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Density Functional Study of the Vibrational Spectra of Octahedral Transition-Metal Hexacarbonyls: Neutral Molecules (M = Cr, Mo, W) and Isoelectronic Ions (M = V, Nb, Ta; Mn, Re; Fe, Ru, Os; Co, Rh, Ir; Pt; Au)

Volker Jonas and Walter Thiel*

Organisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190,
CH-8057 Zürich, Switzerland

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The geometries, harmonic force fields, and charge distributions of the title compounds have been calculated at the level of gradient-corrected density functional theory (DFT) using effective core potential wave functions in conjunction with polarized double- and triple-ζ basis sets. The DFT results are in very good agreement with the available experimental data for both the neutral and ionic systems. Theoretical predictions are made for highly charged hexacarbonyl cations that are as yet unknown (M = Co, Rh, Pt, Au) to facilitate their spectroscopic detection. Trends in the computational results are discussed in terms of bonding models and electrostatic effects, emphasizing the variation of the calculated properties with the total charge of the hexacarbonyls.

1. Introduction

The octahedral hexacarbonyls $[M(CO)_6]$ (M = Cr, Mo, W) are among the prototypical transition-metal complexes.[1] The isoelectronic monoanions $[M(CO)_6]^-$ (M = V, Nb, Ta)[2,3] and monocations $[M(CO)_6]^+$ (M = Mn,[4] Tc,[5] Re[6]) have long been known. More recently, the dianions $[M(CO)_6]^{2-}$ (M = Ti, Zr, Hf),[7] the dications $[M(CO)_6]^{2+}$ (M = Fe,[8] Ru,[9] Os[9]), and the trication $[Ir(CO)_6]^{3+}$ [10] have been synthesized as thermally stable salts and characterized spectroscopically (partially also by X-ray analysis[7]). Related developments include the preparation of highly reduced metal carbonyl anions $[M(CO)_n]^{m-}$ (n = 3−5; m = 3, 4)[11] and of other unusual carbonyl cations such as $[M(CO)_4]^{2+}$ (M = Pd, Pt),[12] $[Cu(CO)_n]^+$ (n = 1−4),[13,14] $[Ag(CO)_n]^+$ (n = 1−4),[13,15] and $[Au(CO)_n]^+$ (n = 1, 2).[16] Some of these latter cations have also been studied theoretically.[17,18] Recent work on homoleptic carbonyl cations of electron-rich metals has been reviewed.[19−21]

The bonding in neutral transition-metal carbonyls is usually described in terms of the Dewar−Chatt−Duncanson model,[22,23] with σ donation from the CO lone pair into an empty metal d_σ orbital and π back-donation from filled metal d_π orbitals into the antibonding π* orbital of CO. This model rationalizes many observed properties quite well, e.g. the shifts in the CO stretching frequencies. It should also be applicable to homoleptic carbonyl cations,[21] in principle, even though it is qualitatively clear that π back-donation will be less important and that electrostatic effects will be strong in these cations. The dominant influence of electrostatics on CO stretching force constants and CO bond lengths has been stressed in a recent theoretical study.[24]

The present paper reports density functional calculations on the vibrational spectra of 16 octahedral hexa-

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carbonyls $[M(CO)_6]^n$, where the charge *n* ranges from −1 to +5. We have established previously that such calculations are reliable for neutral transition-metal carbonyls[25] and carbonyl hydrides.[26] We now confirm that this is also true for charged carbonyl species. The current computational results may therefore be used for the detailed assignment of the observed vibrational spectra. In cases where the cations are still unknown (M = Co, Rh, Pt, Au), the theoretical predictions may facilitate their spectroscopic identification. Finally, the trends in the computational results are related to the bonding and charge distribution in the hexacarbonyls.

2. Theoretical Methods

Gradient-corrected density functional calculations were carried out by using the Gaussian94[27] program system. Gradient corrections for exchange and for correlation were taken from the work of Becke[28] and Perdew,[29] respectively (usually abbreviated as BP or BP86). Two basis sets were employed, labeled ECP1 and ECP2. Both use a quasi-relativistic effective core potential at the transition metal together with the corresponding (8s7p5d)/[6s5p3d] valence basis set.[30] For carbon and oxygen, ECP1 employs the 6-31G(d) basis,[31] whereas ECP2 uses a Dunning (10s6p)/[5s3p] triple-ζ basis supplemented by two sets of d polarization functions.[32] Spherical d functions were applied throughout. Using analytic energy gradients, the molecular geometries were optimized within the constraint of O_h point group symmetry. Second derivatives were obtained by numerical differentiation of the analytic energy gradients. The present computational approach is the same as in our previous studies.[25,26]

3. Results

In most tables of this section, we report both BP86/ECP1 and BP86/ECP2 data to document how the results depend on the chosen basis set. The BP86/ECP2 calculations should generally be more reliable because they employ a larger basis. Therefore, comparisons with experiment will normally refer to BP86/ECP2.

Table 1. Bond Lengths *R* (Å), Vibrational Frequencies *ν* (cm^{-1}),[a] and Force Constants *F* (10^2 N m^{-1}) for CO, CO$^+$, and HCO$^+$

compd	property	exp	BP86/ECP1[b]	BP86/ECP2[b]
CO	*R*(CO)	1.128[c]	1.150	1.138
	ν(CO)	2143[c]	2117[d]	2118[d]
	F(CO)	18.56[c]	18.11	18.11
CO$^+$	*R*(CO)	1.115[c]	1.135	1.123
	ν(CO)	2184[c]	2184	2191
	F(CO)	19.28[c]	19.27	19.40
HCO$^+$	*R*(CO)	1.105[e]	1.125	1.114
	R(CH)	1.097[e]	1.106	1.104
	ν_1(CH)	3089[f]	3187	3134
	ν_2(HCO)	830[f]	828	821
	ν_3(CO)	2184[f]	2176	2176
	F(CO)	21.26[g]	21.29	21.36

[a] Experimental fundamental wavenumbers, theoretical harmonic wavenumbers (see text). Correspondingly for the force constants (10^2 N m^{-1} = 1 mdyn/Å). [b] ECP1 = 6-31G(d), ECP2 = TZ2P. The ECP notation is used for consistency with the other tables. [c] Reference 33. [d] Using the standard int = finegrid option in Gaussian94. The previously quoted value[25] of 2120 cm^{-1} refers to the smaller SG1 grid in Gaussian92/DFT. [e] Reference 34. [f] Reference 35. [g] Reference 36.

