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Molecular Structure and C−O Stretch Frequencies of the Cobalt Carbonyls Co(CO)$_n$, n = 1, 4, As Studied by Density Functional Theory

Hege Ryeng,[†] Odd Gropen,[†] and Ole Swang*,[‡]

Department of Mathematical and Physical Sciences, University of Tromsø, N-9000 Tromsø, Norway, and Department of Hydrocarbon Process Chemistry, SINTEF Applied Chemistry, P. O. Box 124 Blindern, N-0314 Oslo, Norway

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Gas-phase geometries and carbon−oxygen stretch frequencies for the binary cobalt carbonyl molecules CoCO, $Co(CO)_2$, $Co(CO)_3$, and $Co(CO)_4$ have been calculated using quantum chemical DFT methods. The results are compared to earlier experimental results from gas-matrix vibrational spectroscopy. Where experimental results are available, the computed results show good agreement. A reinterpretation of the experimental IR and ESR spectra of $Co(CO)_2$ and $Co(CO)_3$ is proposed.

1. Introduction

Cobalt carbonyl compounds show catalytic activity in hydroformylation reactions,[1] and they can serve as models for catalytic reactions on cobalt metal surfaces, of which Fischer−Tropsch synthesis[2] is a well-known example. Additionally, they are interesting for purely scientific reasons, as binary carbonyl complexes exist for many transition metals. Hence, periodic comparison can give valuable general knowledge. $Co(CO)_4$ was first observed by Keller and Waversik,[3] when they sublimed $Co_2(CO)_8$ at 77 K. Subsequently, the existence of $Co(CO)_4$ has been confirmed in several studies.[4−6] In 1975, Hanlan et al.[1] isolated the mono-, di-, tri-, and tetracarbonyls, in gas matrices of xenon, krypton, and argon under liquid helium temperature and different CO pressures. The molecules were characterized by infrared (IR) and electron spin resonance (ESR) spectroscopy.

Homoleptic carbonyl compounds of other first-row transition metals have been studied both experimentally[7,8] and theoretically.[9−11] For cobalt, the only work we are aware of is the abovementioned experimental study by Hanlan et al., a theoretical paper covering the monocarbonyl,[12] and two theoretical papers concerning the tetracarbonyl exclusively.[13,14] The two latter publications are, however, based on extended Hückel type calculations which do not give reliable geometries or frequencies. Molecular structures of the di- and tricarbonyls have, to the best of our knowledge, not been reported earlier. We have undertaken a systematic theoretical study of the four binary cobalt carbonyls through density functional theoretical (DFT) calculations. DFT has been chosen because of the strong correlation effects encountered in transition metal carbonyl molecules.

2. Computational Details

The reported calculations were all carried out using the program system ADF[15,16] developed by Baerends et al. Slater type orbital (STO) valence basis sets[17] were used for all atoms. The inner shells, i.e. 1s for carbon and oxygen and 1s, 2s, and 2p for cobalt, were kept frozen in their atomic shapes at all times. For cobalt, the 3s and 3p shells were described by two exponents each, the 4s and 3d shells by three exponents each, and the 4p shell by a single exponent. For carbon and oxygen, double zeta valence plus polarization (DZVP) basis sets were employed. Test calculations on CoCO with larger basis sets yielded no improvement, vide infra. Slater exchange and the Vosko−Wilk−Nusair parametrization[18] of the LDA correlation energy, with the gradient corrections of Becke[19] for exchange and of Perdew[20] for correlation were used for the exchange−correlation energies; this functional has been called BP86 in many earlier publications. The gradient corrections were included fully self-consistently. The accuracy of the numerical integration was set to $10^{-5.0}$ for each integral. This is assumed to give a numerical noise level of less than 0.1 kcal/mol in the final energies.[16] All open-shell systems were treated unrestrictedly, with one set of Kohn−Sham orbitals for each spin.

TABLE 1: Symmetry, equilibrium distances (*R*) in Å, angles (*A*) in degrees, relative energy (*E*) for different conformers in kcal/mol, and average binding energy per carbonyl group (*E*(CoC)) for Co(CO)$_n$, *n* = 1−4, in kcal/mol

	CoCO	$Co(CO)_2$		$Co(CO)_3$	$Co(CO)_4$	
sym	$D_{\infty v}$	C_{2v}(B)	$D_{\infty h}$(A)	D_{3h}	C_{3v}	D_{2d}
E		0	7		0	3
E(CoC)	57.5	53.8		47.3	44.1	
R(C−O)	1.170	1.157	1.154	1.156	1.151	1.151
R(Co−C)	1.667	1.784	1.796	1.818		1.813
R(Co−C)$_{ax}$					1.825	
R(Co−C)$_{eq}$					1.794	
A(Co−C−O)		175			177	174
A(C−Co−C)		152				61
A(C$_{ax}$−Co−C$_{eq}$)					98	

3. Results and Discussion

All the binary carbonyls are open-shell systems, and several electronic states were investigated for each in order to ensure that the ground state was found. Specifically, calculations without imposed symmetry were performed for both doublet and quartet multiplicities in order to find the electronic ground state for each system. All systems show doublet ground state multiplicity. Since most of the systems under study are rather easily deformed, matrix effects may influence the geometries significantly. Besides geometrical deformation, the matrix could also facilitate coupling between different electronic states of the molecules. We have not investigated this possibility further, but it may account for some of the discrepancies between calculated and experimental results.

