rosenblum, A. H. Nethercot, Jr., and C. H. Townes, *Phys. Rev.*, **109**, 400 (1958).

is qualitatively comparable and is shown for reference as Figure 1. One of the unique potentials of three-dimensional perspective plots of functions is in the visual demonstration of effects of basis sets. To demonstrate this approach we show in Figure 2 a perspective plot of the electron density difference function (DZ + 3d) - (STO-4G) for a common CO bond length of 2.132 au. The general effect is one of wave-like alternations of electron density (*vide infra*). The larger basis set puts a sharper cusp of electron density at the nuclei at the expense of an immediately surrounding region. The greater flexibility of the larger basis set shows up in the heightened electron density in the internuclear bonding region at the expense of the peripheral lone-pair regions. The larger basis also allows the density in the lone pairs to become more diffuse, undoubtedly to minimize electronic repulsions. This effect is visible in the outermost positive hills in the plot; these hills have low magnitude at any given point but the total volume involved is relatively large and corresponds to substantial net electrons.

For the construction of the potential curves of  $\text{CO } X^1\Sigma^+$ ,  $\text{CO}^+ X^2\Sigma^+$ , and  $\text{CO}^- A^2\Pi$ , three calculations at interatomic distances of 2.0, 2.132, and 2.3 au were performed for each state. The equilibrium values obtained thereby are 2.103, 2.051, and 2.290 au, respectively. The experimental values are 2.132, 2.108, and 2.350 au, respectively,<sup>2</sup> and are all 0.03 to 0.06 au larger than the computed ones. In another calculation<sup>18</sup> with single  $\zeta$  STO's, better agreement with experimental bond lengths was gained by carefully optimizing the orbital exponents, although the total energies were worse. The present calculations show that Clementi's double  $\zeta$  basis set, enriched with polarization functions, is sufficiently flexible to reflect the changes in bond lengths on ionizing valence electrons of carbon monoxide without having to perform the laborious task of optimization of exponents.

(17) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) W. J. Hehre, R. F. Stewart, and J. A. Pople, *Symp. Faraday Soc.*, **2**, 15 (1968).

(18) B. C. Sahni and B. C. Sawhney, *Trans. Faraday Soc.*, **63**, 1 (1967).

Table II. Comparison of Experimental and Calculated Ionization Potentials of Carbon Monoxide (eV)

Orbital	UPS <sup>a</sup>	XPS <sup>b</sup>	Koopmans' theorem			Corresponding hole state	"Adiabatic" values		Relaxation energy		
			This work <sup>c</sup>	Ref 21	MSX <sub>α</sub> <sup>d</sup>		This work <sup>c</sup>	Ref 21	This work	Ref 21	Ref 12c
1σ		542.3	562.79	562.29	551.0	O-1s	542.55	541.57	20.24	20.72	21.38
2σ		296.2	309.62	308.92	305.3	C-1s	298.20	296.87	11.42	12.05	12.31
3σ		38.9	41.78		33.2						
4σ	19.7 (19.65)	19.8	22.19		19.1						
1π	16.9 (16.54)	17.2	17.66		18.5	A <sup>2</sup> Π	15.76		1.90		
5σ	14.0 (14.00)	14.0	15.34		13.1	X <sup>2</sup> Σ <sup>+</sup>	13.93		1.41		

<sup>a</sup> Reference 3; maximum of band given as an approximation to a vertical transition. The 0 ← 0 transitions are given in parentheses.  
<sup>b</sup> Reference 4. <sup>c</sup> Present calculation with (DZ + 3d) basis. <sup>d</sup> Reference 19.

