species (T)·H$^+$. This will be discussed in a separate publication.[22]

Stace[13] has reported process 7 but did not observe process 9 which he attributed to a collision-induced decomposition process. This may indicate that process 9 can occur through both unimolecular decomposition and collision-induced decomposition processes since the present work clearly establishes that process 7 also occurs without collisions.

Summary

Three major types of solvated acetone cluster ions $\{[(CH_3)_2CO]_m{\cdot}H^+, m = 1\text{-}15; [(CH_3)_2CO]_m{\cdot}C_2H_3O^+, m = 1\text{-}17;$ and $[(CH_3)_2CO]_m{\cdot}CH_3^+, m = 1\text{-}10\}$ are observed following the photoionization of neutral acetone clusters. The results are in agreement with the findings in the gas-phase ion-molecule chemistry and demonstrate further the similarity of the ensuing ion chemistry of cluster ion systems which occur via analogous internal ion-molecule reactions.[17,18,23] In the case of prompt ion fragmentation, the branching ratios for yielding methylated and protonated cluster species are independent of cluster size. However, the normalized intensities of the acetylated to protonated cluster ions (upper curve, Figure 3) show nearly a smooth and slightly increasing trend as a function of cluster size. In the time window of several tens of microseconds, all three major types of cluster ions undergo unimolecular decompositions by "boiling off" one acetone molecule.

The most exciting and striking finding of the present work is that the presence of trace amounts of water in the system inhibits the dehydration mechanism of protonated acetone cluster ions. These findings explain the apparent discrepancy between earlier studies. Most importantly, the results provide further evidence for the influence of solvation on reactions in clusters.[24,25]

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Registry No. Acetone, 67-64-1.

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(22) Tzeng, W. B.; Wei, S.; Castleman, A. W., Jr. Metastability of Protonated Acetone Cluster Ions, in preparation.
(23) Klots, C. E.; Compton, R. N. *J. Chem. Phys.* **1978**, *69*, 1636.
(24) Morgan, S.; Castleman, A. W.; Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2867.
(25) Garvey, J. f.; Berstein, R. B. *J. Phys. Chem.* **1986**, *90*, 3577.

Temporary Anion States in Nitrosyl Transition-Metal Complexes Studied by Electron Transmission Spectroscopy and Multiple Scattering Xα Calculations

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Abstract: The electron transmission spectra of $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$, and $Ni(\eta^5\text{-}C_5H_5)NO$ have been recorded in the 0-5-eV energy range. The experimental attachment energy values were reproduced by multiple scattering (MS) Xα calculations, using the transition-state procedure. The calculations also predicted four stable anion states in the iron complex and two stable anion states in the cobalt complex. The experimentally observed stabilization of the anion states with prevailing ligand character, with respect to the corresponding anion states in the free ligands, has been found to be consistent with the calculated charge densities in the neutral states, according to which the central metal has a large negative charge, owing to the acceptor capability of the empty 4s and 4p orbitals. The total electron-scattering cross sections have been calculated with the continuum MS-Xα method.

A knowledge of ionization energies (IEs), electron affinities (EAs), and spatial distributions of frontier molecular orbitals (MOs) is relevant for a better understanding of the chemical bond. The valence occupied MOs of transition-metal complexes have been extensively characterized in energy and nature by UV photoelectron spectroscopy and theoretical studies. The complementary information on the vacant energy levels, however, is scarce.

Electron transmission spectroscopy (ETS)[1] is one of the most powerful means for measuring the various vertical EAs of gas-phase molecular systems. This electron-scattering technique takes advantage of the sharp variations in the total electron-scattering cross section caused by resonance processes, that is, formation of temporary anion states. The energies (AEs) at which electron attachment occurs are the negative of the EAs, and, in a Koopmans' theorem sense, they can be associated with the energies of the empty MOs.

We have recently applied ETS to bis π-ligand,[2,3] mixed π-ligand and carbonyl,[4] and carbonyl[5] complexes. The assignment of the resonances observed in the ET spectra to the corresponding anion states was supported by MS-Xα calculations, using the transition-state procedure, which accurately reproduced the experimental EA and IE data, and described the localization properties of the ion states. The significant stabilization of the anion states with

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(1) Schulz, G. J. *Rev. Mod. Phys.* **1973**, *45*, 378.
(2) Modelli, A.; Foffani, A.; Guerra, M.; Jones, D.; Distefano, G. *Chem. Phys. Lett.* **1983**, *99*, 58.
(3) Burrow, P. D.; Modelli, A.; Guerra, M.; Jordan, K. D. *Chem. Phys. Lett.* **1985**, *118*, 328.
(4) Modelli, A.; Distefano, G.; Guerra, M.; Jones, D. *J. Am. Chem. Soc.* **1987**, *109*, 4440.
(5) Guerra, M.; Jones, D.; Distefano, G.; Foffani, A.; Modelli, A. *J. Am. Chem. Soc.* **1988**, *110*, 375.