Table 2. Bond Lengths (Å)

	exp		BP86/ECP1		BP86/ECP2	
	M−C	C−O	M−C	C−O	M−C	C−O
$[V(CO)_6]^-$	1.945(7)[a]	1.148(7)	1.953	1.180	1.956	1.170
$[Nb(CO)_6]^-$	2.089(5)[b]	1.160(7)	2.127	1.179	2.131	1.169
$[Ta(CO)_6]^-$	2.083(6)[b]	1.149(8)	2.132	1.180	2.132	1.170
$[Cr(CO)_6]$	1.914(2)[c]	1.140(2)	1.903	1.164	1.908	1.154
$[Mo(CO)_6]$	2.063(3)[d]	1.145(2)	2.062	1.164	2.065	1.153
$[W(CO)_6]$	2.058(3)[e]	1.148(3)	2.073	1.165	2.075	1.154
$[Mn(CO)_6]^+$			1.888	1.150	1.892	1.140
$[Re(CO)_6]^+$	2.01(4)[f]	1.13(3)	2.045	1.152	2.047	1.141
$[Fe(CO)_6]^{2+}$			1.903	1.140	1.905	1.130
$[Ru(CO)_6]^{2+}$			2.027	1.141	2.028	1.130
$[Os(CO)_6]^{2+}$			2.043	1.141	2.045	1.130
$[Co(CO)_6]^{3+}$			1.943	1.135	1.942	1.124
$[Rh(CO)_6]^{3+}$			2.057	1.135	2.058	1.124
$[Ir(CO)_6]^{3+}$			2.062	1.135	2.063	1.124
$[Pt(CO)_6]^{4+}$			2.111	1.133	2.111	1.122
$[Au(CO)_6]^{5+}$			2.233	1.136	2.227	1.125

[a] X-ray, ref 37a; average of six values in $[(Ph_3P)_3Cu][V(CO)_6]$. [b] X-ray, ref 38; $[PPN][M(CO)_6]$ (M = Nb, Ta), [PPN] = bis(triphenylphosphine)nitrogen(1+). [c] Neutron diffraction, ref 39. Average X-ray values are 1.916(2) and 1.140(3) Å.[40] [d] Electron diffraction, ref 41. Average X-ray values are 2.059(3) and 1.125(5) Å.[42] [e] Electron diffraction, ref 41. Average X-ray values are 2.048 and 1.135 Å.[43a] An older X-ray analysis yields average values of 2.026 and 1.146 Å.[43b] [f] X-ray, ref 44a; average of six values in $[Re(CO)_6][Re_2F_{11}]$ ranging from 1.89(7) to 2.07(7) Å for Re−C and from 1.12(9) to 1.19(8) Å for C−O.

a. Reference Data. Table 1 collects experimental[33−36] and theoretical results for CO, CO$^+$, and HCO$^+$ ($C_{\infty v}$), which serve as reference compounds in the discussions for the hexacarbonyl species. Here and in the following, the observed fundamental vibrational frequencies are compared with the calculated harmonic frequencies, neglecting any effects of anharmonicity. In Table 1 this choice is made for the sake of consistency with the results for the hexacarbonyls, where both experimental and theoretical anharmonicity corrections are generally not available. In the case of CO and CO$^+$, these corrections amount to 27 and 30 cm^{-1}, respectively.[33]

b. Molecular Structures. Table 2 lists the theoretical equilibrium bond lengths for the title compounds computed at the BP86 level and the available experimental data.[37−44] The experimental values have been obtained by neutron diffraction and gas-phase electron diffraction in the case of the neutral molecules[39,41] and

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by X-ray analysis of $[V(CO)_6]^-$ and $[Re(CO)_6]^+$ salts.[37,38,44] For $[V(CO)_6]^-$, several X-ray structures with different countercations have been published,[37] but only one of them seems reliable concerning the V−C and C−O bond lengths.[37a] In all other experimental structures the $[V(CO)_6]^-$ anion is significantly distorted by the countercation.[37b−g] For $[M(CO)_6]^-$ (M = Nb, Ta), only one structural analysis has been published.[38] For $[M(CO)_6]^+$ (M = Mn, Re), the only experimental structures with isolated hexacarbonyl cations are for $[Re(CO)_6][Re_2F_{11}]$[44a] and $[Re(CO)_6][ReOF_5]$.[44b] In all other structures the counteranion usually forms a σ-bond to one of the carbonyl carbons at the metal.[45] For $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os) and $[Ir(CO)_6]^{3+}$, no structural data are available.