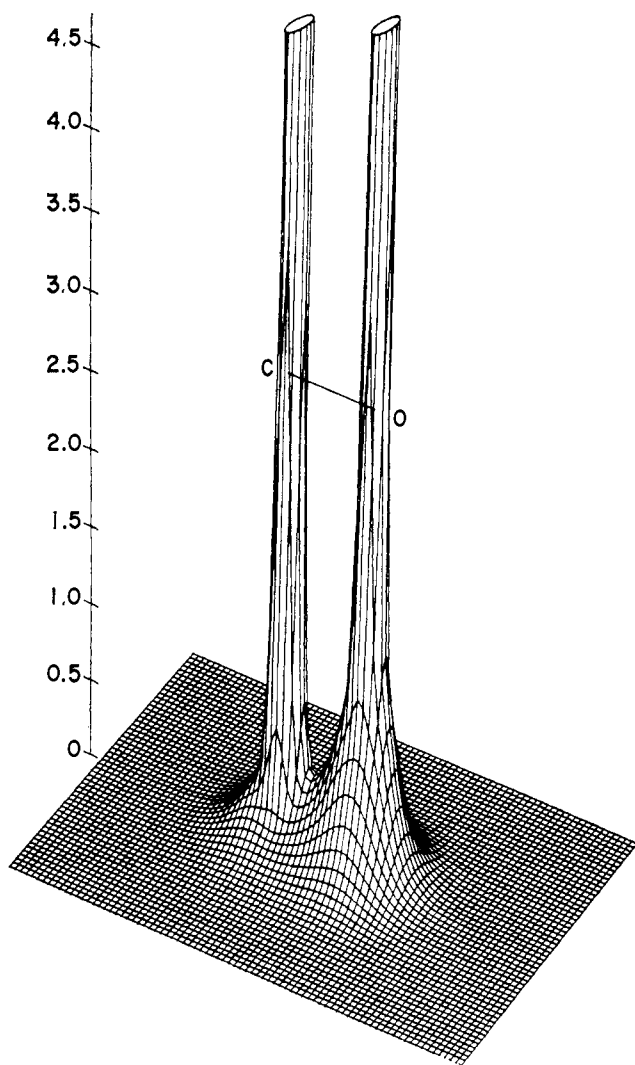


Figure 1. CO total density in a plane. The vertical axis is in electrons per cubic atomic units; the two axes forming the grid plane correspond to two of the geometric axes in the molecule.

Table II shows a comparison of the results of experiment with various theoretical approaches: KT applied to ground state CO, the MSX<sub>α</sub> method, and the values obtained from the calculations of various ionized states compared to the ground state, all at the experimental bond length for CO ( $R_e = 2.132$  au). The calculated results all refer to vertical or Franck-Condon ionizations and probably correspond directly with experimental XPS<sup>4</sup> data. The UPS<sup>3</sup> data for CO show fine structure which allow the assignment of 0 ← 0 or adiabatic transitions. For comparison with the other

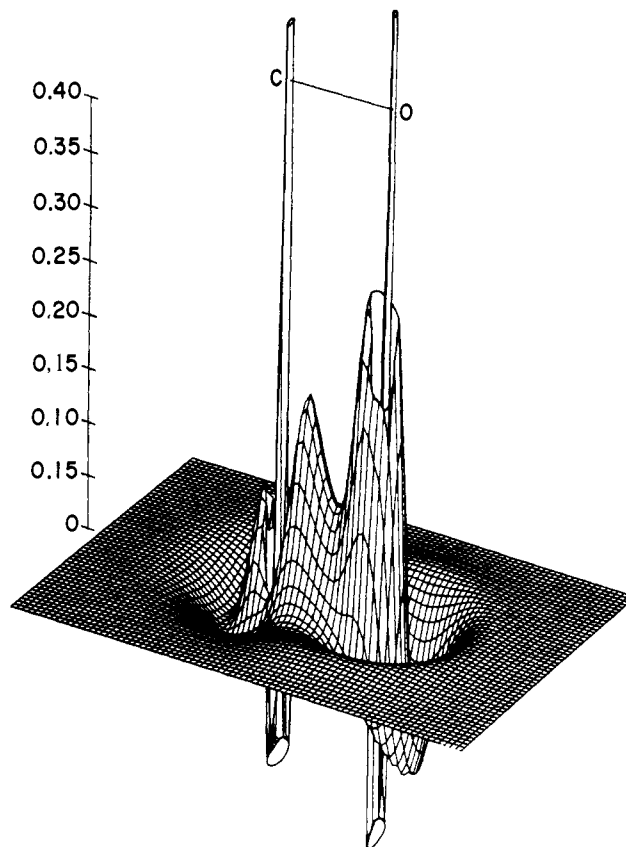


Figure 2. Difference electron density plot of CO to show the effect of basis set; double  $\zeta$  with polarization basis-STO-4G basis. Axes are as defined in Figure 1.

results, the positions of UPS band maxima have been used as estimates of corresponding vertical transitions and are also recorded in Table II. The difference is only significant for ionized states derived from loss of a bonding electron. In Table II this applies only to the 1π MO; the bonding σ MO, 3σ, is too low in energy to be accessible by UPS.