Table I. Atomic Sphere Radii (au)

	r_{metal}	$r_{\text{C(O)}}$	$r_{\text{O(C)}}$	r_{N}	$r_{\text{O(N)}}$	$r_{\text{C(ring)}}$	r_{H}	r_{out}
$Fe(CO)_2(NO)_2$	2.1596	1.6252	1.6428	1.5429	1.5748			7.2935
$Co(CO)_3NO$	2.1414	1.6066	1.6341	1.5261	1.5490			7.2468
$Ni(C_5H_5)NO$	2.2093			1.5557	1.5849	1.7101	1.2753	6.8308

essentially ligand character upon complexation has been found to be consistent with the charge distributions calculated at the MS-Xα level in the neutral ground states of the complexes.[4,5] These data indicated a strong net transfer of negative charge from the ligands to the central metal atom, in contrast with previous theoretical results.

In the present paper, we extend our ETS and MS-Xα investigation to the nitrosyl complexes $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$, and $(\eta^5\text{-}C_5H_5)NiNO$. As for chromium hexacarbonyl and iron pentacarbonyl,[5] we have also compared the ET spectra with the calculated total scattering cross sections. Owing to the difficulties involved in an accurate description of the electron–molecule interaction,[6] this theoretical method has not been as successful as the transition-state procedure in reproducing experimental AE values. In principle, however, this is a more correct approach toward the ET experiment, and it should also provide information on the intensities of resonance processes.

Experimental Details and Computations

Our electron transmission apparatus is in the format devised by Sanche and Schulz[7] and has been previously described.[8] The present spectra have been obtained by using the apparatus in such a mode as to detect the nearly total scattering cross section,[9] unless otherwise stated. To enhance the visibility of the sharp structures that appear in the scattering cross section because of the formation of temporary anion states, the impact energy of the electron beam is modulated with a small ac voltage, and the derivative of the transmitted current is measured directly by a synchronous lock-in amplifier. The energy scales were calibrated with reference to the $(1s^12s^2)$ ^2S anion state of He. The estimated accuracy is ±0.05 or 0.1 eV, depending on the number of decimal places reported.

Multiple scattering Xα calculations[10,11] were carried out on the complexes at their experimental geometries.[12,13] The values of the local exchange parameters (α) were taken from the tabulation of Schwarz,[14] and a valence-weighted average was employed for the inter- and outer-sphere regions. The radii ratios for the atomic spheres were determined by using the nonempirical procedure of Norman,[15] and their absolute values (see Table I) chosen to satisfy the virial ratio $(-2T/V = 1)$ in the neutral complexes. It is important to point out the importance of this nonarbitrary choice of the atomic radii. Their values, in fact, can affect the calculated energy levels and in some cases even their ordering. The stability of the computed AEs was tested by increasing the charge on the Watson sphere from $+4e$ to $+12e$.

The double-counting correction proposed by Herman[16] was used in the normalization process of the molecular orbitals. Partial waves up to $l = 0$ for H, $l = 1$ for C, N, and O, $l = 3$ for Fe, Co, and Ni, and $l = 4$ for the outer sphere were used, respectively. Core orbitals were not frozen during the SCF procedure, and the potentials converged to better than 5×10^{-3} at any point. Ionization energies and attachment energies were computed with the transition-state procedure.[17] The attachment energies were estimated by using a stabilizing positively charged sphere with a radius twice as large as that of the outer sphere. This radius is sufficiently large to ensure the exclusion of any significant presence of charge outside the stabilizing sphere. If this were not the case, all the anion states would not be stabilized to the same extent.

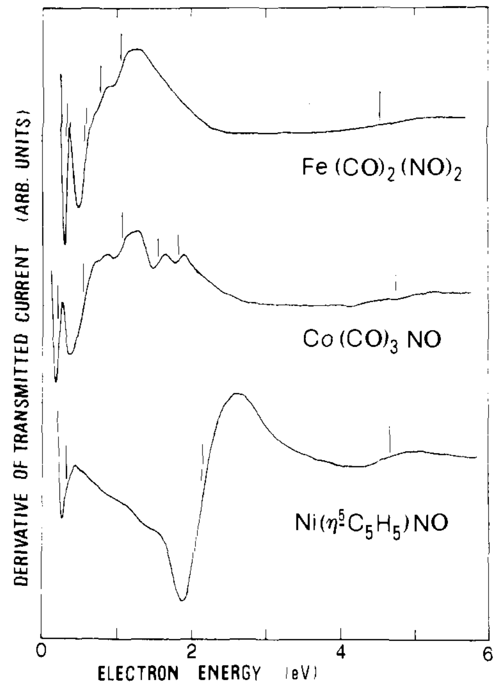

Figure 1. Derivative of the electron current transmitted through iron dicarbonyl dinitrosyl, cobalt tricarbonyl nitrosyl, and nickel cyclopentadienyl nitrosyl vapors, as a function of electron energy.

