Appendix

The Wolfsberg–Helmholz EH calculations with self-consistent charge and configuration (SCCC) were performed on $Fe(C_5H_5)_2$ using a model with D_{5h} symmetry and the following bond distances: $d(C-C) = 1.42$ Å, $d(C-H) = 1.1$ Å, $d(Fe-$center of $C_5H_5) = 1.65$ Å.

The multiexponential radial functions of Richardson[25] were used for 3d, 4s, and 4p orbitals of Fe. Double ζ orbitals of Sakai and Anno[26] were used for 2s(C) and 2p(C) with $H_{2s2s}(C) = -21.4$ eV and $H_{2p2p}(C) = -11.4$ eV. For hydrogen $\zeta = 1.2$ and $H_{1s1s} = -13.6$ eV were chosen. The SCCC iterations for the Fe H_{ii}'s were performed with the parameter set of Basch et al.[27]

In Tables II and V only one representative of degenerate MOs is listed. Also, only coefficients for one selected carbon (C_1) and hydrogen (H_1) are given. Coefficients for the remaining representatives of degenerate MOs and for the remaining carbon and hydrogen atoms are then determined by the D_{5h} symmetry of the ferrocene molecule. The notation π for $2p_z(C)$ and σ for $2p_x$ and $2p_y(C)$ refers to the planar ligand C_5H_5.

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Interaction between Matrix Isolated Nickel Difluoride and Carbon Monoxide. An ab Initio Molecular Orbital Study

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Abstract: The interaction between Ar matrix isolated NiF_2 with CO is studied by an ab initio molecular orbital method. First the electronic structures of NiF_2, CO, and CO^+ are investigated using a Gaussian lobe basis set. The NiF_2 bond angle is found to be 162° in good agreement with the experimental determination; also the NiF bond has a slightly covalent character. The electronic structure of NiF_2CO is then determined and the emphasis is put on the modification of the CO bond from free CO to NiF_2CO. It is shown that the presence of the dipositive nickel atom induces a polarization of the charges leading to a strengthening of the bond. This is consistent with the experimental observation of a 70-cm^{-1} shift of the CO frequency toward higher wavenumbers. Comparison of the dipole moment of the "complex" with the component dipoles shows equally a polarization effect on the CO bond.

I. Introduction

Coordinately unsaturated metal dihalides and diatomic molecules isolated in rare gas matrices can interact as has been

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shown by infrared spectroscopy.[12] If the effect of the matrix on each member of the associated species is known from a separate experiment,[2,4] it is then possible to determine what modifications of the spectra are due to the intermolecular forces.

The goal of the present work is to study the interaction of

Table I. CO and CO$^+$ SCF Orbital and Total Energies for $^1\Sigma^+$ and $^2\Sigma^+$ Ground States[a]

	CO, au	CO$^+$, au
1σ	−20.7195	−21.2130
2σ	−11.4466	−12.0451
3σ	−1.5866	−2.0213
4σ	−0.8052	−1.1934
π	−0.6689	−1.0816
5σ	−0.5767	−1.1415
Total energy	−112.6043	−112.0571

[a] Calculations were performed at the experimental equilibrium internuclear distance of 2.132 au. 1 au (energy) = 27.21 eV; 1 au (distance) = 0.5292 Å.

Table II. CO and CO$^+$ SCF and CI Energy as a Function of Internuclear Distance[a]

R_{CO}	E_{CO}	E_{CO^+}
1.932	−112.5548	−112.0197
	(−112.7175)	(−112.1349)
2.132	−112.6043	−112.0571
	(−112.7175)	(−112.1971)
2.232	−112.6069	−112.0555
	(−112.7266)	(−112.2063)
2.332	−112.6000	−112.0466
	(−112.7256)	(−112.2040)

[a] CI values are in parentheses. Energies and distances are in atomic unit.

NiF$_2$ and CO by means of molecular orbital theory using an ab initio self-consistent field (SCF) approach. The experimental results[2] show that both the spectra of NiF$_2$ and CO are modified in an argon matrix. In particular, the CO stretching frequency is shifted toward higher wavenumbers by about 70 cm^{-1} which makes it closer to the frequency of free CO$^+$. The effect of the matrix on CO alone is known to be a shift of a few wavenumbers.[4] In this work, the electronic structures of CO$^+$, CO, NiF$_2$, and NiF$_2$CO are studied, with emphasis being placed on modifications of the CO bond in going from CO to NiF$_2$CO.

II. Methods

The calculations are of a restricted SCF type using a contracted Gaussian lobe function basis. Orbitals for carbon, oxygen, and fluorine have already been reported,[5] and of these, the five-term p orbitals are split into two groups, (1,2,3) and (4,5). Although this splitting does not affect the energy of the atoms, it could play a part in molecular binding. Qualitatively, nickel fluoride is assumed to have an electronic structure similar to Ni^{2+} (F$^-$)$_2$. The fluorine basis was taken to be that of the negative ion.[6a] For Ni^{2+}, the Gaussian lobe basis set was deduced from the contracted 9s, 5p, 3d Gaussian basis set by Roos et al.,[6b] augmented by another s component and p component as given by Basch et al.[7,8] Summarizing, the basis groups (contractions) for nickel are as follows: s, (1,2,3,4,5) (6,7), (8,9) (10); p, (1,2,3) (4,5) (6); d, (1,2) (3). The Ni^{2+} energy of −1499.4044 au found in ref 6b is lowered to −1500.3113 au by adding the two s and p components. For comparison, Clementi's double ζ basis set leads to an energy of −1506.3702 au, and the principal source of error in the present basis lies in the inner shell orbitals.