"Adiabatic" ionization potentials for CO have been obtained by Connolly, *et al.*,<sup>19</sup> using the multiple scattering method<sup>20</sup> with "muffin-tin" potentials and an X<sub>α</sub> method. Their results are listed in Table II as MSX<sub>α</sub>

(19) J. W. D. Connolly, H. Siegbahn, U. Gelius, and C. Nordling, *J. Chem. Phys.*, **58**, 4265 (1973); we thank Dr. Connolly for preprint communication of this work.

(20) J. C. Slater and K. H. Johnson, *Phys. Rev. B*, **5**, 844 (1972); K. H. Johnson and F. C. Smith, Jr., *Phys. Rev. B*, **5**, 831 (1972); K. H. Johnson, J. G. Norman, Jr., and J. W. D. Connolly in "Computational Methods for Large Molecules and Localized States in Solids," F. Herman, A. D. McLean, and R. K. Nesbet, Ed., Plenum Press, New York, N. Y., 1973.

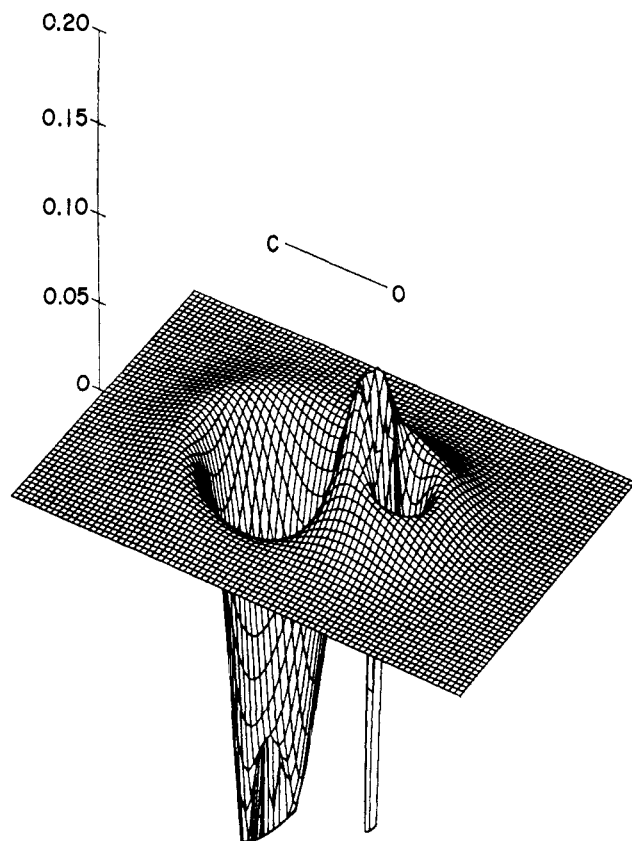


Figure 3. Difference electron density plot to show electronic relaxation in the  $(C^*O)^+$  hole state; Koopmans' theorem-relaxed ion. Axes are as defined in Figure 1.

for comparison with the *ab initio* values. The  $MSX_\alpha$  results for both core and valence shells appear to be in poorer overall agreement with experiment than our  $(DZ + 3d)$  values. Our values agree well with experiment, considering that we may have a correlation error of about 1 eV from the loss of pair correlations with the lost electron.