The cross sections were calculated by using the continuum multiple scattering Xα method (CMS-Xα),[18] at 0.01-eV intervals. The potentials for the continuum calculations were generated from transition-state calculations, according to the method proposed by Davenport et al.[19]

The charge distributions in the neutral molecules were evaluated by partitioning the inter- and outer-sphere charges among the atoms according to the procedure of Case and Karplus,[20] thus avoiding the approximation of attributing all the charge in these regions to the ligands.

The calculations were performed on the VAX 11/780 computer with FPS array processor at the Theoretical Chemistry Group in Bologna.

Results and Discussion

The ET spectra of iron dicarbonyl dinitrosyl, cobalt tricarbonyl nitrosyl, and nickel cyclopentadienyl nitrosyl are shown in Figure 1. The spectra were recorded several times, before and after taking apart and cleaning the monochromator electrodes, on two different ETS instruments with reproducible results. Sample decomposition at the hot filament, in fact, led to metal deposition on the surface of the first electrode, especially for the cobalt complex. However, the absence of signals from the free CO and NO ligands (see Figure 2) in the spectra of the complexes indicates that no significant decomposition occurred in the collision chamber. The spectrum of NO displays a sharp vibrational progression (with an average spacing of approximately 164 meV) starting at about zero energy, which has been assigned to the $^3\Sigma^-$ ground anion state.[21,22] According to photodetachment studies,[23] the ground vibrational component is slightly stable (24 meV). The two

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(6) Lane, N. F. *Rev. Mod. Phys.* **1980**, *52*, 29.

(7) Sanche, L.; Schulz, G. J. *J. Phys. Rev.* **1972**, *A5*, 1672.

(8) Modelli, A.; Jones, D.; Distefano, G. *Chem. Phys. Lett.* **1982**, *86*, 434.

(9) Johnston, A. R.; Burrow, P. D. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *25*, 119.

(10) Schwarz, K. *Adv. Quantum Chem.* **1972**, *6*, 1.

(11) Johnson, K. H. *Adv. Quantum Chem.* **1972**, *7*, 143.

(12) Brokway, L. O.; Anderson, J. S. *Trans. Faraday Soc.* **1937**, *33*, 1233.

(13) Sutton, L. E. *Chem. Soc. London, Spec. Publ.* **1958**, 11.

(14) Schwarz, K. *Phys. Rev.* **1972**, *B5*, 2466.

(15) Norman, J. G., Jr. *J. Chem. Phys.* **1974**, *61*, 4630.

(16) Herman, F. *Electrons in Finite and Infinite Structures*; Phariseau, P., Sheire, L. Eds.; Plenum Press: New York, 1977.

(17) Slater, J. C. In *Computational Methods in Band Theory*; Plenum Press: New York, 1981.

(18) Dehmer, J. L.; Dill, D. In *Electron-molecule and Photon-molecule Collisions*; Rescigno, T., McKoy, V., Schneider, B., Eds.; Plenum Press: New York, 1978.

(19) Davenport, J. V.; Ho, W.; Schrieffer, J. R. *Phys. Rev.* **1978**, *B17*, 3115.

(20) Case, D. A.; Karplus, M. *Chem. Phys. Lett.* **1976**, *39*, 33.

(21) Schulz, G. J. *Rev. Mod. Phys.* **1973**, *45*, 423.

(22) Burrow, P. D. *Chem. Phys. Lett.* **1974**, *26*, 265.

(23) Siegel, M. W.; Celotta, R. J.; Hall, J. L.; Levine, J.; Bennett, R. A. *Phys. Rev.* **1972**, *A6*, 607.

Table II. Experimental and Calculated AEs and IEs in Iron Dicarbonyl Dinitrosyl and the Calculated Transition-State Charge Distributions[a]

	energy		charge distribution, %						
sym (C_{2v})	exptl	Xα	Fe	C	O(CO)	N	O(NO)	int	out
	AE								
A_2	1.05	1.3	4	21	7	0	0	19	49
B_2	0.76	1.0	2	16	8	0	0	31	43
B_1	0.55	0.9	5	17	7	1	1	26	43
A_1	0.31	0.6	6	9	8	1	0	45	31
B_2		−0.7	29	5	2	29	15	19	1
A_1		−0.9	30	0	0	24	13	28	5
A_2		−1.1	16	1	0	37	23	22	1
B_1		−1.2	13	1	1	38	24	22	1
	IE								
A_1	8.56	7.9	56	3	5	6	7	23	0
B_1	8.97	8.0	59	1	5	7	8	20	0
B_2	8.97	8.0	37	4	2	11	18	28	0
A_1	9.74	9.2	69	0	3	3	11	14	0
A_2	9.74	9.2	71	0	4	3	9	13	0

[a] Experimental IE values taken from ref 24.

