Analysis of Transition-Metal Carbonyl Auger Line Shapes

D. R. Jennison, G. D. Stucky, R. R. Rye, and J. A. Kelber
Sandia National Laboratories, Albuquerque, New Mexico 87185
(Received 12 August 1980)

The carbon Auger line shapes obtained from three diverse gas-phase transition-metal carbonyls are analyzed. Some features in the line shape directly reflect the amount of π backbonding. The analysis indicates that the dominant initial state is the adiabatically relaxed ground state. The final-state holes are either localized on the same ligand or described by a state consisting of one hole on a ligand and the other on the metal atom. The latter state may be viewed as a π-backbonding–assisted interatomic decay.

PACS numbers: 33.50.Hv, 33.10.Cs

In addition to their central position in inorganic chemistry, the transition-metal carbonyls have long been of interest to the surface science community as models for CO chemisorption. Despite extensive experimental and theoretical studies, however, there is still extensive debate concerning the role of π backbonding[1] and the assignment of the features visible in the x-ray photoelectron spectra (XPS) of the carbon and oxygen 1*s* levels, particularly as to the nature of the lowest-energy core-hole state.[2-4]

We have obtained, using previously described experimental techniques,[5] essentially identical Auger spectra for a set of gas-phase transition-metal carbonyls systematically chosen to probe bonding variations. We analyze here the carbon line shape and explain the origin of the differences first noted by Plummer, Salaneck, and Miller[6] between the carbonyl and CO spectra. This represents the first theoretical analysis of the Auger line shapes of a transition-metal complex. Since the Auger line shape is largely determined by the Auger initial-state valence configuration,[7] (i.e., in the molecule containing a core hole) we are able to discriminate between the adiabatically relaxed and the shakeup initial states. We find that the adiabatic initial state dominates the Auger spectrum, and thus we assign this state to the largest amplitude XPS peak, which is also lowest in energy in agreement with the *ab initio* calculations of Loubriel[2] and of Messmer and Lamson.[4] We show that the presence of π backbonding directly contributes to features observed in the Auger spectra and that the magnitude predicted by the Hartree-Fock theory seems correct. Thus, Auger spectroscopy provides the first direct experimental evidence for the presence of π backbonding.

Due to the presence of satellites and of large shakeup state mixing in the deep valence region of unsaturated molecules,[8] we focus here on the shallow valence transitions.

We calculate the energy of the Auger transition by assuming an independent-particle model. The Auger-electron energy, E_A, is found from the appropriate experimental core and valence ionization potentials, I, and from the effective final-state hole-hole interaction,[9] $U_{\rm eff}$:

$$E_A(c,j,k,s) = I_c - I_k - I_j - U_{\rm eff}(j,k,s), \qquad (1)$$

where we explicitly note the spin dependence. We approximate $U_{\rm eff}$ by calculating the bare hole-hole interaction using ground state orbitals[10] (or other appropriate hole wave functions; see below), but we note that each hole also interacts with the electronic polarization field induced by the other hole. For itinerant holes, this latter effect is somewhat averaged as to reduce its importance[10]; however, this polarization energy is known to be important for localized states.[7,11] By comparing the calculated and experimental values of $U_{\rm eff}$, and recognizing the effect of polarization, we derive information about the degree of localization of the final-state holes.

We calculate the transition probabilities as previously described.[7,12] There are four major factors: atomic-like Auger matrix elements over the local basis set; the initial-state valence atomic (as opposed to overlap) charge populations; the nonorthogonality between the initial state and final state valence orbitals caused by the initial state relaxation; and configuration mixing with the low-lying virtual orbitals. This latter effect has been shown to be of restricted importance.[12] All calculations were done in the restricted Hartree-Fock approximation with use of a modified version of the HONDO 76 program with double-zeta accuracy contracted Gaussian basis sets of Dunning (for C and O), and of Roos, Veillard, and Vinot as extended by Hay (for Ni).[13]

Since an understanding of CO is basic to the carbonyls, theory and experiment are compared

for CO in Fig. 1. We find that although the 5σ orbital is 3 eV less bound than the 1π,[14] the large calculated U_{eff} produced by the almost lone-pair character of the 5σ makes the theoretical $5\sigma^{-1}1\pi^{-1}$ final-state configuration (U_{eff} = 12 eV) higher in Auger-electron energy than the $5\sigma^{-2}$ (U_{eff} = 17 eV). The peak in the experimental spectrum assigned to the $5\sigma^{-2}$ configuration is an unusually sharp Auger feature[15] similar to that observed for the $5\sigma^{-1}$ in the ultraviolet photoelectron spectroscopy spectrum,[14] an observation which argues for the correctness of the assignment. We note that while the one-electron theory describes the simple O(*KVV*) spectrum of CO extremely well, significant satellites due to the virtual 2π orbital, and configuration-interaction (CI) effects[12] are present in the C(*KVV*) spectrum. However, all major features may still be assigned and understood. We also note that the alternate theoretical approach based upon limited configuration-interaction calculations does not reproduce the experimental spectrum[16] although this comparison is not completely fair as our method is not *ab initio* since we use empirical ionization potentials[6] in Eq. (1). A complete analysis of CO may be found in Ref. 17.