### Discussion

The energy difference between that given by KT and actual calculation of the hole state is usually referred to as the "relaxation energy." The values compared in Table III show that such relaxation energies are signifi-

Table III. Comparison of Relaxation Energies (eV) in Various Environments

	C	CH <sub>4</sub>	CO
C <sub>1s</sub>	13.0 <sup>a</sup>	13.9, <sup>b</sup> 14.4 <sup>c</sup>	11.42, <sup>d</sup> 12.05, <sup>e</sup> 12.31 <sup>c</sup>
	O	OH <sub>2</sub>	CO
O <sub>1s</sub>	18.0 <sup>a</sup>	20.0, <sup>b</sup> 20.15 <sup>c</sup>	20.24, <sup>d</sup> 20.72, <sup>e</sup> 21.38 <sup>c</sup>

<sup>a</sup> Reference 6a. <sup>b</sup> Reference 12b. <sup>c</sup> Reference 12c. <sup>d</sup> This work. <sup>e</sup> Reference 21.

cantly dependent on molecular environment and demonstrate further the care that must be used in basing experimental "shifts" on KT results. Our results for the relaxation energies of the core hole states of CO differ significantly from those of Hillier, *et al.*,<sup>12c</sup> who performed a limited CI on the ions using the virtual orbitals

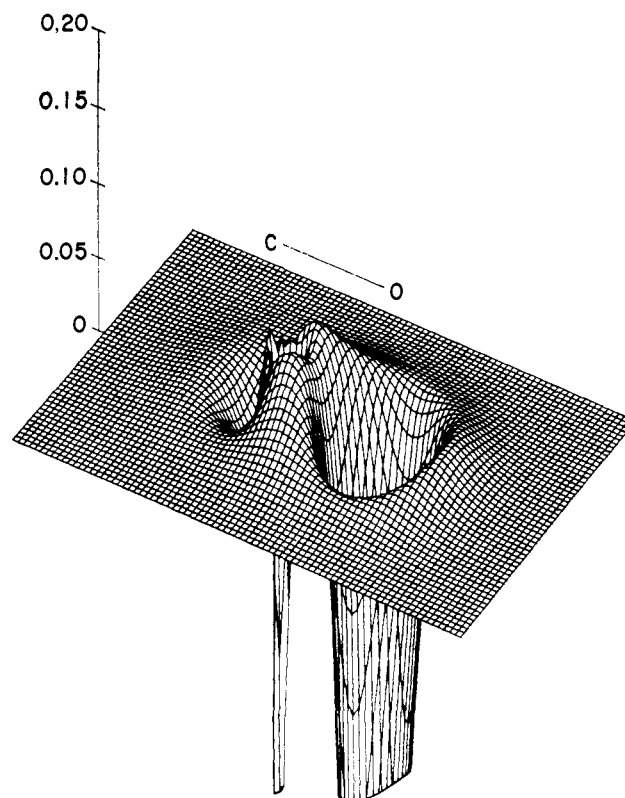


Figure 4. Electron density difference plot to show electronic relaxation in the  $(CO^*)^+$  hole state; Koopmans' theorem-relaxed ion. Axes are as defined in Figure 1.

of neutral ground state CO; however, both results show the same direction of effect and are of comparable magnitude compared to the isolated C and O atoms. Moreover, the core hole states have also been calculated more recently by Schrenk and Bagus<sup>21</sup> using a larger SCF basis set, 7s6p3d2f. Their results for the two core ionized states fall between our smaller basis set results and the limited CI results of Hillier, *et al.*,<sup>12c</sup>

The relaxation effect itself is made more visible by an electron density difference map in which the electron density calculated for a hole state is subtracted from that given by KT (*i.e.*, the ground state minus the electron density of one electron in the  $1\sigma$  or  $2\sigma$  MO). Figures 3 and 4 show such plots for the carbon and oxygen 1s-hole states, respectively, of CO. As may be expected, the major change is in the immediate vicinity of the nucleus whose core electron has been lost. The other electron in the same space orbital from which ionization has occurred is affected most by the missing electron. The loss of screening by the emitted electron produces the greatest amount of orbital contraction in the orbital of its former mate. This remaining electron crowds closer to the nucleus to produce a sharp positive peak not visible in Figures 3 and 4. This feature is buried within the deep well of the immediately surrounding region.