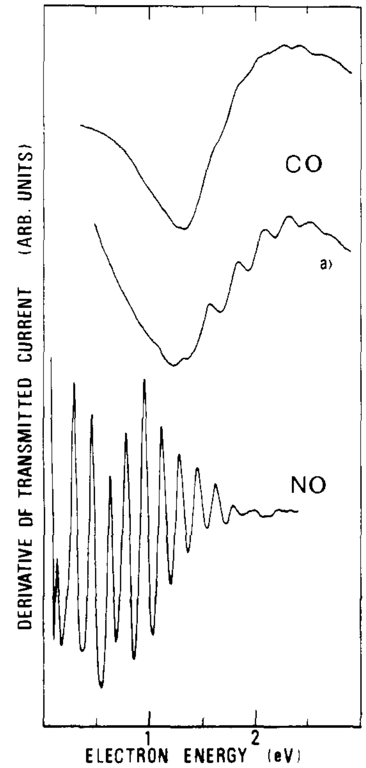

Figure 2. Derivative of the electron current transmitted through carbon monoxide and nitrogen monoxide vapors, as a function of electron energy: (a) spectrum recorded in the "low-rejection mode", that is, correlated to the backscattering cross section.

resonances located at 1.55 and 1.79 eV in the spectrum of the cobalt complex could have indicated the possible presence of free CO. These features are, in fact, unusually sharp, considering their energy range, and very close in energy to the two most intense structures (1.49 and 1.77 eV; see Figure 2) observed in the "low-rejection" (that is, correlated to the backscattering cross section[9]) spectrum of CO. However, in the "high-rejection" spectrum of CO, recorded under the same instrumental conditions used for the complexes, the fine structure of the π^* resonance centered at 1.7 eV is hardly visible, thus indicating that the two highest lying sharp resonances belong to the complex. This is confirmed by both the calculated AEs and cross sections (see below).

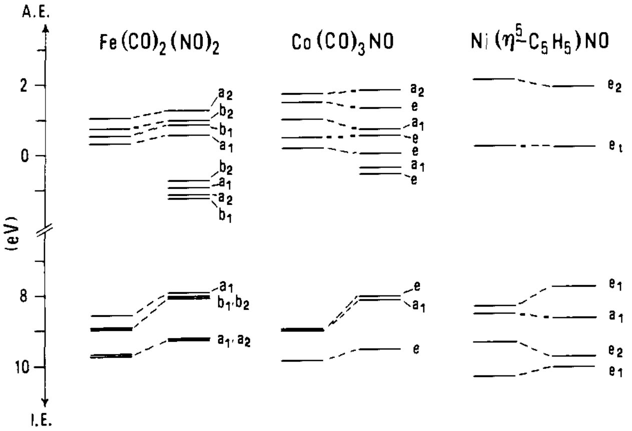

Figure 3. Correlation diagram between experimental (left) and MS-Xα (right) AE and IE values of iron dicarbonyl dinitrosyl, cobalt tricarbonyl nitrosyl, and nickel cyclopentadienyl nitrosyl. Experimental IE values taken from ref 24 and 25.

As far as the reliability of the ET experiment is concerned, it should be pointed out that resonances at very low energy always deserve particular attention. As reviewed by Johnston and Burrow,[9] there are low-energy artifacts inherent to the technique that may be confused with real signals. In the spectra of all three complexes under examination, a resonance partially superimposed on the electron beam signal is present. These features, however, are not shifted in energy by changing the tuning of the instrument and are also detected in the "low-rejection" spectra (not shown here), where retardation cusps are not present at low energy. This makes us confident about the presence of the first resonance observed in the three complexes, in agreement with the results of the calculations (see below).

$Fe(CO)_2(NO)_2$. Each CO ligand possesses a doubly degenerate empty π^* orbital, the NO ligand has one more electron with respect to CO, and the iron atom has one empty d orbital. Eight nondegenerate empty MOs are thus expected at low energy in the C_{2v} symmetry of iron dicarbonyl dinitrosyl. The ET spectrum shows four resonances below 1.1 eV, no signal being observed around 1.7 eV, that is, the energy of the π^* resonance in the free CO ligand. This suggests the occurrence of four stable anion states, not observable in ETS. The experimental AEs, as well as the IEs, are well reproduced by the MS-Xα calculations, using the transition-state procedure, as shown by the correlation diagram of Figure 3. The calculations confirm the presence of four stable anion states and predict a positive EA of 1.2 eV. The experimental and calculated AE and IE values, together with the localization properties of the corresponding ion states, calculated by using the transition-state procedure, are reported in Table II. The four unstable anion states are predicted to be associated with electron capture into empty orbitals of essentially CO character. On the

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(24) Hillier, I. H.; Guest, M. F.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1974**, *27*, 215.