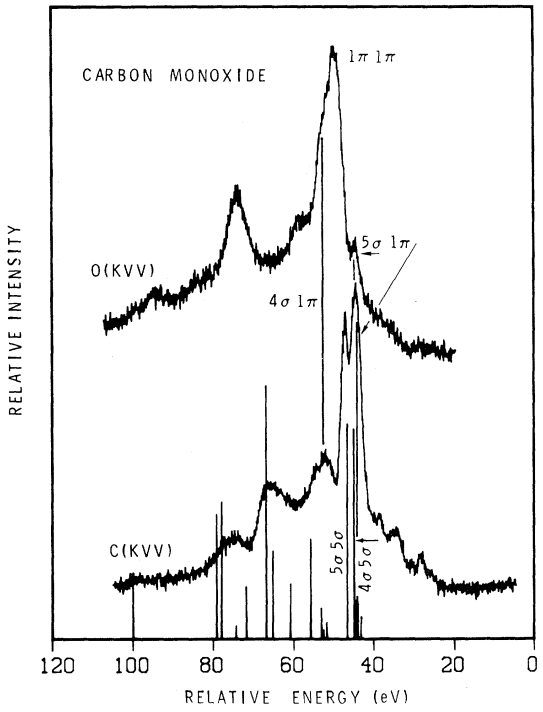

FIG. 1. Theory and experiment for gas-phase CO. Position and amplitudes of the theoretical vertical transitions are indicated by the lower set of lines. The contributions of the 5σ orbital, which is almost a lone pair on the carbon, are greatly diminished in the oxygen spectrum. The alignment of the carbon and oxygen spectra was achieved by subtracting in Eq. (1) the core-hole binding energy from Ref. 6. The triplet state transitions have too little amplitude to be observed. The two shallow transitions common to both spectra are labeled by connecting lines.

In order to study the universality of the C(*KVV*) carbonyl spectrum, we measured the spectra of $Mo(CO)_6$, $Fe(CO)_5$, and $Co(CO)_3NO$ with coordination numbers 6, 5, and 4, respectively. These curves, seen in Fig. 2, may be compared to the C(*KVV*) spectrum of $Cr(CO)_6$ reported by Plummer, Salaneck, and Miller.[6] Since no apparent differences exist, we note that the Auger analysis is a sufficiently local probe that it does not register, from the point of view of the carbon atoms, changes in the metal-atom coordination number. For this reason we may select a computationally simple carbonyl, $Ni(CO)_4$, in order to understand general carbonyl line shapes.

Upon comparing the above gas-phase carbonyls to gas-phase CO, and to the ionization potential shifts of Ref. 6, we find strong evidence to indicate that the final-state holes (in those states

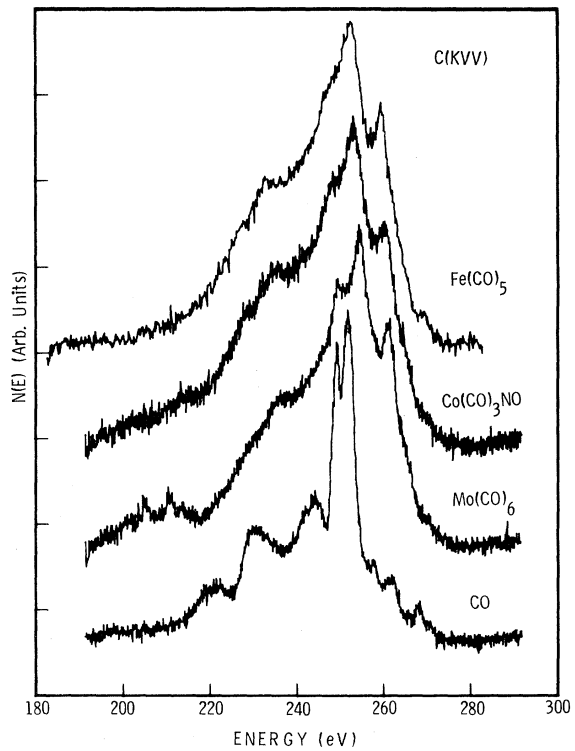

FIG. 2. Carbon *KVV* Auger spectrum of $Mo(CO)_6$, $Fe(CO)_5$, and $Co(CO)_3NO$ compared with CO.