The calculated bond lengths are generally in good agreement with the experimental values, for both the ECP1 and ECP2 basis sets. The agreement is best for the neutral hexacarbonyls of the chromium group (typically within 0.02 Å; see ref 25 for a more detailed discussion). For $[M(CO)_6]^-$ (M = V, Nb, Ta) and $[Re(CO)_6]^+$, the calculated bond lengths are somewhat larger than the observed X-ray values (see Table 2), which may partially be due to solid-state effects.

c. Vibrational Frequencies. Our previous investigation of nine neutral transition-metal carbonyls[25] and eight neutral carbonyl hydrides[26] has shown that the deviations $\Delta\nu = \nu_{\text{exp}} - \omega_{\text{calc}}$ between the observed fundamental wavenumbers and the calculated (BP86) harmonic wavenumbers are surprisingly small. For a given type of vibration, the remaining systematic errors may be taken into account by a constant offset ω_{shift} to arrive at predicted wavenumbers $\nu_{\text{pred}} = \omega_{\text{calc}} + \omega_{\text{shift}}$. In the case of the CO stretching vibrations, we find an optimum value of $\omega_{\text{shift}} = 28.3\ \text{cm}^{-1}$ at the BP86/ECP2 level (consistent with an error of 25 cm^{-1} for free CO), which leads to an rms deviation $\delta_{\text{rms}} = 5.6\ \text{cm}^{-1}$ of ν_{pred} for those 39 vibrations where experimental gas-phase data are available[25,26] (see Figure 1). Similar corrections may be derived for other modes, e.g. for the 24 MC stretching vibrations[25,26] with $\omega_{\text{shift}} = -13.0\ \text{cm}^{-1}$ and $\delta_{\text{rms}} = 4.9\ \text{cm}^{-1}$ at the BP86/ECP2 level (see Figure 2). The overall agreement between ν_{exp} and ω_{calc} (BP86/ECP2, uncorrected) in the range below 900 cm^{-1} is illustrated in Figure 3. These comparisons for the neutral carbonyls[25] and carbonyl hydrides[26] indicate the accuracy which may presently be expected for the hexacarbonyl ions.

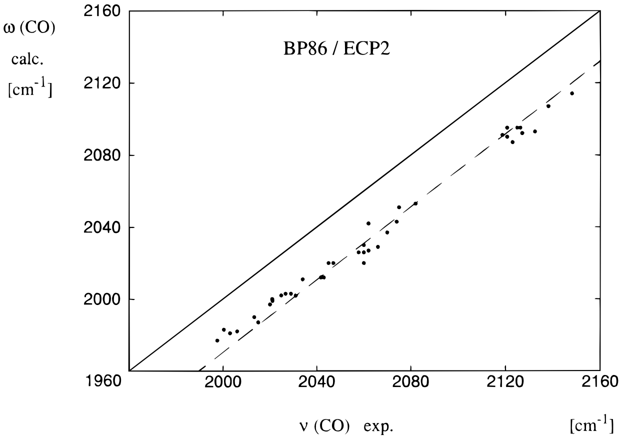

Figure 1. Calculated vs experimental CO vibrational frequencies in transition-metal carbonyls and carbonyl hydrides.[25,26] Correlation lines with unit slope are shown (unshifted as well as shifted by $-28.3\ \text{cm}^{-1}$; see text).

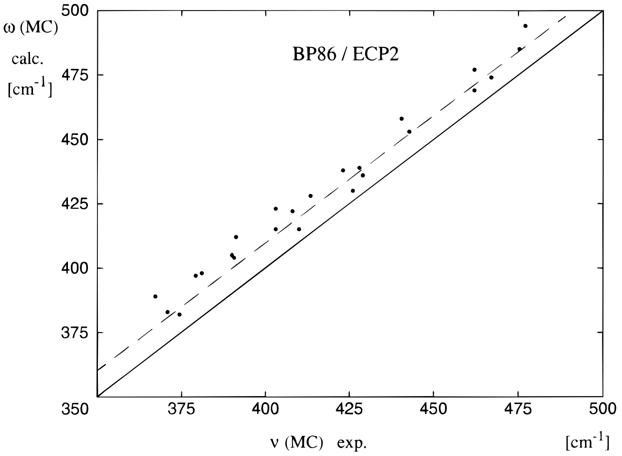

Figure 2. Calculated vs experimental MC vibrational frequencies in transition-metal carbonyls and carbonyl hydrides.[25,26] Correlation lines with unit slope are shown (unshifted as well as shifted by $+13.0\ \text{cm}^{-1}$; see text).

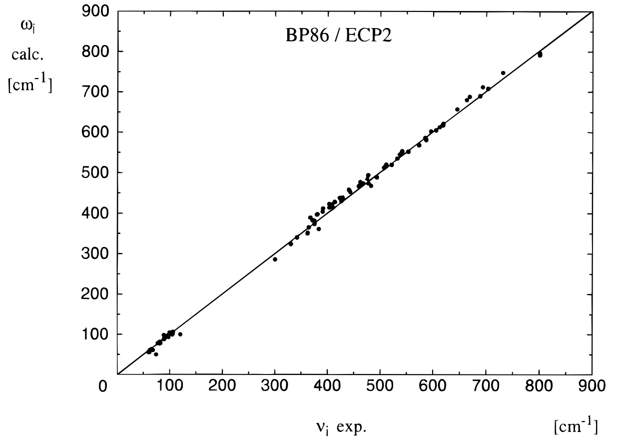

Figure 3. Calculated vs experimental vibrational frequencies below 900 cm^{-1} in transition-metal carbonyls and carbonyl hydrides.[25,26] The ideal correlation line with unit slope is shown.