Valence orbitals are also affected by the loss of a core electron. An important difference between Figures 3 and 4 results from the greater  $\pi$ -electron density at oxygen. In the carbon core hole state, the valence electrons migrating inward are primarily from the  $\sigma$  orbitals,  $3\sigma$  and  $4\sigma$  and especially from the  $5\sigma$  orbital

(21) H. Schrenk and P. S. Bagus, unpublished results.

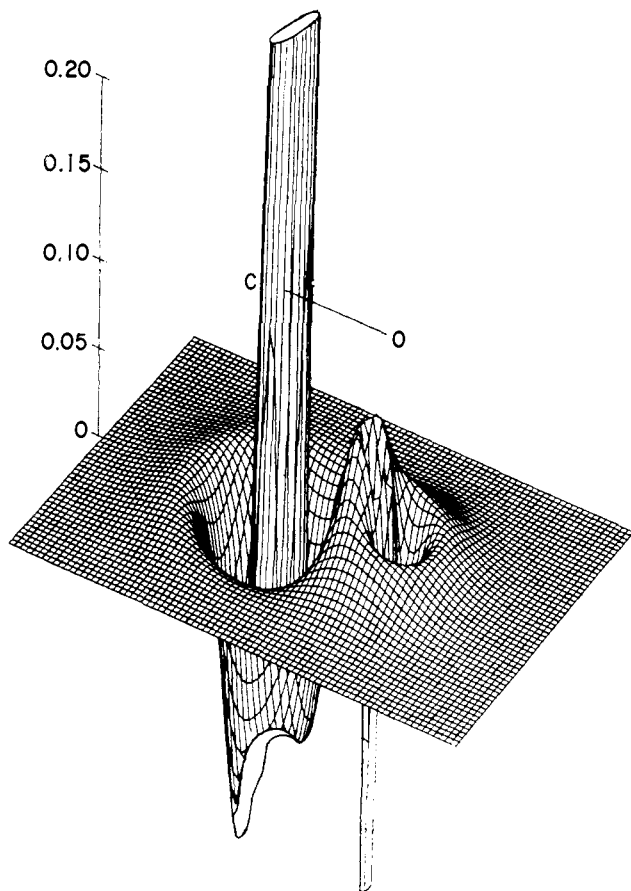


Figure 5. Electron density difference plot,  $\text{CO}-(\text{C}^*\text{O})^+$ , derived from the molecule and ion SCF wave functions. Axes are as defined in Figure 1.

(the lone pair on carbon). In the oxygen core hole state the  $3\sigma$  and  $4\sigma$  orbitals again contract, but contraction of the  $1\pi$  orbital now becomes apparent. The contraction of this  $\pi$  orbital is responsible for the twin-humped feature between the nuclei in Figure 4. These relaxation differences between the C and O hole states are already inherent in the electron density distributions in the parent carbon monoxide (Figure 1). Even in the Mulliken population, the  $\pi$  density in CO itself is considerably more skewed than the  $\sigma$  density. Looking at the valence populations, we find the total  $P_C/P_O$  ratio for the  $\sigma$  orbitals is 0.732, whereas the same ratio for the  $1\pi$  orbital is only 0.316; *i.e.*, the  $\pi$ -electron density is closer to the oxygen. Siu and Davidson<sup>22</sup> also made a similar observation: "The center of charge of the  $\pi$  electrons is located about 0.25 of the way from O toward C as would be expected from the contribution of three  $\pi$  electrons from O and only one from C." Proximity to a localized hole seems to form an important criterion for maximum contraction and would be expected from simple electrostatic consideration. These differences are also reflected in Table IV which shows the energy changes in orbitals for the various states. The variations discussed so far, together with the data in Table III, are related to the bonding situation in the molecule and we must therefore expect some fluctuation in relaxation energies with molecular environment. The changes observed are not large, but they are readily

(22) A. K. Q. Siu and E. R. Davidson, *Int. J. Quantum Chem.*, **4**, 223 (1970).