Configuration interaction (CI) studies employed the scheme due to Whitten and Hackmeyer.[9]

III. Results and Discussion

Carbon Monoxide. Carbon monoxide and CO$^+$ are studied, and energies are computed at various internuclear distances. Effects of a limited CI have also been taken into consideration.

Table III. CO and CO$^+$ Minimum Energy, Equilibrium Internuclear Distance, and Force Constant

		R_{CO}, au	E, au	k, mdyn/Å
	Calcd SCF	2.20	−112.6073[b]	16.10
CO	Calcd CI	2.27	−112.7275	15.80
	Exptl	2.132[a]	−113.377[c]	18.55[d]
	Calcd SCF	2.16	−112.0577	16.29
CO$^+$	Calcd CI	2.26	−112.2068	17.88
	Exptl	2.1074[a]	−112.8621[d]	19.22[d]

[a] Reference 11. [b] The present value obtained with a [30/10] basis should be compared to the following: (1) the Hartree–Fock limit −112.8211 au (C. Hollister and O. Sinanoglu, *J. Am. Chem. Soc.*, **88**, 13 (1966)); (2) −112.6762 au, a [42,20] calculation made at R = 2.132 au by H. Basch, M. B. Robin and N. A. Kuebler, *J. Chem. Phys.*, **47**, 1201 (1967), and (3) −112.550 au, a [24/8] calculation made at R = 2.175 au by J. Demuynk and A. Veillard, *Theor. Chim. Acta*, **28**, 241 (1973). [c] B. J. Ransil, *Rev. Mod. Phys.*, **32**, 239 (1960). [d] Calculated from experimental data: 2170 cm^{-1} (CO stretching), 2214 cm^{-1} (CO$^+$ stretching), and 14.01 eV (ionization potential), as given by G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. I, Van Nostrand, Princeton, N.J., 1950.

Table I shows the calculated SCF eigenvalues of CO at the experimental equilibrium internuclear distance for the $^1\Sigma^+$ state, and these agree fairly well with results already published.[10] Table I also gives values for the $^2\Sigma^+$ state of CO$^+$ (at the same internuclear distance as in CO). Orbital energies are lowered significantly on the loss of one electron, and the 5σ and π orbitals change order. This is in agreement with results of Sahni et al.,[11] who report an unrestricted Hartree–Fock treatment. Table II gives the energies of CO and CO$^+$ as a function of the internuclear distance. In the CI calculations using SCF MOs, two orbitals were kept in an invariant core. For the $^1\Sigma^+$ state of CO, 11 orbitals outside the core were selected for the generation of configurations from 6 parents (see ref 9). For the $^2\Sigma^+$ state of CO$^+$, 9 such orbitals were included. Finally, 158 determinants were generated for the $^1\Sigma^+$ state and 111 for the $^2\Sigma^+$ state. In both cases the energy is lowered by a little more than 0.1 au from the SCF value. The vertical ionization energy at R = 2.132 au goes from 14.9 eV at the SCF level to 14.2 eV on CI, the observed value being 14.01 eV.[10] The dipole moment goes from −0.256 (SCF) to −0.076 au (CI), the observed value being −0.047 au (0.12 D), the negative sign indicating the orientation C$^-$ O$^+$.

The equilibrium bond length, minimal energy, and force constants have been calculated using a polynomial fit to the energy curve for the SCF and CI calculations; results are tabulated in Table III. The observed bond length decrease and force constant increase in going from CO to CO$^+$ are reflected qualitatively by both the SCF and CI calculations.

Figure 1 shows the 5σ, weakly antibonding orbital, density. Figure 2 gives the total density difference, $\rho(CO) - \rho(CO^+)$, showing a depletion of electrons near the C and O nuclei. Mulliken population analyses of CO and CO$^+$ are given in Table IV. In CO$^+$, the loss of one electron is mostly felt by the σ population of the carbon (−0.85 e) and little by the σ population of the oxygen (−0.15 e), which is not surprising since the 5σ orbital is mainly localized on the carbon atom. However, there is a redistribution of the π population, reducing the net loss of charge of the carbon to 0.7 e, and lowering the difference of π charge between carbon and oxygen. This is consistent with an increase of the force constant in going from CO to CO$^+$.