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Table 3. Vibrational Frequencies (cm^{-1}) for $[M(CO)_6]^-$ (M = V, Nb, Ta)

			exp[a] (soln)	BP86/ECP1	$\Delta\nu$	BP86/ECP2	$\Delta\nu$
				$[V(CO)_6]^-$			
A_{1g}	ν_1	[CO]	2020	2008	−12	1994	−26
A_{1g}	ν_2	[MC]	374	388	+14	385	+11
E_g	ν_3	[CO]	1894	1910	+16	1887	−7
E_g	ν_4	[MC]	393	398	+5	396	+3
T_{1g}	ν_5	[δ(MCO)]	356[b]	359	+3	365	+9
T_{1u}	ν_6	[CO]	1858	1894	+36	1869	+11
T_{1u}	ν_7	[δ(MCO)]	650	673	+23	669	+19
T_{1u}	ν_8	[MC]	460	464	+4	465	+5
T_{1u}	ν_9	[δ(CMC)]	92[c]	87	−5	80	−12
T_{2g}	ν_{10}	[δ(MCO)]	517	512	−5	512	−5
T_{2g}	ν_{11}	[δ(CMC)]	84	80	−4	78	−6
T_{2u}	ν_{12}	[δ(MCO)]	506	507	+1	506	0
T_{2u}	ν_{13}	[δ(CMC)]		49		46	
				$[Nb(CO)_6]^-$			
A_{1g}	ν_1	[CO]		2008		1995	
A_{1g}	ν_2	[MC]		390		385	
E_g	ν_3	[CO]		1906		1886	
E_g	ν_4	[MC]		381		377	
T_{1g}	ν_5	[δ(MCO)]		331		332	
T_{1u}	ν_6	[CO]	1864	1891	+27	1870	+6
T_{1u}	ν_7	[δ(MCO)]		581		574	
T_{1u}	ν_8	[MC]		397		390	
T_{1u}	ν_9	[δ(CMC)]		71		64	
T_{2g}	ν_{10}	[δ(MCO)]		449		445	
T_{2g}	ν_{11}	[δ(CMC)]		73		68	
T_{2u}	ν_{12}	[δ(MCO)]		495		491	
T_{2u}	ν_{13}	[δ(CMC)]		48		42	
				$[Ta(CO)_6]^-$			
A_{1g}	ν_1	[CO]		2008		1995	
A_{1g}	ν_2	[MC]		401		398	
E_g	ν_3	[CO]		1904		1883	
E_g	ν_4	[MC]		392		390	
T_{1g}	ν_5	[δ(MCO)]		338		343	
T_{1u}	ν_6	[CO]	1859	1890	+31	1868	+9
T_{1u}	ν_7	[δ(MCO)]		556		552	
T_{1u}	ν_8	[MC]		381		377	
T_{1u}	ν_9	[δ(CMC)]		69		62	
T_{2g}	ν_{10}	[δ(MCO)]		439		439	
T_{2g}	ν_{11}	[δ(CMC)]		75		70	
T_{2u}	ν_{12}	[δ(MCO)]		496		496	
T_{2u}	ν_{13}	[δ(CMC)]		49		44	

[a] Reference 46 for M = V; values for $[(CH_3)_4N][V(CO)_6]$ from CH_3CN solution. Reference 38 for M = Nb, Ta; values for $[PPN][M(CO)_6]$ from acetone solution. [b] Calculated from observed combination bands. [c] Tetrachloroethane solution.

Table 4. Vibrational Frequencies (cm^{-1}) for $[M(CO)_6]^+$ (M = Mn, Re)

			exp[a]	BP86/ECP1	$\Delta\nu$	BP86/ECP2	$\Delta\nu$
				$[Mn(CO)_6]^+$			
A_{1g}	ν_1	[CO]	2192	2171	−21	2168	−24
A_{1g}	ν_2	[MC]	384	389	+5	387	+3
E_g	ν_3	[CO]	2125	2110	−15	2105	−20
E_g	ν_4	[MC]	390	387	−3	386	−4
T_{1g}	ν_5	[δ(MCO)]	347	348	+1	355	+8
T_{1u}	ν_6	[CO]	2095	2092	−3	2086	−9
T_{1u}	ν_7	[δ(MCO)]	636	661	+25	660	+24
T_{1u}	ν_8	[MC]	412	420	+8	421	+9
T_{1u}	ν_9	[δ(CMC)]	101	114	+13	110	+9
T_{2g}	ν_{10}	[δ(MCO)]	520[b]	532	+12	533	+13
T_{2g}	ν_{11}	[δ(CMC)]		97		95	
T_{2u}	ν_{12}	[δ(MCO)]	500	510	+10	510	+10
T_{2u}	ν_{13}	[δ(CMC)]		71		71	
				$[Re(CO)_6]^+$			
A_{1g}	ν_1	[CO]	2197	2178	−21	2178	−21
A_{1g}	ν_2	[MC]	441	443	+2	440	−1
E_g	ν_3	[CO]	2122	2106	−16	2103	−19
E_g	ν_4	[MC]	426	421	−5	418	−8
T_{1g}	ν_5	[δ(MCO)]	354[c]	350	−4	350	−4
T_{1u}	ν_6	[CO]	2085	2083	−2	2080	−5
T_{1u}	ν_7	[δ(MCO)]	584	594	+10	587	+3
T_{1u}	ν_8	[MC]	356	371	+15	366	+10
T_{1u}	ν_9	[δ(CMC)]	82	97	+15	92	+10
T_{2g}	ν_{10}	[δ(MCO)]	486	484	−2	480	−6
T_{2g}	ν_{11}	[δ(CMC)]	82	94	+12	89	+7
T_{2u}	ν_{12}	[δ(MCO)]	522[c]	528	+6	525	+3
T_{2u}	ν_{13}	[δ(CMC)]		72		69	

[a] Values for solid $[Mn(CO)_6][PF_6]$;[48] values for $[Re(CO)_6][AsF_6]$ from CH_3CN solution.[46] [b] The value for ν_{10} has been changed from 500 to 520 cm^{-1} after checking the original data (see Table I of ref 48). [c] Calculated from observed combination bands.

The calculated harmonic wavenumbers for the title compounds, as well as the available observed fundamental wavenumbers[8−10,38,46−48] and the corresponding deviations $\Delta\nu$ are collected in Tables 3−7 (ions) and in Table S1 of the Supporting Information (neutral molecules[25]). The experimental data for the neutral molecules (M = Cr, Mo, W) have been obtained in the gas phase, while those for the ions refer to the solid state (M = Mn, Fe, Ru, Os, Ir) or to solution (M = V, Nb, Ta, Re). Hence, comparisons between theory and experiment are complicated by solid-state and solvent shifts in the case of the ions.