(25) Evans, S.; Guesi, M. F.; Hillier, I. H.; Orchard, A. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 417.

Table III. Experimental and Calculated AEs and IEs in Cobalt Tricarbonyl Nitrosyl and the Calculated Transition-State Charge Distributions[a]

	energy		charge distribution, %						
sym (C_{3v})	exptl	Xα	Co	C	O(CO)	N	O(NO)	INT	OUT
	AE								
A_2	1.79	1.9	1	42	20	0	0	36	1
E	1.55	1.4	3	19	7	0	0	17	54
A_1	1.08	0.8	5	15	6	0	0	26	48
E	0.55	0.6	5	10	11	1	0	49	24
E	0.24	0.1	7	7	5	1	0	49	32
A_1		−0.3	10	6	6	1	0	53	25
E		−0.5	19	2	1	34	21	22	1
	IE								
E	8.90	8.0	53	6	6	4	7	24	0
A_1	8.90	8.1	70	2	6	3	1	18	0
E	9.82	9.5	78	1	5	1	4	11	0

[a] Experimental IE values taken from ref 24.

Table IV. Experimental and Calculated AEs and IEs in Nickel Cyclopentadienyl Nitrosyl and the Calculated Transition-State Charge Distributions[a]

	energy		charge distribution, %						
sym (C_{5v})	exptl	Xα	Ni	C	H	N	O	INT	OUT
	AE								
E_2	2.21	2.0	2	22	0	0	0	19	57
E_1	0.26	0.3	18	6	0	18	16	32	10
	IE								
E_1	8.29	7.7	28	32	0	3	7	29	1
A_1	8.48	8.6	84	1	0	2	0	13	0
E_2	9.30	9.7	94	1	0	0	0	5	0
E_1	10.27	10.0	59	23	0	0	3	14	1

[a] Experimental IE values taken from ref 25.

other hand, the orbitals associated with the four stable anion states are predicted to possess mainly NO character, but with large contributions from the iron atom. Both experiment and calculations indicate the occurrence of a significant EA increase of the ligands upon complexation. In fact, the mean energy (0.7 eV) of the four anion states essentially localized at the carbonyl ligands and the mean energy (−1.0 eV) calculated for the four stable anion states are about 1 eV lower than the energies of the ground anion states in the free CO and NO ligands, respectively. This result is analogous to that previously found for bisbenzenechromium,[3] complexes with mixed π and carbonyl ligands,[4] and carbonyl complexes.[5] For all these complexes, the EA increase of the ligands upon complexation has been found consistent with the net transfer of negative charge from the ligands to the central metal predicted by the charge distributions calculated at the MS-Xα level in the neutral states.[4,5]

The ET spectrum displays a broad low-intensity signal, centered at about 4.5 eV, which is probably to be ascribed to a core-excited shape resonance. In agreement, the calculations do not predict the occurrence of simple electron capture in this energy range.

The calculated IEs are in good agreement with experiment. The calculated localization properties predict a significant contribution of the NO group to all the five outermost MOs, especially for the b_2 orbital. This seems to be in contrast with the relative intensity changes of the low-energy photoelectron bands on going from the He(I) to the He(II) exciting radiations, from which it has been deduced that the two innermost MOs possess mainly NO character.[26] We note, however, that once the effect of the sharply rising base line in the He(I) spectrum is taken into account, these changes do not appear to be very significant. Moreover, Hillier and co-workers have underlined[27] that He(I)/He(II) relative intensity data are subject to a whole series of effects that often render simple rules and trends unreliable for assignment purposes.

$Co(CO)_3NO$. Cobalt tricarbonyl nitrosyl is isoelectronic with iron dicarbonyl dinitrosyl but possesses higher symmetry (C_{3v}). The eight empty orbitals thus transform into three doubly degenerate (e) and two singly degenerate (a_1 and a_2) orbitals. The MS-Xα calculations, however, predict the occurrence of two additional stable (0.5 and 0.3 eV below zero energy) anion states (see Figure 3 and Table III). The number of calculated anion states suggests that electron capture into σ^* (e and a_1) metal–carbonyl empty orbitals also contributes to the observed spectrum. Analogous results were obtained for complexes with similar $-M(CO)_3$ geometry.[4] The agreement between the calculated and experimental AE values is very good. According to the calculated localization properties (see Table III) the ground anion state possesses mainly NO character, but with large contribution from the metal atom. The remaining anion states are predicted to have mainly CO character, their NO character being very small or negligible and their metal contribution decreasing with increasing energy.

Comparison between the energies of the ground anion states in the cobalt complex and in free NO and between the mean energy of the highest lying anion states of the complex with the π anion state of free CO indicates a significant EA increase of the ligands upon complexation, in line with the observation made above for the iron complex.