Nickel Difluoride. Self-consistent field calculations have been performed for different angular conformations of NiF$_2$ with the NiF internuclear distance fixed at R = 3.79 au.[12] The ground state was found to be a triplet and Table V gives the energy as a function of bond angle. Fitting these points by a polynomial leads to an equilibrium bond angle of 161.6°. The
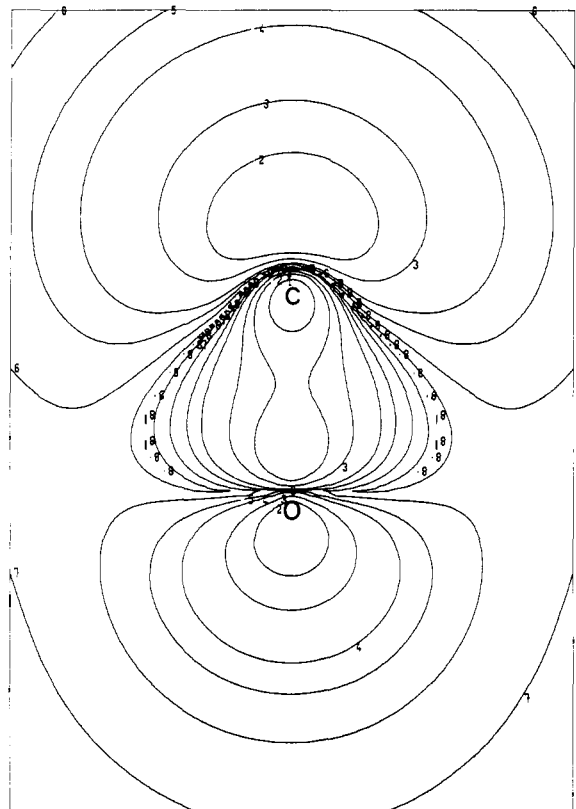
Figure 1. Density contour of the 5σ molecular orbital of CO in the xy plane. Density range from 0.4 to 1×10^{-5} e/(au)^3. Level 8: denotes zero density contour.
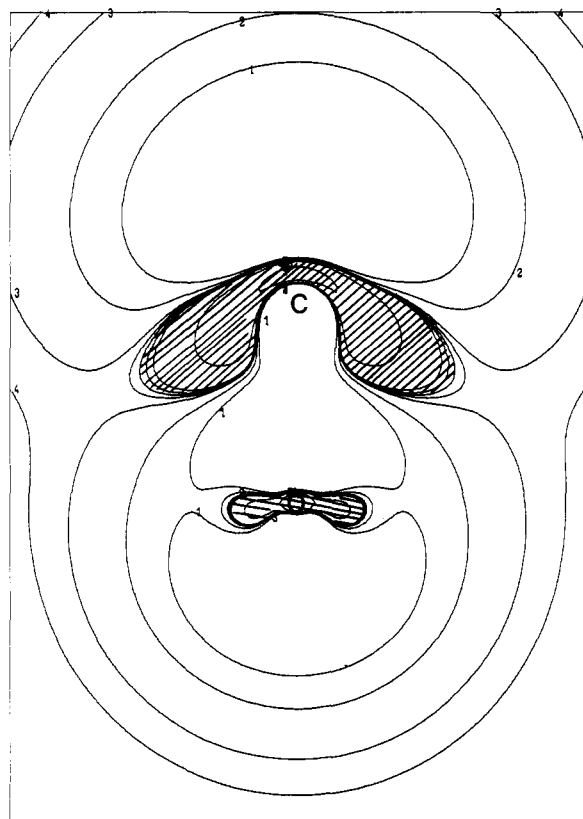

Figure 2. Difference of total density, $\rho[CO] - \rho[CO^+]$, in the xy plane. Density range from 0.01 to -0.04 e/(au)^3. Negative density denoted by ruled areas.

Figure 3. Orbital energy levels of F$^-$, Ni^{2+}, and NiF$_2$.
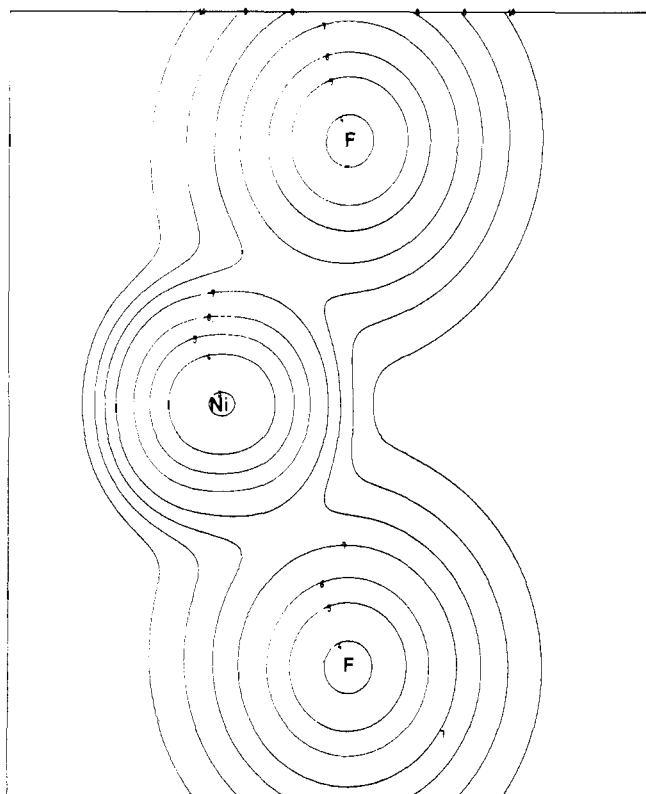
Figure 4. Nickel difluoride total density in the xy plane. Density range from 5 to 1×10^{-4} e/(au)^3.

Table IV. CO and CO$^+$ Population Analysis for $R = 2.132$ au[a]

	s population on carbon	p population on carbon	s population on oxygen	p population on oxygen
CO	3.619	1.876	3.893	4.612
	(3.605)	(1.895)	(3.894)	(4.607)
CO$^+$	3.084	1.711	3.956	4.249
	(3.049)	(1.870)	(3.948)	(4.133)

[a] CI values are in parentheses.

Table V. NiF$_2$ Energy vs. Bond Angle

θ, deg	E, au
152	$-1698.245\ 59$
166	$-1698.259\ 56$
180	$-1698.198\ 02$

infrared spectra of NiF$_2$ trapped in an Ar matrix reveals natural isotope shifts of the NiF antisymmetric stretching frequency.[3] From these shifts the bond angle was calculated as
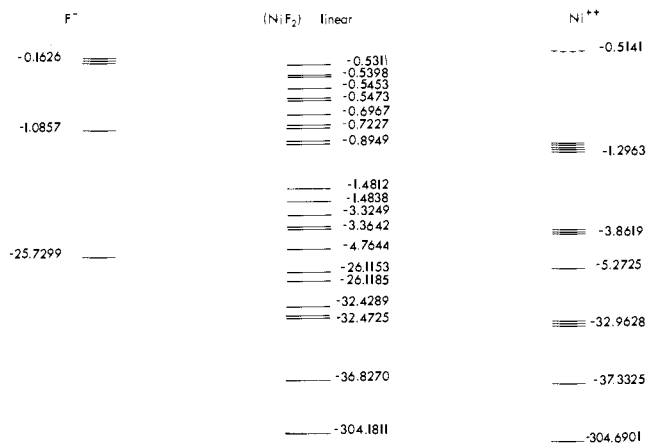
Table VI. NiF_2 Population Analysis ($\theta = 152°$)