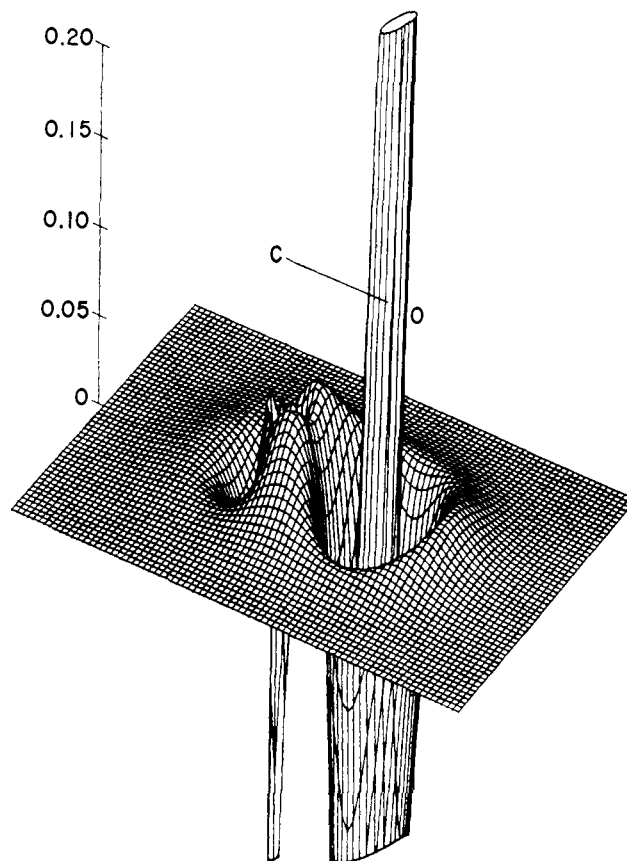


Figure 6. Electron density difference plot,  $\text{CO}-(\text{CO}^*)^+$ , derived from the molecule and ion SCF wave functions. Axes are as defined in Figure 1.

Table IV. Orbital Energies of Carbon Monoxide States and Related Ions

	$1\sigma$	$2\sigma$	$3\sigma$
$\text{CO } X^1\Sigma^-$	-20.681863	-11.378165	-1.535507
$\text{CO}^+ X^2\Sigma^-$	-21.110054	-11.898605	-1.932492
$\text{CO}^+ A^2\Pi$	-21.194117	-11.850855	-2.018591
$\text{CO}^+$ (C-1s hole)	-21.260064	-14.105020	-2.096291
$\text{CO}^-$ (O-1s hole)	-24.006130	-11.905300	-2.148050
$\text{NO}^+$	-21.253971	-16.307323	-2.126288
$\text{CF}^+$	-26.895188	-11.898760	-2.272950
	$4\sigma$	$5\sigma$	$1\pi$
$\text{CO } X^1\Sigma^+$	-0.815404	-0.563756	-0.648900
$\text{CO}^+ X^2\Sigma^+$	-1.178168	-1.137869	-1.026907
$\text{CO}^- A^2\Pi$	-1.269643	-0.950959	-1.148607
$\text{CO}^+$ (C-1s hole)	-1.334460	-1.136693	-1.145505
$\text{CO}^+$ (O-1s hole)	-1.394801	-0.991742	-1.251418
$\text{NO}^+$	-1.391000	-1.160064	-1.135324
$\text{CF}^+$	-1.407409	-0.986907	-1.232898

discernible in the type of difference function described above.

The magnitude of the orbital energy change upon ionization, seen in Table IV, exhibits a sharp change from valence ionization (0.4 to 0.6 au) to core ionization (about 3.3 au). The effect is caused mostly by the Coulombic potential of the generated positive charge. These arguments tacitly assume the core hole states to be localized. To validate this hypothesis we generated Figures 5 and 6, in which the electron densities of the core hole states are subtracted from the electron density of the CO ground state. The results show a common