TABLE I. CO and NiCO orbital ionization potentials and electron charge distributions. Orbital atomic and overlap populations are normalized on two electrons per orbital, although only nearest-neighbor overlap populations are shown. I is the ionization potential used in Eq. (1). Orbitals in NiCO are labeled by their parentages since the mixing is not large in the ground state.

			Ground state					Auger initial state (C $1s^{-1}$)				
Molecule	Orbital	I[a] (eV)	Ni	Ni-C	C	C-O	O	Ni	Ni-C	C	C-O	O
CO	5σ	14.0	···	···	1.88	−0.19	0.31	···	···	1.79	0.04	0.17
	1π	16.8	···	···	0.29	0.38	1.34	···	···	0.59	0.38	1.03
NiCO	$3d\sigma$	8.5	1.95	0.02	0.04	−0.01	0.02	1.92	−0.07	0.15	−0.01	0.02
	$3d\pi$	8.5	1.86	0.06	0.03	−0.04	0.11	1.54	−0.07	0.15	−0.01	0.35
	5σ	13.9	0.25	0.50	0.98	0.02	0.30	0.11	0.14	1.01	0.13	0.62
	1π	14.8	0.01	0.00	0.33	0.39	1.26	0.02	0.02	0.63	0.39	0.94

[a]Ref. 6.

producing the major features) are localized on one CO ligand. If the holes are described in terms of molecular orbitals, which are delocalized over all the ligands, a U_{eff} of ~6 eV is calculated. However, the experimentally observed U_{eff} for the singlet $5\sigma^{-1}1\pi^{-1}$ transition of gas-phase $Mo(CO)_6$ is ~11 eV, which may be compared to the CO value of ~13 eV. Since this small difference may be understood in terms of the polarization response of the rest of the molecule, it is incorrect to analyze the Auger lines in terms of orbitals delocalized over all ligands as would result from a calculation on $Ni(CO)_4$. However, we take advantage of the flexibility inherent in the theory as formulated in Eq. (1) and proceed to analyze the spectra using localized orbitals generated by a model NiCO molecule. We note that this localization is consistent with previous theoretical work[9] in that U_{eff}(delocalized) $-U_{\text{eff}}$(localized) ~5 eV is larger than the relevant 5σ and 1π "bandwidths" of $\lesssim 1$ eV.[2]

The changes in the population analysis seen in CO versus NiCO are found in Table I. We find σ donation of $0.5e^-$ per CO and π backbonding of $0.2e^-$ per CO in fair agreement with the calculations of many workers.[1] Upon the introduction of a carbon or oxygen 1s hole, we find pronounced alterations to the charge distributions, as also seen by Loubriel using a multiple-scattering $X\alpha$ (MS$X\alpha$) method.[2] While the predominantly $3d\sigma$ and $3d\pi$ orbitals have too little ground-state charge density on the CO to take a visible part in an Auger decay originating on the ligand, the initial-state populations indicate that a decay producing one hole in a predominantly $3d$ orbital and one on the ligand should be clearly visible in the C(KVV) spectrum, and also, although relatively less intense, in the O(KVV). The initial-state π backbonding is thus directly responsible for the magnitude of the high-energy feature seen in the C(KVV) spectrum. This feature may be viewed as a backbonding-assisted interatomic Auger decay.

We finally note that the level of agreement between carbonyl theory and experiment, shown in Fig. 3, implies that the initial-state configuration was correctly assigned, i.e., that the dominant initial state is the adiabatically relaxed state. Using our 2π orbitals, we find that a change

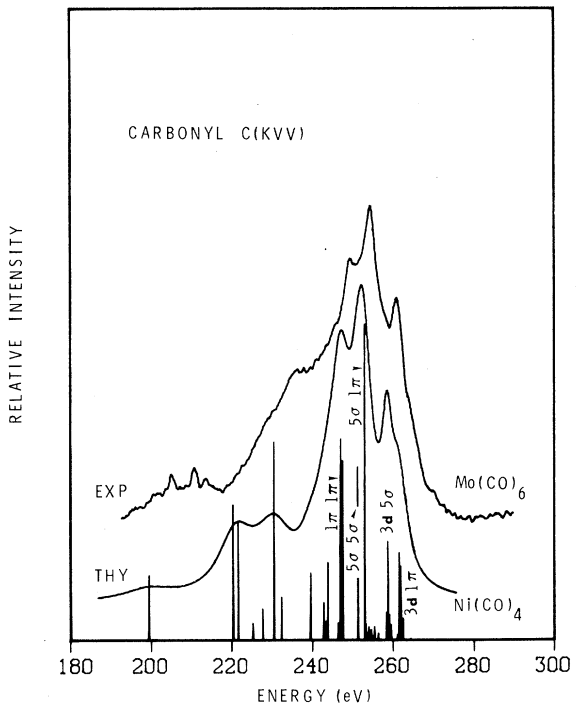

FIG. 3. Theory and experiment are compared for the carbonyl C(KVV) Auger spectrum.