The calculations do not predict the occurrence of a shape resonance in the energy range of the weak signal observed at about 4.7 eV. This feature is thus ascribed to a core-excited shape resonance.

The MS-Xα calculations also reproduce satisfactorily the IE values. The present iron and cobalt nitrosyl complexes constitute a good test for demonstrating the adequacy of the transition-state procedure in accounting for orbital relaxation occurring during photoionization. Ab initio calculations[24] have, in fact, pointed out that for these complexes the IEs calculated assuming the validity of Koopmans' theorem lead to serious errors and that ΔSCF calculations are necessary for reproducing the experimental observations.

$Ni(C_5H_5)NO$. The open-shell cyclopentadienyl ligand possesses one empty $e_2(\pi^*)$ orbital and one electron vacancy in the filled $e_1(\pi)$ orbital. This Ni complex of C_{5v} symmetry is thus expected to possess only two low-energy (and doubly degenerate) empty orbitals, one with mainly nitrosyl character and the other with

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(26) Guest, M. F.; Hillier, I. H.; McDowell, A. A.; Berry, M. *Mol. Phys.* **1980**, *41*, 519.

(27) Moncrieff, D.; Hillier, I. H.; Saunders, V. R.; von Niessen, W. *Chem. Phys. Lett.* **1986**, *131*, 545.

mainly cyclopentadienyl character. In agreement, the ET spectrum displays two resonances located at 0.26 and 2.21 eV, and no stable anion states are predicted by the calculations. The calculated AE values accurately reproduce experiment, and inspection of the calculated localization properties (see Table IV) confirms that while the higher lying anion state (E_2) is essentially cyclopentadienyl in character, the ground anion state (E_1) mainly possesses nitrosyl character, but with a sizeable contribution from the Ni atom. This suggests strong mixing of the empty π^*(NO) orbital with the filled orbitals of proper symmetry. In spite of the destabilization of the LUMO resulting from this mixing, the ground anion state is at about the same energy as in the free NO ligand. Once again, this is in line with the stabilization of the ligand anion states upon complexation, as observed above for the iron and cobalt complexes.

The ET spectrum of nickel cyclopentadienyl nitrosyl also displays a (probably core-excited) resonance located at about 4.7 eV.

Ab initio calculations have demonstrated that orbital relaxation accompanying ionization from the metal e_2 and a_1 (d) MOs is much larger than that for the two e_1 MOs. Allowing for orbital relaxation by using ΔSCF calculations leads to IE values fairly close to experiment, although the sequence predicted for the first three ionization events is opposite to that deduced experimentally ($E_1 < A_1 < E_2$) from relative band intensities and from the IE shifts produced by ring methylation.[25] The present MS-Xα calculations (see Figure 3 and Table IV) give IE values close to experiment and also reproduce the experimental assignment. Inspection of the calculated localization properties (see Table IV) shows that the a_1 and e_2 filled orbitals are essentially Ni 3d in character, while the two e_1 MOs, associated with the first and fourth ionization events, derive from strong mixing between the nickel and cyclopentadienyl fragment orbitals. It has been pointed out[25] that the first IE value is about 1 eV lower than the $E_1(\pi)$ IE measured in other cyclopentadienyl complexes (about 9.3 eV), and that this could be due to a negative charge density at the ring. In our opinion, this energy shift can be simply explained in terms of the large destabilization experienced by the outermost e_1 orbital, owing to the strong π/d mixing mentioned above. This also accounts for the IE from the innermost e_1 counterpart orbital (which experiences an energy shift in the opposite direction), 1.4 eV higher than the mean IE from the a_1 and e_2 (d) orbitals. Comparison between the energies of ion states essentially localized at the cyclopentadienyl ligand would be more suitable for drawing conclusions about its charge (although final-state effects should also be taken into account). On this point, we note that the energy (2.21 eV) of the $e_2(\pi^*)$ resonance in nickel cyclopentadienyl nitrosyl is about 0.5 eV lower than that of the π^* resonance (associated with essentially cyclopentadienyl orbitals) in ferrocene.[2] This indicates that the ring ligand is more positive in the Ni complex, whereas a comparison of its first IE (8.3 eV) with the mean IE (9.0 eV) from the mainly ring π orbitals of ferrocene would lead to the opposite conclusion.