	Ni						F		
1s	2.000	$2p_x$	1.949	$3d_{x^2}$	1.566	s	0.939	p_x	1.970
2s	1.997	$2p_y$	1.949	$3d_{y^2-z^2}$	1.454	s'	1.032	p_y	1.969
3s	1.992	$2p_z$	1.949	Subtotal	3.020	s''	2.029	p_z	1.985
4s	0.118	Total 2p	5.847	$3d_{xy}$	1.996	Total	4.000	Total	5.924
Total	6.107	$3p_x$	2.052	$3d_{xz}$	1.030				
		$3p_y$	2.050	$3d_{yz}$	1.999				
		$3p_z$	2.051	Subtotal	5.025				
		Total 3p	6.153	Total d	8.045				
		Total p	12.000						
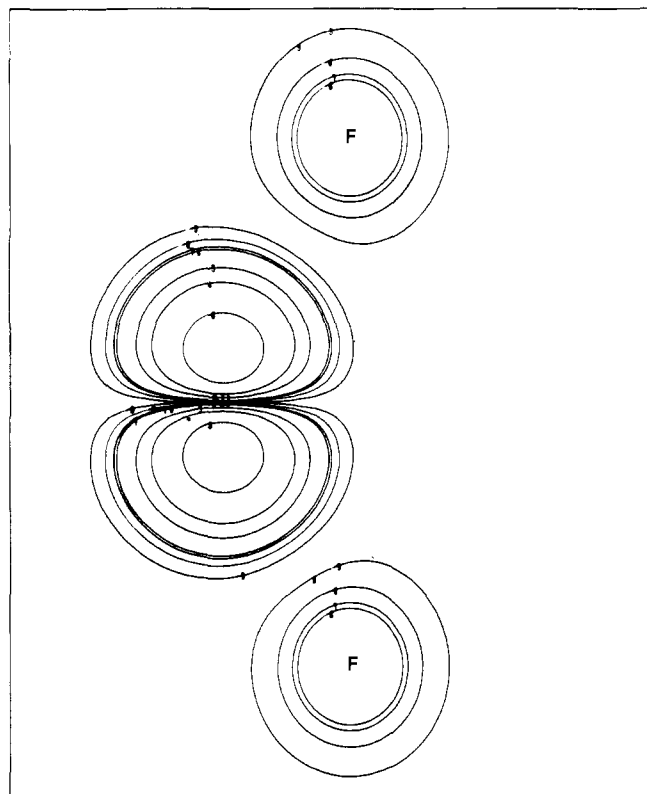
Figure 5. Nickel difluoride a_2 open shell orbital. Density contour in the $Z = 1$ plane; density range from 0.5 to 5 × 10^{-5} e/(au)^3.

Figure 6. Nickel difluoride a_1 open shell orbital. Density contour in the xy plane; density range from 0.5 to 5 × 10^{-5} e/(au)^3.

152° neglecting anharmonicity. If anharmonicity is taken into account, the angle is found to be in the range 157-164°,[3] and thus there is good agreement between the experimental and theoretical value. The calculated minimum energy is −1698.263 30 au showing that the NiF_2 species is bound with respect to Ni^{2+} + 2F$^-$ taken at infinite separation. The stabilization energy is 569.7 kcal/mol which compares fairly well with the thermodynamic estimate of 655 kcal/mol.[13]

In Figure 3, an orbital energy diagram depicts the combination of Ni^{2+} and F$^-$ levels to give the orbital energies of NiF_2 for a linear FNiF structure. Of the two singly occupied orbitals, one is of dσ-pσ type and the other dπ-π. The fluorine energy levels are lowered on approaching Ni^{2+} and those of the nickel levels are raised. The fluorine nickel bond acquires some covalent character and the 4s orbital of nickel, which was empty in Ni^{2+}, now participates in the bonding. In the case of a bent configuration of C_{2v} symmetry, the two singly occupied orbitals are now of a_1 and a_2 symmetry. Qualitatively, these can still be described as of dσ-pσ and dπ-pπ type although the a_1 symmetry contains some s, p_y, and p_x character. In Table VI is summarized the population analysis of bent NiF_2 with $\theta = 152°$. The s plus d total population of nickel increases by an amount 0.152 e compared to Ni^{2+}, equal to the pσ and pπ

electron loss of the fluorine atoms, while the p population of Ni remains the same. Density contours in Figures 4-6 emphasize the quasi-linearity of the molecule (here $\theta = 152°$) and the nearly atomic character of the two singly occupied orbitals; $\phi(a_2) = d_\pi - \lambda(p_\pi^F + p_\pi^{F'})$ and $\phi(a_1) = d_\sigma - \lambda'(p_\sigma^F + p_\sigma^{F'})$ where λ and λ' are small.