of initial-state configuration to a low-lying shake-up state (such as the $3d\delta^3 2\pi^1)^3$ would alter the relative Auger decay probability for $3d^{-1}$ ($1\pi^{-1}$ or $5\sigma^{-1}$) state creation by a factor of at least 2.4. However, if the 2π were occupied, it would also provide a spectator electron for the $5\sigma 1\pi$ transition and the lower states of Fig. 3 but not for the higher states. Our calculations of hole-hole interactions show that this would shift the energy of $5\sigma 1\pi$ relative to $3d5\sigma$ and $3d1\pi$ by ~ 10 eV, thus destroying the agreement of Fig. 3. Thus the observed magnitude of the "interatomic" decay in the carbon spectrum and the relative energies of the final states both argue against the dominance of the shakeup initial state.

We wish to thank G. M. Loubriel for stimulating discussions, for reading the manuscript, and for pointing out the problem of the initial-state assignments. This was supported by the U. S. Department of Energy under Contract DE-AC04-76-DP00789. Sandia National Laboratories is a U. S. Department of Energy facility.

[1]J. B. Johnson and W. G. Klemperer, J. Am. Chem. Soc. 99, 7132 (1977); B. E. Bursten, D. G. Freier, and R. F. Fenske, Inorg. Chem. 19, 1810 (1980); D. E. Sherwood and M. B. Hall, Inorg. Chem. 19, 1805 (1980); S. Larsson and M. Braga, Int. J. Quantum Chem. 15, 1 (1979).

[2]G. Loubriel, Phys. Rev. B 20, 5339 (1979).

[3]P. S. Bagus and K. Hermann, Surf. Sci. 89, 588 (1979).

[4]R. P. Messmer and S. H. Lamson, Chem. Phys. Lett. 65, 465 (1979), and unpublished.

[5]R. R. Rye, T. E. Madey, J. E. Houston, and P. H. Holloway, J. Chem. Phys. 619, 1504 (1978).

[6]E. W. Plummer, W. R. Salaneck, and J. S. Miller, Phys. Rev. B 18, 1673 (1978).

[7]D. R. Jennison, to be published.

[8]L. S. Cederbaum, W. Domcke, J. Schirmer, W. von Niessen, G. H. F. Diercksen, and W. P. Kraemer, J. Chem. Phys. 69, 1591 (1978), and references therein.

[9]General theories of hole-hole correlation have been based on U_{eff}. See G. A. Sawatzky, Phys. Rev. Lett. 39, 504 (1977); M. Cini, Phys. Rev. B 17, 2788 (1978), and Solid State Commun. 24, 681 (1977), and 20, 605 (1976).

[10]D. R. Jennison, Chem. Phys. Lett. 69, 435 (1980).

[11]S. P. Kowalczyk, R. A. Pollak, F. R. McFeely, L. Ley, and D. A. Shirley, Phys. Rev. B 8, 2387 (1973).

[12]D. R. Jennison, J. A. Kelber, and R. R. Rye, Chem. Phys. Lett. 77, 604 (1981).

[13]M. Dupuis, J. Rys, and H. King, computer code (unpublished), available (catalog no. 10, program no. 336 of 1977) from Quantum Chemistry Program Exchange, Chemistry Building, Room 204, Indiana University, Bloomington, Indiana 47401; T. H. Dunning, Jr., J. Chem. Phys. 53, 2823 (1970); B. Roos, A. Veillard, and G. Vinot, Theor. Chim. Acta 20, 1 (1971). The $(12s, 6p, 5d)$ set was augmented by two p functions of the same exponent as the last two s functions and by a d function as described in P. J. Hay, J. Chem. Phys. 66, 4377 (1977).

[14]D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley, New York, 1970), p. 49.

[15]W. E. Moddeman, T. A. Carlson, M. O. Krause, B. P. Pullen, W. E. Bull, and G. K. Schweitzer, J. Chem. Phys. 55, 2317 (1971).

[16]I. H. Hillier and J. Kendrick, Mol. Phys. 31, 849 (1976). The inappropriateness of this peak assignment is clearly evident as a major transition is assigned to a triplet final state whose amplitude in the absence of spin-orbit coupling is exactly zero.

[17]J. A. Kelber, D. R. Jennison, and R. R. Rye, to be published.