For the neutral molecules $[M(CO)_6]$ (M = Cr, Mo, W), the observed solvent shifts $\Delta\nu_s$ relative to the gas phase range from −21 to +12 cm^{-1} (see Table S1). Those for the CO stretching modes (ν_1, ν_3, ν_6) are more uniform and lie between −21 and −4 cm^{-1}. The solvent shifts for the ungerade vibrations (ν_6, T_{1u}) are almost twice as large as those for the gerade vibrations (ν_1, A_{1g} and ν_3, E_g), presumably due to the fact that the solvent can better stabilize the dipolar charge distribution generated during a T_{1u} motion. Larger solvent shifts for less symmetrical CO stretching modes are also found in other molecules, e.g. in $[HMn(CO)_5]$, $[HRe(CO)_5]$, $[Fe(CO)_5]$, $[HCo(CO)_4]$, and $[Ni(CO)_4]$.[25,26] On the basis of these data, one may generally expect solvent shifts $\Delta\nu_s$ on the order of ±20 cm^{-1} and estimate more specific shifts for the CO stretching modes (ca. −5 to −10 cm^{-1} for ν_1 and ν_3, ca. −15 to −20 cm^{-1} for ν_6).

In the following, we discuss the results for the hexacarbonyl ions individually (Tables 3−7). Those for the neutral molecules (Table S1) have been considered before.[25]

The experimental data in Table 3 are nearly complete for $[V(CO)_6]^-$, whereas only the infrared active CO stretching frequency ν_6 has been reported for $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$. ν_6 is strongly dependent on the solvent and the countercation.[38,46] It varies between 1851 and 1877 cm^{-1} for $[V(CO)_6]^-$, 1857 and 1876 cm^{-1} for $[Nb(CO)_6]^-$, and 1852 and 1875 cm^{-1} for $[Ta(CO)_6]^-$, so that a meaningful comparison with theory is difficult. The most detailed experimental spectrum for $[V(CO)_6]^-$ comes from acetonitrile solution with $[(CH_3)_4N]^+$ or $[Na(diglyme)_2]^+$ as counterions, which should be rather uncoordinating.[46] The deviations $\Delta\nu$ (BP86/ECP2) for the three CO stretching modes are −26, −7, and +11 cm^{-1}, respectively. Correcting for the specific solvent shifts (see above) brings these deviations into the usual range[25,26] (see Figure 1). For the other vibrations in $[V(CO)_6]^-$, the average absolute deviation $\Delta\nu$ is 8 cm^{-1}, with a maximum deviation of 19 cm^{-1}. This would

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Table 5. Vibrational Frequencies (cm^{-1}) for $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os)

			exp[a] (solid)	BP86/ECP1	$\Delta\nu$	BP86/ECP2	$\Delta\nu$
				$[Fe(CO)_6]^{2+}$			
A_{1g}	ν_1	[CO]	2241	2220	−21	2221	−20
A_{1g}	ν_2	[MC]		361		361	
E_g	ν_3	[CO]	2220	2186	−34	2188	−32
E_g	ν_4	[MC]	348	353	+5	355	+7
T_{1g}	ν_5	[δ(MCO)]		333		338	
T_{1u}	ν_6	[CO]	2204	2172	−32	2173	−31
T_{1u}	ν_7	[δ(MCO)]	558	605	+47	608	+50
T_{1u}	ν_8	[MC]	338	378	+40	380	+42
T_{1u}	ν_9	[δ(CMC)]		120		117	
T_{2g}	ν_{10}	[δ(MCO)]		508		508	
T_{2g}	ν_{11}	[δ(CMC)]	138	100	−38	98	−40
T_{2u}	ν_{12}	[δ(MCO)]		476		478	
T_{2u}	ν_{13}	[δ(CMC)]		77		77	
				$[Ru(CO)_6]^{2+}$			
A_{1g}	ν_1	[CO]	2254	2230	−24	2235	−19
A_{1g}	ν_2	[MC]		404		401	
E_g	ν_3	[CO]	2222	2187	−35	2192	−30
E_g	ν_4	[MC]	382	378	−4	377	−5
T_{1g}	ν_5	[δ(MCO)]		332		329	
T_{1u}	ν_6	[CO]	2199	2168	−31	2172	−27
T_{1u}	ν_7	[δ(MCO)]	557	580	+23	572	+15
T_{1u}	ν_8	[MC]	336	342	+6	337	+1
T_{1u}	ν_9	[δ(CMC)]		111		106	
T_{2g}	ν_{10}	[δ(MCO)]		474		468	
T_{2g}	ν_{11}	[δ(CMC)]	131	95	−36	91	−40
T_{2u}	ν_{12}	[δ(MCO)]		495		490	
T_{2u}	ν_{13}	[δ(CMC)]		78		75	
				$[Os(CO)_6]^{2+}$			
A_{1g}	ν_1	[CO]	2259	2234	−25	2237	−22
A_{1g}	ν_2	[MC]		434		428	
E_g	ν_3	[CO]	2218	2186	−32	2188	−30
E_g	ν_4	[MC]		406		401	
T_{1g}	ν_5	[δ(MCO)]		341		339	
T_{1u}	ν_6	[CO]	2190	2163	−27	2166	−24
T_{1u}	ν_7	[δ(MCO)]	562	574	+12	567	+5
T_{1u}	ν_8	[MC]	346	338	−8	336	−10
T_{1u}	ν_9	[δ(CMC)]		105		101	
T_{2g}	ν_{10}	[δ(MCO)]		478		471	
T_{2g}	ν_{11}	[δ(CMC)]	132	98	−34	93	−39
T_{2u}	ν_{12}	[δ(MCO)]		513		509	
T_{2u}	ν_{13}	[δ(CMC)]		80		77	

[a] Reference 8 for M = Fe; ref 9 for M = Ru, Os; values obtained for $[M(CO)_6][Sb_2F_{11}]_2$.