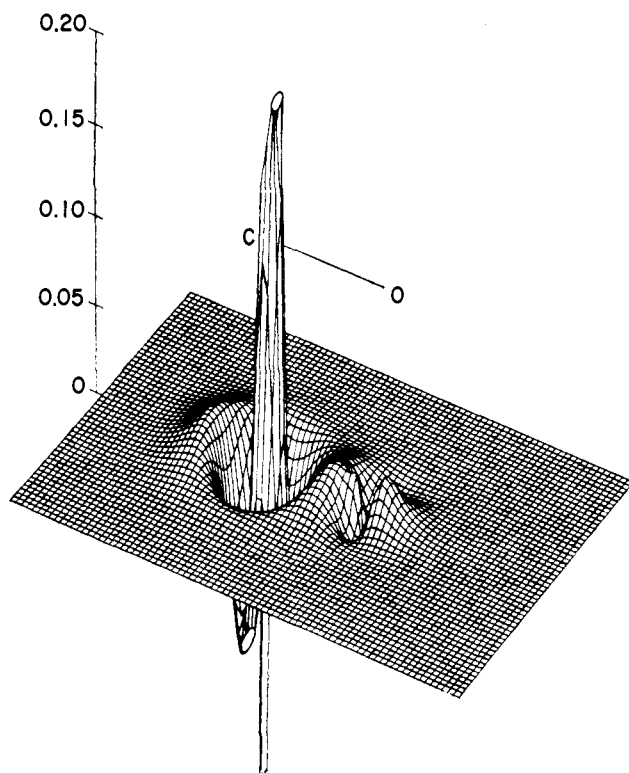


Figure 7. Electron density difference plot to evaluate the quasi-thermodynamic approach;  $(C^*O)^-$  SCF valence density- $NO^+$  SCF valence density. The  $NO^-$  bond distance is equal to  $CO^+$ . Axes are as defined in Figure 1.

pattern. Removal of one 1s electron causes an *increase* in the electron density right at the nucleus because of the reduced screening. Electron density is lost massively from an immediately surrounding shell and there are definite changes in the internuclear bonding region. The plots are not dissimilar to Figures 3 and 4 except for the region close to the nucleus and show, therefore, that the emitted 1s electron was highly localized about a specific nucleus.

Jolly's<sup>13</sup> empirical but quasi-thermochemical approach to the correlation of ESCA chemical shifts has been highly successful. The method is based on the assumption that valence electrons contract on generation of a core hole as if the nuclear charge had increased by one; *i.e.*, the nucleus of atomic number  $Z$  with only one corresponding core electron is replaced by the nucleus of atomic number  $Z + 1$  with its normal complement of two core electrons. For the core ionized states of CO this would mean comparing the valence densities of  $(C^*O)^+$  with  $NO^+$  and those of  $(CO^*)^+$  with  $CF^+$ . To evaluate this "equivalent cores" approach in terms of electron density patterns we calculated  $NO^+$  and  $CF^+$  at the CO bond distance with basis sets comparable to those used in the CO calculations. The electron density functions were used for difference plots with the corresponding hole-state carbon monoxide functions; these electron density difference plots are shown in Figures 7 and 8. The changes are seen to be rather small, except in the region of ionization, thus giving a qualitative pictorial verification of Jolly's treatment. In particular, the changes in the bonding region and around the other atom are relatively small. This result agrees with the recent formal deriva-