NiF_2CO. Analysis of the IR spectrum of NiF_2CO in an argon matrix shows that the carbonyl is bonded to the nickel atom through carbon.[2] NiF_2CO is a planar system of C_{2v} symmetry. In the molecule, both the NiF_2 and CO stretching frequencies are perturbed, the CO frequency increasing from 2148 to 2214 cm^{-1}. As suggested previously by other authors,[14] it is of interest first to determine the modification of the CO bond vibration due to its incorporation into NiF_2CO. We have performed an approximate vibrational analysis of NiF_2CO using Wilson's[15] FG matrix method and have calculated the change in the CO frequency by perturbation theory with a diagonal force field. Keeping the CO force constant equal to 18.55 mdyn/Å, and choosing the NiC force constant to have

Table VII. NiF_2CO. Energy vs. Ni⋯C Distance

$R_{Ni⋯C}$, au	E, au
3.80	−1810.7484
4.25	−1810.7528
4.48	−1810.7511

Table VIII. NiF$_2$CO Mulliken Population Analysis. $R_{Ni\cdots C}$ = 4.25 au, CO Direction along y Axis

	Ni					F			C			O	
1s	2.000	2p$_x$	1.949	3d$_{x^2}$	1.585	s	0.939	p$_x$	1.972	s	3.354	s	3.950
2s	1.997	2p$_y$	1.949	3d$_{y^2-z^2}$	1.444	s'	1.032	p$_y$	1.972	p$_x$	0.608	p$_x$	1.402
3s	1.992	2p$_z$	1.949	Subtotal	3.029	s''	2.028	p$_z$	1.988	p$_y$	0.992	p$_y$	1.722
4s	0.077	Subtotal	5.847	3d$_{xy}$	1.988	Total	3.999	Total	5.932	p$_z$	0.616	p$_z$	1.392
Total	6.066	3p$_x$	2.052	3d$_{xz}$	1.025					Total	5.570	Total	8.466
		3p$_y$	2.052	3d$_{yz}$	1.992								
		3p$_z$	2.051	Subtotal	5.005								
		Subtotal	6.155	Total	8.034								
		Total	12.002										
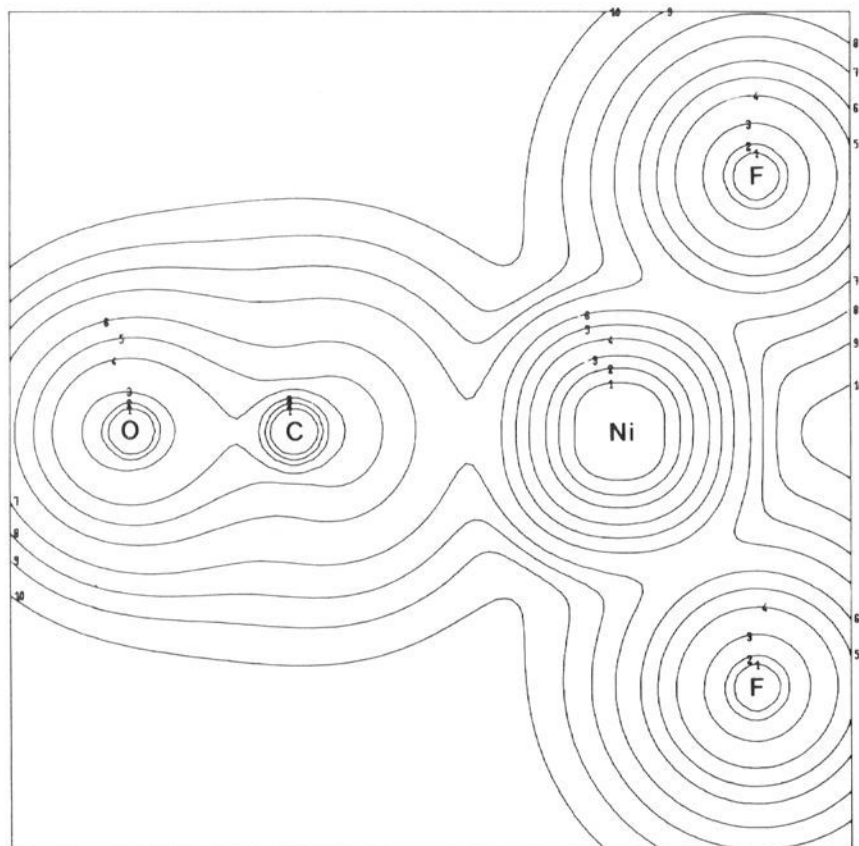
Figure 7. NiF$_2$CO total density in the xy plane. Density range from 4 to 4×10^{-3} e/(au)^3.
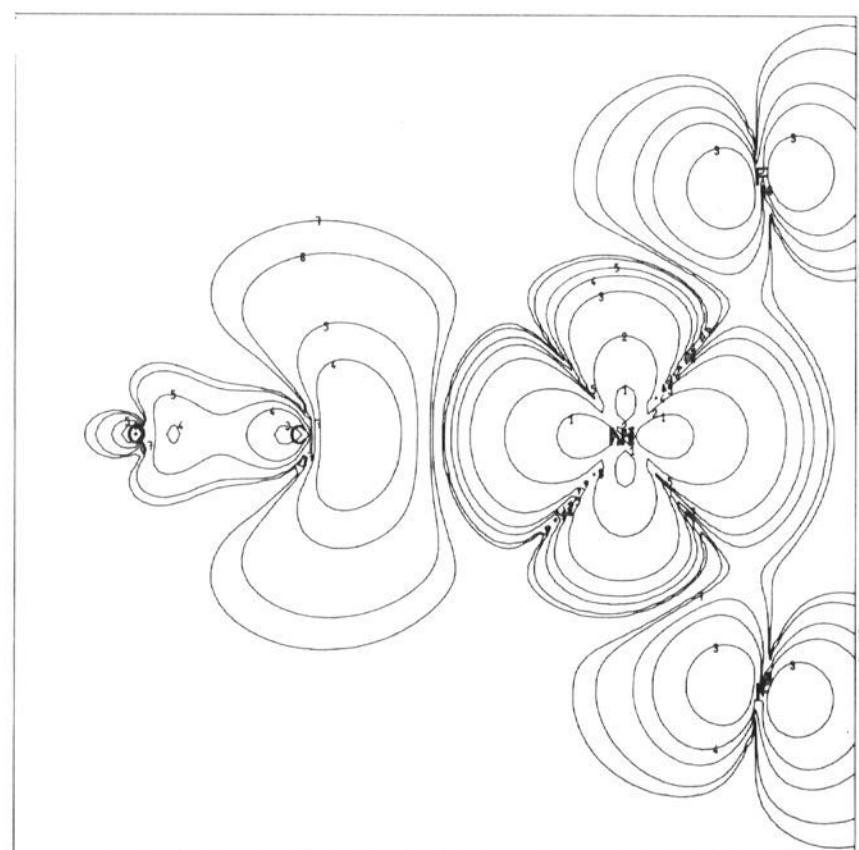
Figure 8. NiF$_2$CO a$_1$ open shell orbital. Density contour in the xy plane. Density range from 0.4 to 5×10^{-5} e/(au)^3.