Table 6. Vibrational Frequencies (cm^{-1}) for $[Ir(CO)_6]^{3+}$

			exp[a] (solid)	BP86/ECP1	$\Delta\nu$	BP86/ECP2	$\Delta\nu$
A_{1g}	ν_1	[CO]	2295	2266	−29	2272	−23
A_{1g}	ν_2	[MC]		404		402	
E_g	ν_3	[CO]	2276	2239	−37	2245	−31
E_g	ν_4	[MC]		374		373	
T_{1g}	ν_5	[δ(MCO)]		332		326	
T_{1u}	ν_6	[CO]	2254	2222	−32	2228	−26
T_{1u}	ν_7	[δ(MCO)]	531	536	+5	528	−3
T_{1u}	ν_8	[MC]		317		319	
T_{1u}	ν_9	[δ(CMC)]		112		107	
T_{2g}	ν_{10}	[δ(MCO)]		458		449	
T_{2g}	ν_{11}	[δ(CMC)]		100		95	
T_{2u}	ν_{12}	[δ(MCO)]		483		477	
T_{2u}	ν_{13}	[δ(CMC)]		85		83	

[a] Reference 10; values obtained for $[Ir(CO)_6][Sb_2F_{11}]_3$.

suggest that the analogous theoretical predictions for $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ should also be fairly accurate.

The vibrational spectra of $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$ are known both in solution and in the solid state.[46,48] These spectra are quite similar, since the differences between solution and solid state do not exceed 5 cm^{-1}. Table 4 compares the available experimental[46,48] and theoretical wavenumbers. The agreement is very good, as in the case of the neutral hexacarbonyls (Table S1). Concerning the CO stretching modes, the deviations between the calculated (BP86/ECP2) and the observed values are −24, −20, −9 cm^{-1} for $[Mn(CO)_6]^+$ and −21, −19, −5 cm^{-1} for $[Re(CO)_6]^+$. Again, these deviations move more into the usual range when the solvent shifts are accounted for (see above). For the other modes, the average absolute deviations are 10 cm^{-1} for $[Mn(CO)_6]^+$ and 6 cm^{-1} for $[Re(CO)_6]^+$, with maximum deviations of 24 and 10 cm^{-1}, respectively.

Table 7. Vibrational Frequencies (cm^{-1}) for $[Co(CO)_6]^{3+}$, $[Rh(CO)_6]^{3+}$, $[Pt(CO)_6]^{4+}$, and $[Au(CO)_6]^{5+}$

			$[Co(CO)_6]^{3+}$		$[Rh(CO)_6]^{3+}$	
			BP86/ ECP1	BP86/ ECP2	BP86/ ECP1	BP86/ ECP2
A_{1g}	ν_1	[CO]	2243	2248	2257	2264
A_{1g}	ν_2	[MC]	326	330	368	366
E_g	ν_3	[CO]	2232	2237	2237	2244
E_g	ν_4	[MC]	315	320	344	343
T_{1g}	ν_5	[δ(MCO)]	318	321	316	312
T_{1u}	ν_6	[CO]	2222	2226	2223	2230
T_{1u}	ν_7	[δ(MCO)]	532	538	522	516
T_{1u}	ν_8	[MC]	347	348	320	318
T_{1u}	ν_9	[δ(CMC)]	121	120	114	110
T_{2g}	ν_{10}	[δ(MCO)]	468	467	437	432
T_{2g}	ν_{11}	[δ(CMC)]	100	98	95	91
T_{2u}	ν_{12}	[δ(MCO)]	424	428	450	445
T_{2u}	ν_{13}	[δ(CMC)]	79	79	81	79

			$[Pt(CO)_6]^{4+}$		$[Au(CO)_6]^{5+}$	
			BP86/ ECP1	BP86/ ECP2	BP86/ ECP1	BP86/ ECP2
A_{1g}	ν_1	[CO]	2266	2273	2221	2228
A_{1g}	ν_2	[MC]	355	356	247	256
E_g	ν_3	[CO]	2254	2261	2216	2224
E_g	ν_4	[MC]	323	325	194	206
T_{1g}	ν_5	[δ(MCO)]	320	311	304	292
T_{1u}	ν_6	[CO]	2242	2249	2211	2217
T_{1u}	ν_7	[δ(MCO)]	481	474	407	400
T_{1u}	ν_8	[MC]	304	308	250	257
T_{1u}	ν_9	[δ(CMC)]	114	110	108	105
T_{2g}	ν_{10}	[δ(MCO)]	423	414	370	363
T_{2g}	ν_{11}	[δ(CMC)]	100	94	93	89
T_{2u}	ν_{12}	[δ(MCO)]	439	431	374	366
T_{2u}	ν_{13}	[δ(CMC)]	86	84	78	77

Table 5 lists the calculated wavenumbers of the dications $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os) along with the experimental data for the corresponding $[Sb_2F_{11}]^-$ salts.[8,9] The deviations for the CO stretching vibrations (ν_1, ν_3, ν_6) are quite uniform and are of the usual magnitude (between −19 and −32 cm^{-1}) without applying any solid-state correction. In the spectral region between 300 and 600 cm^{-1}, the published assignments (ν_4, ν_7, ν_8) are confirmed for M = Ru, Os,[9] while there are some discrepancies for M = Fe.[8] The BP86/ECP2 calculations reproduce the observed value of ν_7 (δ(MCO), infrared allowed) for M = Ru, Os to within 15 cm^{-1} but yield a value for M = Fe that is too high by 50 cm^{-1} and would much better fit another feature in the experimental infrared spectrum around 600 cm^{-1}. Likewise, for the two MC stretching modes (ν_4, ν_8), the BP86/ECP2 results are within 10 cm^{-1} of experiment in four out of five cases (including ν_4 for M = Fe), but there is a difference of 42 cm^{-1} with ν_8 for M = Fe (whose infrared intensity is computed to be quite small; see below). Finally, in the low-frequency region, the calculations consistently underestimate the value of ν_{11} (δ(CMC)) from the solid-state spectra (M = Fe, Ru, Os).