Charge Distributions. In transition-metal complexes previously studied,[3-5] we observed a significant stabilization of ligand anion states which, for symmetry reasons, do not mix with the metal, with respect to the corresponding anion states in the free ligands. This experimental finding was explained in terms of the charge distributions calculated in the neutral states at the MS-Xα level. The MS-Xα calculations, in contrast with LCAO calculations, predicted, in fact, a large net transfer of negative charge from the ligands to the metal. As mentioned above, the ET spectra indicate a sizeable electron affinity increase of the ligands upon complexation also in the nitrosyl complexes under investigation. This experimental finding could in principle be due to several factors, as, for instance, final-state effects (that is, the repulsive effect of adding an electron is likely to be smaller in the complex than in the free ligand, due to the greater delocalization of the extra electron in the former) or to neutral-state effects, such as a positive charge density at the ligands. The charge densities calculated in the neutral states at the MS-Xα level are consistent with the observed ligand anion state stabilization. A positive charge density is, in fact, calculated for all the ligands, while the central metal is predicted to have a large (about 0.7*e*) negative charge. In particular, as shown in Table V, the calculations predict the occurrence of a transfer of negative charge from the metal d orbitals to the ligands, but an even larger one from the ligands to the empty 4s and 4p metal orbitals, thus pointing out the importance of the role played by the latter orbitals in the chemical bond. These theoretical results are in line with the linear MNO geometry in the present complexes. The nitrosyl ligand, in fact, coordinates (formally) as NO^+ to give a linear MNO group or as NO^- with a MNO angle of about 120°. In agreement, the bond angle affects chemical and physical properties correlated to the charge distribution, such as the susceptibility of nitrogen to electrophilic attack in the bent form and the nitrogen NMR chemical shift.[28] It is to be noted that once again the MS-Xα results are opposite to those predicted by LCAO methods. According to ab initio calculations,[24,29] in fact, the metal atom has a large positive charge (Fe +1.0*e*, Co +0.6*e*, Ni +0.8*e*), and the ligands (mainly NO in the iron and cobalt complexes and the cyclopentadienyl ring in the nickel complex) a large negative charge. Of course, the hypothesis of an ionic $(C_5H_5)^-(NiNO)^+$ bond in the nickel complex derived from these calculations[29] can be dismissed on the basis of the present results. We have already suggested[5] two possible sources of the systematic discrepancies in the calculated charge densities between the two theoretical approaches.

Table V. Calculated Charge Densities in the Neutral Ground States of Iron Dicarbonyl Dinitrosyl, Cobalt Tricarbonyl Nitrosyl, and Nickel Cyclopentadienyl Nitrosyl[a]

	metal	nitrosyls	carbonyls	C_5H_5
$Fe(CO)_2(NO)_2$	−0.75 ($d^{7.29}s^{0.40}p^{0.95}f^{0.14}$)	+0.54	+0.22	
$Co(CO)_3NO$	−0.78 ($d^{8.22}s^{0.45}p^{1.01}f^{0.10}$	+0.36	+0.42	
$Ni(C_5H_5)NO$	−0.74 ($d^{9.21}s^{0.57}p^{0.82}f^{0.14}$)	+0.29		+0.45

[a] The numbers in parentheses give the metal orbital populations above [Ar].

Calculated Scattering Cross Sections. Although MS-Xα calculations using the transition-state procedure, where all the states are shifted to lower energy and treated as bound states, have been shown to closely reproduce the experimental AE values in transition-metal complexes,[2-5] direct calculation of the electron–molecule scattering cross section is, in principle, a more correct theoretical approach toward the ET experiment. Although an accurate description of electron-molecule interactions presents difficulties,[6] it is worth exploring the reliability of this approach. Dehmer and Dill[18] have demonstrated that the continuum multiple scattering Xα method satisfactorily reproduces the scattering cross section in diatomic molecules. In larger molecular systems, such as $Cr(CO)_6$ and $Fe(CO)_5$, we obtained less accurate results.[5] It is to be recalled that the calculations are performed with fixed nuclei. As a consequence, the Franck–Condon profile is lost, the resonance width being determined only by the shape of the potential (that is, by the anion lifetime). For each complex, the calculations were carried out using the transition-state potential corresponding to occupation of the lowest unoccupied MO for describing the short-range electron–molecule interactions. For the Ni complex, we verified that the choice of a different transition-state potential (e.g., e_2) does not significantly change the results. Figure 4 reports the derivative with respect to energy (to facilitate comparison with the ET experiment) of the total scattering cross sections calculated in iron dicarbonyl dinitrosyl, cobalt tricarbonyl nitrosyl, and nickel cyclopentadienyl nitrosyl. The calculated cross sections present striking features, for opposite reasons. The energies of the resonances are in excellent agreement with the ET spectra (the maximum deviation is 0.2 eV), and their assignment is the same as that obtained with the transition-state calculations. An additional result consists in the predicted relative intensities, which closely parallel experiment. Regarding this, the

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(28) Bell, L. K.; Mingos, D. M. P.; Tew, D. G.; Larkworthy, L. F.; Sandell, B.; Povey, D. C.; Mason, J. *J. Chem. Soc., Chem. Commun.* **1983**, 125, and references therein.

(29) Hillier, I. H.; Saunders, V. R. *Mol. Phys.* **1972**, *23*, 449.