Table IX. CO Comparative Population Analysis

Molecule	s + p$_\sigma$ on carbon	s + p$_\sigma$ on oxygen	π on carbon	π on oxygen
CO	4.491	5.509	1.004	2.996
NiF$_2$CO	4.346	5.672	1.224	2.794
CO$^+$	3.642	5.358	1.153	2.691
	0.7	0.3		
CO^a	4.3	5.6		

^{a} Estimated value, derived from CO$^+$.

Table X. CO, NiF$_2$, and NiF$_2$CO Dipole and Quadrupole Moment Components Relative to the Center of Mass, from SCF Calculations^a

	y	xx	yy	zz
CO	−0.256	−7.8267	−10.1067	−7.8267
	(−0.096)	(−7.5271)	(−9.0805)	(−7.5271)
NiF$_2$	+3.219	−16.1696	−35.1792	−15.1208
NiF$_2$CO	+3.716	−43.9253	−32.8349	−23.6806

^{a} Values are in atomic units. Results in parentheses are from ref 10.
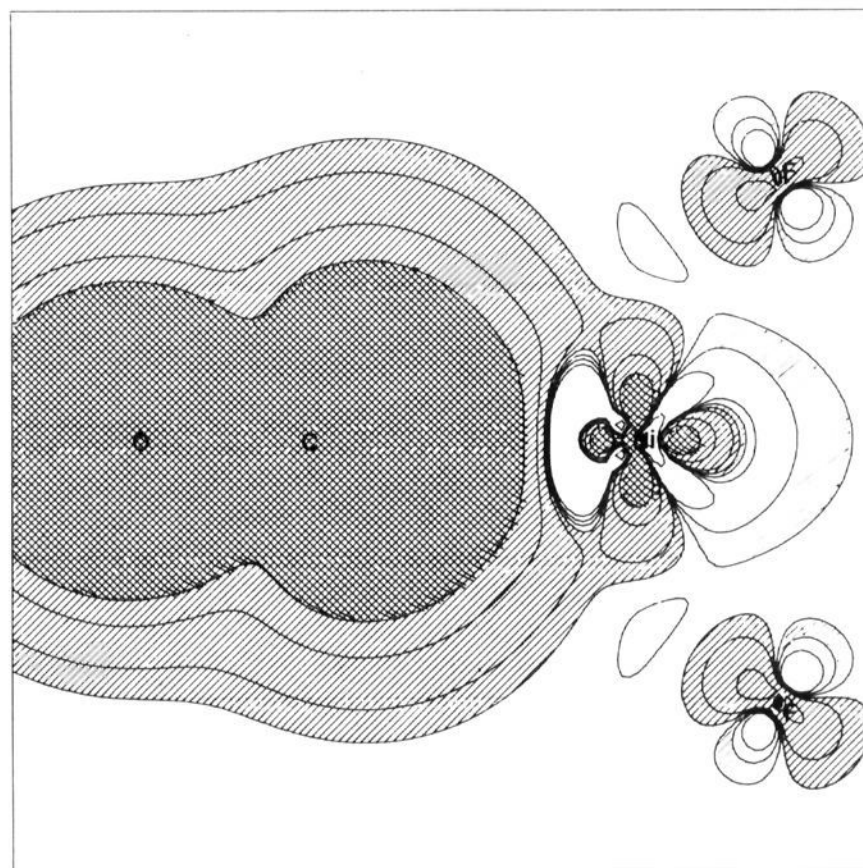
Figure 9. Difference of total density, $\rho[\text{NiF}_2\text{CO}] - \rho[\text{NiF}_2]$, in the xy plane. Negative density denoted by white enclosed areas. Density range from 0.01 to −0.04 e/(au)^3.

the same value as in nickel carbonyl, 2.1 mdyn/Å at an internuclear distance of 1.82 Å,[16] gives a CO frequency shift of 49 cm^{-1}. If k = 0.5 mdyn/Å for NiC, a value corresponding to

a moderately strong nonbonded interaction, the CO frequency shift becomes 10 cm^{-1}; thus, the NiC force constant, reflecting the strength of the NiC bond, has a direct effect on the CO frequency shift distinct from any changes in CO bonding.

In order to investigate the bonding of CO to NiF_2 and changes in the CO bond on formation of NiF_2CO, SCF calculations were performed on NiF_2CO employing the same basis as used for NiF_2 and CO. The NiF_2 bond angle and the CO internuclear distance were kept equal to 152° and 2.132 au and three different NiC distances were tried around 2 Å which is a typical value encountered for nickel carbonyls. In all cases, the complex remained in a triplet ground state. Results in Table VII show a slight energy minimum at $R_{NiC} = 2.25$ Å, but the system is unbound by $\sim$0.1 au with respect to $NiF_2 + CO$ at infinite separation. Thus, it is possible that the slight minimum is simply an artifact of the relatively small basis SCF treatment. CI would be expected to favor stabilization of the complex relative to separated NiF_2 and CO, but a gain of 0.1 au is not likely. It is possible, of course, that the association is due to matrix effects, and this conclusion would be consistent with the fact that the NiF_2CO species has not been identified in the gas phase. In the following, we assume that the NiF_2 and CO are positioned at a NiC distance of 2.25 Å and proceed to study the effect of such an association on the electronic structure.