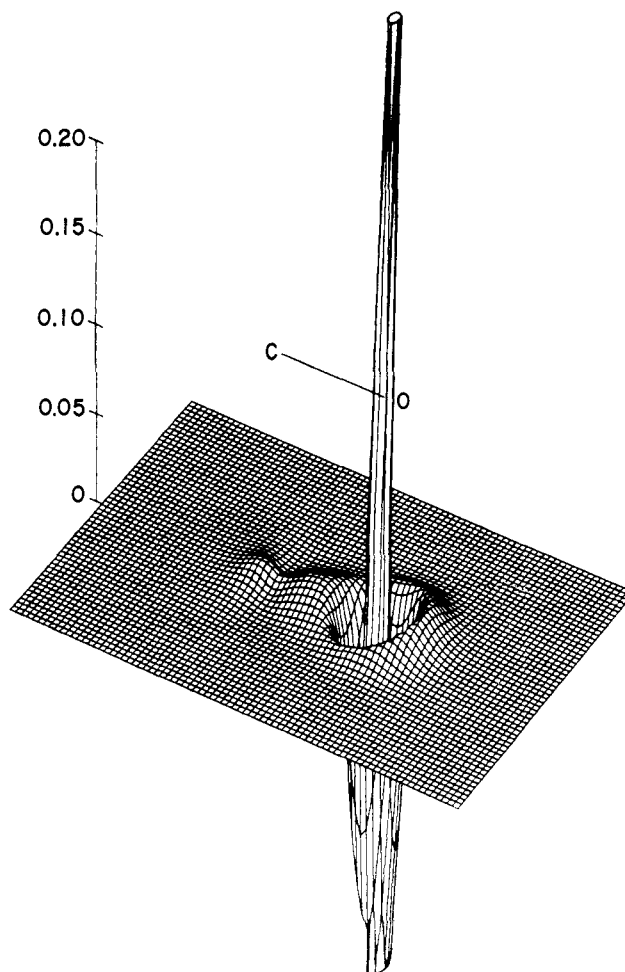


Figure 8. Electron density difference plot to evaluate the quasi-thermodynamic approach;  $(CO^*)^-$  SCF valence density- $CF^+$  SCF valence density. The  $CF^+$  bond distance is equal to  $CO^+$ . Axes are as defined in Figure 1.

tion of Shirley<sup>23</sup> who showed that Jolly's empirical treatment is essentially equivalent to Schwartz's quantum mechanical potential model.<sup>24</sup>

If the exponents for the ionized states had been optimized a more accurate description of the electron density of the ions would have been obtained. For the core shell ions, we expect that the optimized exponents would lie between those of ground state CO and ground state  $NO^+$  or  $CF^+$ . (Bagus<sup>12a</sup> has shown, for example, that the optimized exponents for the 1s-hole  $Ne^+$  are between those for Ne and  $Na^+$ .) This improvement in the ionic electron density could result in a flattening of the differences in Figures 7 and 8; however, such an effect may well be small since the core ionization potentials obtained by Schrenk and Bagus<sup>21</sup> with a larger basis set are within 1.1 eV of the present values. This indicates that our smaller basis set has sufficient flexibility to account for more than 90% of the relaxation effects.

An interesting corollary of the success of the equivalent cores approach is apparent in a comparison of the orbital energies of the two core hole states of CO with those of  $NO^+$  and  $CF^+$ . As summarized in Table IV, the

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orbital energies of  $(C^*O)^+$  are remarkably similar to those of  $NO^+$  except for  $2\sigma$ , which is mostly the  $C_{1s}$  and  $N_{1s}$  orbitals, respectively. The other MO's are much the same in terms of orbital energy for a carbon core hole as for a nitrogen nucleus. A similar comparison holds for  $(CO^*)^+$  with  $CF^+$ ; in this case, the MO energies are much the same except for  $1\sigma$ , the  $O_{1s}$  and  $F_{1s}$  orbitals, respectively.

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## SCF-X $\alpha$ Scattered Wave Studies on Bonding and Ionization Potentials. I. Hexafluorides of Group VI Elements

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**Abstract:** A SCF-X $\alpha$ -SW calculation has been carried out for the hexafluorides of the group VI elements S, Se, and Te. The bonding of these molecules is compared by using the charge distribution in different spatial regions in these molecules. The central atom–ligand bond is found to increase in polarity as one moves from S to Te. In contrast to simple overlap arguments, the  $e_g$  level is always higher in energy than the  $t_{2g}$  level. The calculated ionization spectra agree well with the experimental measurements. Finally, the d orbital participation has been studied for SF<sub>6</sub>. The inclusion of d components is necessary in order to reproduce the experimental level ordering. However, its effect on the charge distribution (and possibly also on the bonding) is minor.

Molecules containing elements of the groups VI to VIII in their higher valence states have received considerable attention,<sup>2–8</sup> since they involve atoms which exceed the number of valences permitted on the basis of the Langmuir–Lewis theory of bonding.<sup>9</sup> For this reason they have been called hypervalent molecules.<sup>6</sup> A number of explanations, based either on valence bond<sup>3,7,9</sup> or on molecular orbital theory,<sup>2,3,6–9</sup> have been proposed to elucidate the bonding nature of these molecules. Among the molecules of MX<sub>6</sub> type, sulfur hexafluoride, SF<sub>6</sub>, might be the most thoroughly studied system, both experimentally<sup>10–17</sup> and theoretically.<sup>18–28</sup>

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