Table 8. Stretching Force Constants F (10^2 N m^{-1})

compd	exp[a] F(CO)	BP86/ECP2[b] F(CO)	BP86/ECP2[b] F(MC)
$[V(CO)_6]^-$	14.55[c]	14.47	2.33
$[Nb(CO)_6]^-$		14.54	2.04
$[Ta(CO)_6]^-$		14.46	2.21
$[Cr(CO)_6]$	16.64[d]	16.27	2.36
$[Mo(CO)_6]$	16.66[d]	16.30	2.21
$[W(CO)_6]$	16.60[d]	16.20	2.43
$[Mn(CO)_6]^+$	18.2[e]	17.92	2.11
$[Re(CO)_6]^+$	18.01[c]	17.82	2.40
$[Fe(CO)_6]^{2+}$	19.82[f]	19.20	1.77
$[Ru(CO)_6]^{2+}$	19.82[g]	19.22	1.89
$[Os(CO)_6]^{2+}$	19.76[g]	19.13	2.16
$[Co(CO)_6]^{3+}$		19.88	1.49
$[Rh(CO)_6]^{3+}$		19.96	1.62
$[Ir(CO)_6]^{3+}$	20.8[h]	19.94	1.92
$[Pt(CO)_6]^{4+}$		20.10	1.60
$[Au(CO)_6]^{5+}$		19.50	0.87

[a] From energy factored force fields designed to reproduce the observed fundamental frequencies.[49] See original papers for the values of these frequencies. [b] Harmonic force constants. [c] Reference 46. [d] Reference 47, gas-phase data; results for solution data 16.45, 16.46, 16.35. [e] Reference 21. [f] Reference 8. [g] Reference 9. [h] Reference 10.

Table 9. Infrared Intensities:[a] Theoretical Absolute Values and Experimental Relative Intensities

compd	A_i (km/mol)[b] ν_6	ν_7	ν_8	ν_9	I_{rel}[c] ν_6	ν_7	ν_8	ν_9
$[V(CO)_6]^-$	6986	364	18	2	vs	vs	s	
$[Nb(CO)_6]^-$	7701	194	56	2	vs			
$[Ta(CO)_6]^-$	7791	123	53	3	vs			
$[Cr(CO)_6]$	4842	484	52	3	vvs	vs	s	m
$[Mo(CO)_6]$	5383	285	108	3	vvs	vs	s	m
$[W(CO)_6]$	5616	192	124	2	vvs	vs	s	m
$[Mn(CO)_6]^+$	2733	446	65	4	2000	800	500	
$[Re(CO)_6]^+$	3443	243	158	0	vs	vs	vs	
$[Fe(CO)_6]^{2+}$	1039	310	26	3	s	m	w	
$[Ru(CO)_6]^{2+}$	1254	280	61	1	s	s	m	
$[Os(CO)_6]^{2+}$	1540	245	120	0	s	s	m	
$[Co(CO)_6]^{3+}$	157	168	0	3				
$[Rh(CO)_6]^{3+}$	221	193	7	0				
$[Ir(CO)_6]^{3+}$	372	216	53	2	s	s		
$[Pt(CO)_6]^{4+}$	3	174	19	4				
$[Au(CO)_6]^{5+}$	137	134	53	6				

[a] For the infrared allowed T_{1u} modes. [b] From BP86/ECP2 calculations. [c] Experimental data in standard notation: ref 46 for M = V, Re; ref 38 for M = Nb, Ta; ref 47 for M = Cr, Mo, W; ref 48 for M = Mn; ref 8 for M = Fe; ref 9 for M = Ru, Os; ref 10 for M = Ir. Numerical relative intensities are given for M = Mn.

Table 6 contains the theoretical results for the trication $[Ir(CO)_6]^{3+}$ together with the experimental data[10] for $[Ir(CO)_6][Sb_2F_{11}]_3$. This compound exhibits the highest reported CO stretching frequency reported to date, i.e. 2295 cm^{-1} for ν_1 (BP86/ECP2: 2272 cm^{-1}). The deviations between theory and experiment for the CO stretching modes are again consistent and are in the usual range (between −23 and −31 cm^{-1}). The other observed bands have not yet been assigned, but it seems clear from the present calculations that the strong infrared band at 531 cm^{-1} corresponds to ν_7 (BP86/ECP2: 528 cm^{-1}).

The other trications $[M(CO)_6]^{3+}$ (M = Co, Rh) are still unknown; therefore, the theoretical predictions in Table 7 may be helpful in future attempts to identify them by vibrational spectroscopy. The same applies to the even more highly charged cations $[Pt(CO)_6]^{4+}$ and $[Au(CO)_6]^{5+}$ (see also Table 7). Although it may be quite difficult to generate these cations,[21] they correspond to minima on the BP86 potential surface and should therefore, at least in principle, be observable.