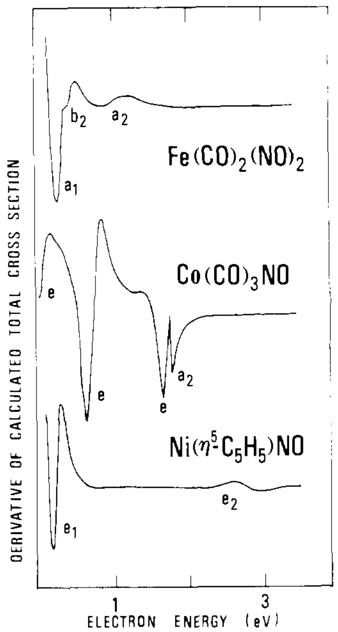

Figure 4. Derivative of the calculated total electron-scattering cross section in iron dicarbonyl dinitrosyl, cobalt tricarbonyl nitrosyl, and nickel cyclopentadienyl nitrosyl, as a function of electron energy.

only serious discrepancy relates to the two resonances in nickel cyclopentadienyl nitrosyl. However, the small intensity of the first resonance in the ET spectrum could, at least in part, be due to its overlap with the intense electron beam signal. On the other hand, the exceptional correspondence of these theoretical results with experiment is counterbalanced by the nearly total absence of signal in the b_1 channel for the iron complex and in the a_1 channel for the cobalt complex, so that the calculations do not reproduce the second and third resonances, respectively, in these two complexes. These two resonances were not found by the calculations even using the corresponding transition-state potentials. The results could probably improve by using higher angular momentum basis functions in the atomic and outer-sphere regions.

Conclusions

The present MS-Xα calculations, including the correction of the overlap between atomic spheres, closely reproduce the AE values measured in the ET spectra of the nitrosyl transition-metal complexes under investigation. Iron dicarbonyl dinitrosyl and cobalt tricarbonyl nitrosyl are predicted to have a positive EA of 1.2 and 0.5 eV, respectively. According to the calculated localization properties, in all three complexes the ground anion state possesses mainly nitrosyl character, but with a large contribution from the metal atom.

The calculated electron–molecule total scattering cross sections display features with energies and relative intensities in good agreement with experiment and reproduce the assignment given by the transition-state calculations. This approach, however, did not detect one resonance in the iron and cobalt complexes.

The experimentally observed stabilization of the anion states with mainly ligand character, with respect to the free ligands, is consistent with the sizeable net transfer of negative charge (about 0.7*e*) from the ligands to the metal predicted by the charge densities calculated for the neutral ground states of the complexes. These results are in line with those previously obtained in ETS and MS-Xα studies of transition-metal complexes and in contrast with the charge densities calculated with LCAO methods.

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^{27}Al Cross Polarization of Aluminas. The NMR Spectroscopy of Surface Aluminum Atoms

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Abstract: The selective cross polarization of surface aluminum atoms is demonstrated and applied to γ- and α-aluminas. The relatively high hydration levels of the γ-alumina surface (out of the bottle) allow the observance of two surface species. Upon dehydration only one, somewhat broader resonance, with lower signal-to-noise ratio, can be resolved. Upon extensive dehydration this signal disappears. By comparison to Boehmite and α-alumina, these resonances are assigned to surface octahedral sites (3.0 ppm) and tetrahedral sites ($\sim$62.0 ppm). All chemical shifts are reported relative to Al(NO$_3$)$_3$$\cdot xH_2$O. It is demonstrated that these resonances represent surface Brønsted sites, and that they are not contaminated by Lewis acid sites or subsurface species. The Lewis acid sites can be selectively observed by replacing the surface hydroxyl protons with deuterons and adsoring a Lewis base probe, pyridine, on the surface. In this case the ^{1}H's on the pyridine provide the polarization for the ^{27}Al resonance. The α-alumina used in this study appears to have a low number of surface hydroxyls concomitant with its low surface area (5.5 m^2/g). This is reflected in the low (relative to γ-alumina) ^{27}Al signal-to-noise ratio obtained with this sample. Overall, this approach appears to be an excellent way to nondestructively characterize these surfaces. More importantly, the success of surface selective cross polarization methodology illustrates that other nuclides are equally amenable to such experiments, and that this approach could be very useful as a general surface chemistry method for characterization of surfaces.

NMR spectroscopy has proven to be a powerful tool for the elucidation of molecular structures in a wide variety of conditions and phases. An area which has not received the attention it should is the application of solid-state NMR methods to the selective observation of the surface of systems of catalytic interest. The essential goals of such research would be the characterization of surfaces, structural identification, quantifying molecular motion, and following surface chemistry, while not being hampered by resonances associated with the bulk material. In a series of seminal papers,[1-7] Sindorf and Maciel have directly addressed some of these

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