The NiC distance of 2.25 Å is somewhat shorter than the sum of the van der Waals radius of carbon and the ionic radius of dipositive nickel (1.65 Å + 0.72 Å = 2.37 Å). At this distance, inspection of the SCF orbital energy levels shows a slight shift from the corresponding levels in NiF_2 and CO (increased energies for NiF_2 and lower energies for CO). The closed shell orbitals retain their nickel difluoride or carbonyl character. The most prominent feature is the participation of C and O orbitals, mainly the C 2s, in the $d_\sigma-p_\sigma$ open-shell orbital.

Table VIII gives a Mulliken population analysis of NiF_2CO. If we compare the NiF_2 region to an isolated NiF_2, we note that the total p population remains the same, but the d population decreases by 0.01 e. The d_σ charge increases slightly while d_π decreases. The 4s orbital is depleted by 0.04 e while the fluorine $p_x p_y$ orbitals gain 0.005 e. For the CO region, we find that it retains essentially a cylindrical symmetry: p_x and p_z population are nearly identical. The carbon atom loses σ charge but gains back more π charge; for oxygen, the reverse is observed. There is a total transfer of 0.04 e from nickel difluoride to the carbonyl. We give in Table IX a comparative analysis of the population of the CO bond in CO, NiF_2CO, and CO^+. Recalling the earlier discussion, in going from CO to CO^+ there was a redistribution of both σ and π charge resulting in a net loss of 0.7 e from C and 0.3 e from O. In NiF_2CO, we find that it is possible to reproduce the σ population in the CO region by adding 0.7 e on C and 0.3 e on O to the σ population of CO^+, implying that the CO bond has been modified compared to CO in a manner that qualitatively leads to its strengthening.

Figure 7 shows the total electron density of the NiF_2CO complex in the xy plane. Figure 8 illustrates density contours of the singly occupied orbital of a_1 symmetry, composed of the a_1 occupied orbital of NiF_2 and a CO orbital of antibonding character. Figures 9 and 10 refer to the total density difference between the complex and its component molecules: NiF_2 for Figure 9, and CO for Figure 10. White areas correspond to negative densities and it is seen that they exist especially between carbon and oxygen, and to a lesser extent on the atoms themselves. The interatomic transfers of charge are not always reflected by Mulliken populations where negative contributions can be compensated by atomic contributions of opposite sign when density is integrated.

Further evidence for a polarization of the electronic distribution of CO on formation of NiF_2CO can be obtained from an analysis of the dipole moment. In Table X, dipole and quadrupole moments of NiF_2, CO, CO^+, and NiF_2CO are tabulated. Adding vectorially the dipole moments of CO and NiF_2 gives a resultant moment of 2.96 au, differing from that of NiF_2CO by 0.75 au. Transferring 0.04 e from NiF_2 to CO
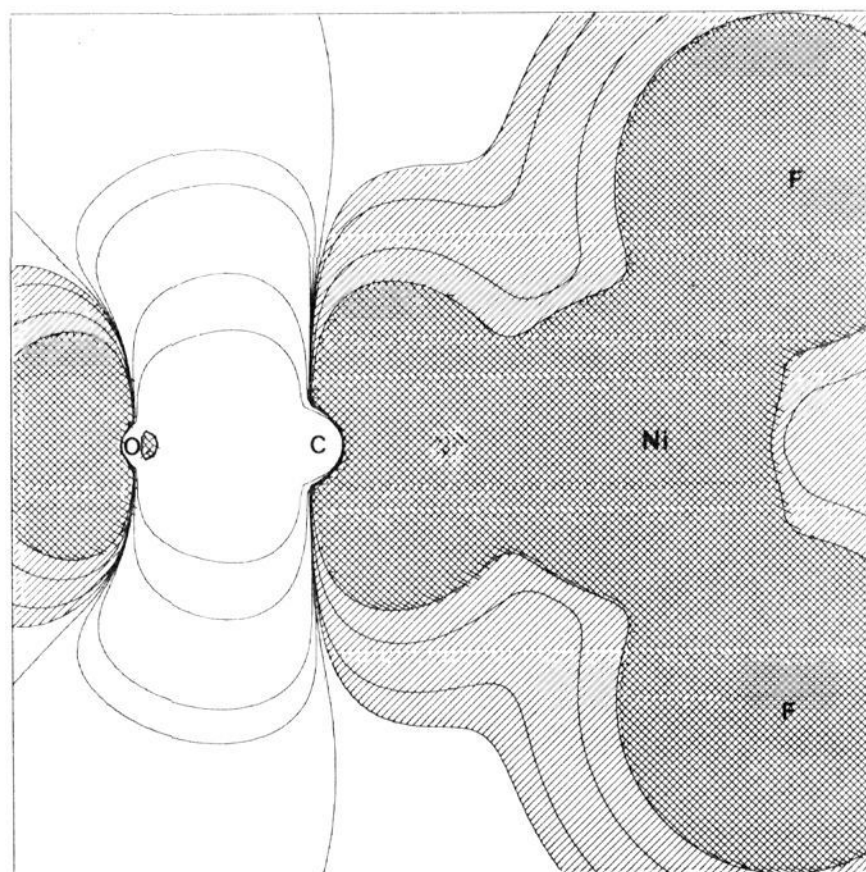

Figure 10. Difference of total density, $\rho[NiF_2CO] - \rho[CO]$, in the xy plane. Negative density denoted by white enclosed areas. Density range from 0.01 to -0.04 e/(au)^3.

reduces the difference, but further changes in the polarization of NiF_2 or CO are needed to account for the discrepancy.