The geometries of all the binary carbonyls are compared in Table 1, and their C−O stretch frequencies are summarized in Table 2.

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[*] Author to whom correspondence should be addressed.

[†] University of Tromsø.

[‡] SINTEF Applied Chemistry.

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TABLE 2: Calculated and experimental C−O stretch frequencies and calculated absorption intensities for Co(CO)$_n$, n = 1−4

	calculated[a]				experimental	
system	sym	Γ	ω (cm^{-1})	int. (km/mol)	sym	ω
CO	$C_{\infty v}$	Σ	2107	64	$C_{\infty v}$	2133[c]
CoCO	$C_{\infty v}$	Σ	1979	686	$C_{\infty v}$	1959[b]
Co(CO)$_2$	C_{2v}	A$_1$	2052	59	$D_{\infty h}$	
		B$_2$	1956	2075		1925[b]
Co(CO)$_3$	D_{3h}	A′	2083	0		
		E′	1994	1290	C_{3v}	1989[b]
Co(CO)$_4$	C_{3v}	A$_1$	2075	6	C_{3v}	2107[b]
		A$_1$	2006	636		2029[b]
		E$_1$	1998	1062		2011[b]
HCo(CO)$_4$	C_{3v}	A$_1$	2082	59		2119[d]
		A$_1$	2032	298		2055[d]
		E$_1$	2000	1004		2030[d]

[a] Present work. [b] Reference 1. [c] Reference 25. [d] Reference 26.

TABLE 3: Geometries and C−O stretch frequencies for HCo(CO)$_4$ and CO. Distances (R) in Å, angles (A) in degrees, and frequencies (ω) in cm^{-1}

	HCo(CO)$_4$		CO	
	calc[a]	exp[b]	calc[a]	exp[c]
R(Co−H)	1.490	1.556		
R(Co−C$_{ax}$)	1.801	1.764		
R(Co−C$_{eq}$)	1.813	1.818		
R(C−O)	1.151	1.141	1.139	1.128
A(H−Co−C$_{ax}$)	180	180		
A(H−Co−C$_{eq}$)	81	80.3		
A(Co−(C−O)$_{eq}$)	177	172.6		
A(Co−(C−O)$_{ax}$)	180	180		
A(Co$_{eq}$−Co$_{eq}$)	117	117.3		
ω_1	2060	2092[d]	1980	2130
ω_2	2005	2028[d]		
ω_3	1973	2003[d]		

[a] Present work. [b] Reference 24 [c] Reference 25. [d] Reference 26.

TABLE 4: Bonding distances (R) in Å, and C−O stretch frequency (ω), in cm^{-1} for CoCO in its ground state calculated with DZVP and TZVP basis sets on carbon and oxygen. Basis set A: DZVP. B: DZVP on carbon and TZVP on oxygen. C: TZVP. The experimental geometry is unknown

	basis			
	A	B	C	exp[a]
R(Co−C)	1.667	1.670	1.671	
R(C−O)	1.170	1.169	1.171	
frequency	1987	1993	1983	1959

[a] Reference 1.

3.1. CO and HCo(CO)$_4$. The closed-shell molecules CO and HCo(CO)$_4$ have both been well characterized experimentally, and hence they may serve as examples for evaluating the accuracy of the applied theoretical methods. The latter molecule has C_{3v} symmetry; it can be regarded as a trigonal bipyramid with the hydrogen atom in an apical position. Several theoretical studies of HCo(CO)$_4$ have been reported earlier.[21−23] In Table 3, experimental and calculated data for these molecules are compared. The calculated bond distances show a discrepancy with experiment of 0.04 Å for Co−C bonds, 0.01 Å for C−O bonds, and 5° for the angles. This is slightly worse than typical performance of the methods in use, which is probably a result of the very strong correlation effects in the molecules under study. The discrepancy in vibrational frequencies is about 2%, the calculated frequencies being lower than the experimental ones.