Summarizing, the CO bond is polarized by the field of the dipositive Ni, the actual transfer of charge from NiF_2 to CO is small, and the combined σ, π character of this donation implies very weak NiC bonding. The results of the energy computation directly support this contention since NiF_2CO is not bound, as a free molecule, compared to NiF_2 and CO. The matrix is therefore required for association of the species. The shallow energy minimum, which as noted may simply be an artifact of the present level of treatment, would lead to a force constant for the NiC bond on the order of that due to a van der Waals interaction. Thus, the effect of the NiC force constant on the perturbation of the CO frequency would be only on the order of a few wavenumbers. Since the matrix effects are known to be small, it follows that the 70-cm^{-1} CO frequency shift, observed experimentally on NiF_2CO association in an argon matrix, is due to an electronic modification of the CO bond. As described above, both π and σ polarizations occur. Similar interpretations have been proposed by other authors studying the properties of CO adsorbed on metals.[14,17,18] The proposal that there could be σ transfer from carbon with π back-donation from the nickel[17] is not found to apply in the NiF_2CO system.

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Molecular Orbitals from Group Orbitals. 6. Quantitative Evaluation and Nature of the Stabilizing and Destabilizing Orbital Interactions in Difluoroethylenes and Fluoropropenes

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Abstract: Ab initio SCF–MO calculations, with extensive geometry optimization at the STO-3G level, have been performed on the three isomeric difluoroethylenes and on the 1- and 2-fluoropropenes. For the fluoropropenes, this basis set reproduces the principal experimental differences between the isomers, viz., (1) the relative stabilities are 2- > *cis*-1 > *trans*-1; (2) the F–C–CH$_3$ angle in 2-fluoropropene is significantly smaller than 120°; (3) eclipsed conformations (methyl CH eclipsed to C=C) are more stable than staggered conformations; (4) the methyl rotational barrier is lower in *cis*-1-fluoropropene than in *trans*-1-fluoropropene. For the difluoroethylenes, the STO-3G basis set incorrectly predicts the trans isomer to be more stable than the cis; however, the preferred stability of the 1,1 isomer and the small FCF angle in this compound are reproduced correctly. The results have been analyzed in terms of a recently described perturbational molecular orbital procedure which calculates orbital interactions between molecular fragments quantitatively using fragments and fragment orbitals derived from the ab initio wave functions. Two fragmentation modes have been examined: method a, in which XFC$_2$H$_2$ is dissected into XF and C$_2$H$_2$; and method b, in which XFC$_2$H$_2$ is dissected into X and FC$_2$H$_2$. Method a predicts incorrectly that the 1,1-disubstituted alkenes are much less stable than the 1,2 isomers. On the other hand, use of the FC$_2$H$_2$ fragment orbitals of method b leads to an internally consistent description of the stereochemical behavior of all six molecules. Only the π-type fragment orbitals are needed to achieve agreement with the various trends in the total energies. The reason for this is that only these orbitals contribute to the highest occupied molecular orbitals (HOMOs) of the various molecules and, in all cases, the stereochemical behavior of the HOMO parallels that of the total energy. The quantitative results are supplemented by a detailed qualitative description of the nature and origin of the fragment orbitals, the relative magnitudes of the different orbital interactions, and the importance of overlap effects. This discussion includes a set of simple rules, based on second-order perturbation theory, for obtaining the orbitals, and the relative magnitudes of the atomic coefficients in these orbitals, in a general fragment C=C–X.

One of the most useful concepts in stereochemistry is that the geometries of molecules can be rationalized in terms of a minimization of repulsive forces between bonds, between nuclei, and between lone pairs. The valence shell electron pair repulsion model (VSEPR)[1] is a well-known example of the successful application of this concept to geminal effects, i.e., effects associated with bonds, nuclei, and lone pairs grouped about a central atom. Extensions of such thinking, from geminal effects to vicinal effects, can be found in textbooks of organic chemistry and conformational analysis. Thus, the gauche conformation of *n*-butane is said to be less stable than the anti conformation because of "steric repulsion between the methyl groups";[2] alternatively, ". . . the instability of the gauche form of butane may be ascribed entirely to the Me··Me interaction".[3]

Empirical force field calculations[4] treat "steric repulsion" explicitly in terms of explicit relations for nonbonded repulsive interaction energies of the van der Waals type. However, to achieve quantitative agreement with experiment, it is also necessary to include, inter alia, London attractive forces in the

description of nonbonded interactions, as can be seen upon inspection of the well-known Hill,[5] Lennard–Jones,[6] and Buckingham potentials[7] which are employed in force field methods.

Thus, the notion that intramolecular *attractive* forces play a significant role in conformational analysis is as firmly established as is the concept of minimization of repulsive forces. Nevertheless, the discovery[8] of conformational effects, associated especially with the presence of lone electron pairs and/or polar bonds, which seem to be at variance with the concept of minimization of repulsive forces, came as a surprise, and this "surprise" has triggered extensive discussion in recent years into the nature and the magnitude of intramolecular attraction. Unfortunately, the force field method cannot yet be applied reliably to this problem, because of a lack of suitable potential functions for nonhydrocarbon molecules,[9] with the result that progress in the *qualitative* understanding of attractive effects has been achieved principally by the application of molecular orbital and, especially, perturbational molecular orbital (PMO)[10] methods.