3.2. CoCO. For CoCO, a series of calculations were carried out with different combinations of basis sets in order to evaluate their performance. The results are shown in Table 4. We note that bonding distances change by 0.01 Å and the stretch frequency by 6 cm^{-1} upon increasing the basis set size. As no significant improvement is gained by going to the TZVP basis, the DZVP set has been used for all subsequent calculations.

We find a linear ground state geometry for the CoCO molecule. Test calculations with start geometries of lower symmetry converge to $C_{\infty v}$. Our C−O stretch frequency is 20 cm^{-1} higher than the experimental value.

The only earlier theoretical work on CoCO we are aware of is that of Adamon and Lelj,[12] who report DFT results for monocarbonyls of all first-row transition metals. Their C−O stretch frequency is 2020 cm^{-1}, compared to the present value of 1981 and the experimental value of 1959 cm^{-1}. Their Co−C and C−O distances are 2 pm shorter and 4 pm longer than the present results, respectively. The discrepancies can be explained by differences in the computational methods; Adamon and Lelj use a B3LYP functional and Gaussian basis sets optimized for Hartree−Fock calculations.

3.3. Co(CO)$_2$. We have found no earlier theoretical studies of the Co(CO)$_2$ molecule. In our calculations, it shows two minima (bent C_{2v} and linear $D_{\infty h}$) which are nearly degenerate and divided by a very small energy barrier. The bent structure is more stable by 7 kcal/mol, and has a C−Co−C bonding angle of 152°. Upon diminishing the angle, the energy rises rapidly, while an increase in the angle is accompanied by a very slow energy rise. The C−O stretch modes have vibration frequencies of 1956 and 2052 cm^{-1} of B$_2$ and A$_1$ symmetry, respectively. Hanlan et al. find only one IR C−O stretch adsorption for this molecule (at 1925 cm^{-1}, 31 cm^{-1} below our value), indicating a linear geometry. This result can be explained by the very soft bending potential of the molecule. The failure to observe the A$_1$ frequency may be due to matrix effects straightening the molecule out into something closer to a linear geometry, or to the very weak IR absorption intensity of the A$_1$ mode. We have computed the absorption intensities of the A$_1$ and B$_2$ modes to be 59 and 2075 km/mol, respectively. While these computed intensities not can be regarded as quantitative, the factor of 35 indicates a real physical difference. We would, however, not like to draw firm conclusions from the calculated intensities: For the tricarbonyl (vide infra), the A$_1$ mode was observed experimentally despite the calculated intensity of only 6 km/mol.

3.4. Co(CO)$_3$. No theoretical results on this molecule seem to have been reported. The calculated geometry is planar trigonal, with D_{3h} symmetry. Calculations with C_{3v} symmetry restrictions and starting geometry converge to D_{3h}. This is in line with experimental IR results of Hanlan et al.,[1] in which only one C−O mode is observed in the spectrum. Their ESR results, however, indicate C_{3v} geometry, and they claim that small differences from a planar geometry is not easily observed by IR. From our calculations, the "umbrella" deformation of the molecule is rather soft, 1 kcal/mol being sufficient to bend the CO groups more than 5° out of plane. Hence, the molecule might have C_{3v} symmetry in the noble gas matrix even if the gas phase ground state is planar. Our asymmetric C−O stretch frequency of 1994 cm^{-1} is 5 cm^{-1} higher than the experimental value, 1989 cm^{-1}.

3.5. Co(CO)$_4$. There are many possible symmetries for this system. Geometry optimizations were performed with T_d, D_{2d}, C_{3v}, and C_{2v} symmetry restrictions. Their relative energies were 14, 2, 0, and 6 kcal/mol, indicating that the ground state geometry has C_{3v} symmetry. Furthermore, a geometry optimization without any symmetry restrictions and a T_d starting geometry converged to C_{3v}. The structure is tetragonal pyramidal, with the apical Co−C bond 0.03 Å longer than the basal ones. From symmetry, this system has 3 IR-active C−O modes, which is in line with the observed spectrum.[1] The present A_1, A_1, and E_1 C−O stretch frequencies are 37, 23, and 30 cm^{-1} lower than the experimental ones, respectively.

4. Concluding Remarks

The present computed results show good agreement with experiment in the cases that experimental results are available. The discrepancies between computed and experimental stretch frequencies are somewhat larger than usually found for the applied methods. This may be explained by the very strong correlation effects encountered in the systems under study, and is in line with earlier work. However, the worst case is only 37 cm^{-1} off. Interestingly, the present results are too low for the closed-shell systems CO and $HCo(CO)_4$, and too high for the open-shell homoleptic carbonyls. A possible explanation, besides the multiplicity differences, are the influence of matrix effects on the experimental values for the open-shell systems. To the best of our knowledge, geometries of $Co(CO)_2$ and $Co(CO)_3$ have not been reported earlier. The present results extend the description of these systems offered by earlier experimental IR studies.[1]

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