In an overall assessment, the current density functional calculations yield vibrational frequencies for the charged hexacarbonyls which are of quality similar to that for the neutral hexacarbonyls.[25] For example, the theoretical and experimental CO stretching frequencies in $[M(CO)_6]$ (M = Cr, Mo, W) and $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os) show completely analogous patterns with regard to relative magnitudes, shifts, and correlations (see Figure S1 in the Supporting Information). Such comparisons (and the data in Tables 3−7 and S1) suggest that the calculations provide realistic predictions for unknown hexacarbonyls (M = Co, Rh, Pt, Au) and that the computational results may be used for a reliable analysis of trends among differently charged hexacarbonyls (see section 4).

d. Force Constants. Table 8 lists experimental and theoretical stretching force constants for the title compounds. The experimental values are derived from the Cotton−Kraihanzel treatment,[49] which neglects any coupling between CO stretching and other modes and does not correct the observed frequencies for anharmonicity effects. The BP86/ECP2 values represent harmonic force constants. The comparisons between theory and experiment in Table 8 are analogous to those in Tables 3−6 and S1. Since the CO stretching frequencies are generally slightly underestimated at the BP86/ECP2 level, the same also applies to the CO stretching force constants F(CO). However, the overall variation of F(CO) with the total charge is reproduced nicely, as well as the detailed variation within a group (see, for example, the chromium group, Cr vs Mo vs W). Experimentally, the highest CO stretching force constant has been reported[10] for $[Ir(CO)_6]^{3+}$. According to the calculations, F(CO) should still be slightly higher for the yet unknown $[Pt(CO)_6]^{4+}$ ion.

e. Infrared Intensities. Table 9 documents the calculated (BP86/ECP2) intensities for the four infrared-active vibrations of the hexacarbonyls. Comparison with the experimental relative intensities[8−10,38,46−48] shows that the calculations correctly describe the major qualitative intensity variations in the experimental infrared spectra. The CO stretching mode ν_6 normally gives rise to the strongest infrared band. However, its intensity is predicted to be rather low for the highly charged cations and is even close to zero for $[Pt(CO)_6]^{4+}$. This might complicate the spectroscopic identification of this species.

f. Charge Distributions. Table 10 presents atomic charges obtained from a natural population analysis (NPA)[50,51] at the BP86/ECP2 level. The partitioning of the electron density into atomic contributions is not unique, of course, but different types of population analyses usually lead to similar trends in related

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Table 10. Atomic Charges from Natural Population Analysis[a,b]

compd	q_M	q_C	q_O	$q_C + q_O$	$q_C - q_O$
$[V(CO)_6]^-$	−1.60	0.61	−0.51	0.10	1.12
$[Nb(CO)_6]^-$	−1.22	0.54	−0.50	0.04	1.04
$[Ta(CO)_6]^-$	−0.78	0.46	−0.50	−0.04	0.96
$[Cr(CO)_6]$	−1.35	0.64	−0.42	0.22	1.06
$[Mo(CO)_6]$	−1.16	0.60	−0.40	0.20	1.00
$[W(CO)_6]$	−0.95	0.56	−0.40	0.16	0.96
$[Mn(CO)_6]^+$	−0.98	0.65	−0.32	0.33	0.97
$[Re(CO)_6]^+$	−0.69	0.58	−0.30	0.28	0.88
$[Fe(CO)_6]^{2+}$	−0.49	0.63	−0.21	0.42	0.84
$[Ru(CO)_6]^{2+}$	−0.51	0.63	−0.21	0.42	0.84
$[Os(CO)_6]^{2+}$	−0.35	0.60	−0.20	0.40	0.80
$[Co(CO)_6]^{3+}$	0.04	0.60	−0.11	0.49	0.71
$[Rh(CO)_6]^{3+}$	0.01	0.61	−0.11	0.50	0.72
$[Ir(CO)_6]^{3+}$	0.11	0.59	−0.11	0.48	0.70
$[Pt(CO)_6]^{4+}$	0.60	0.58	−0.01	0.57	0.59
$[Au(CO)_6]^{5+}$	1.04	0.59	0.07	0.66	0.52

[a] BP86/ECP2 values in units of e. [b] Free CO: $q_C = 0.46$, $q_O = -0.46$, $q_C - q_O = 0.92$.

molecules. We have chosen NPA because it is well-established and is rather insensitive to basis set effects. In the hexacarbonyl series $[M(CO)_6]^n$, where the total charge n varies between −1 and +5, the computed NPA charges behave quite regularly. The charges at carbon are almost constant at $q_C \approx 0.6$ (in units of e). With increasing n, oxygen loses electron density (mostly out of the p_π orbitals) according to $q_O \approx -0.4 + 0.1n$. As a consequence, the total positive charge on the CO ligand increases as $q_C + q_O \approx 0.2 + 0.1n$, while the polarity within the CO unit decreases as $q_C - q_O \approx 1.0 - 0.1n$. These relations are admittedly an oversimplification of the data (see Table 10), but they capture the essential qualitative trends in the NPA charges.

In the case of $[Pt(CO)_6]^{4+}$, the polarity within CO is already quite low, and the NPA charges of Pt and C are almost the same (0.60 and 0.58, respectively). It is therefore qualitatively plausible that the nuclear motion along the T_{1u} CO stretching mode will generate only a small dipole moment and, hence, only a small infrared intensity for ν_6 (see above). This argument neglects the charge flux during the nuclear motion, however, which is implicitly included in an alternative population analysis based on generalized atomic polar tensors (GAPT).[52] The GAPT charges are obtained from the trace of the derivatives of the dipole moment components with respect to the nuclear coordinates and are thus directly linked to the infrared intensities.[52] For $[Pt(CO)_6]^{4+}$, these charges are $q_{Pt} = 0.42$, $q_C = 0.44$, and $q_O = 0.16$, which implies an explanation completely analogous to that in the NPA case for the very small infrared intensity of the ν_6 band (see above).

We have evaluated the GAPT charges for all hexacarbonyls considered presently. The charge variations are more pronounced for GAPT than for NPA, but the basic overall trends are analogous, so that there is no need to discuss the GAPT charges in detail. It seems noteworthy, however, that $q_C - q_O$ changes from +0.28 to −0.10 when going from $[Pt(CO)_6]^{4+}$ to $[Au(CO)_6]^{5+}$, indicating a reversal of CO polarity in the GAPT analysis.

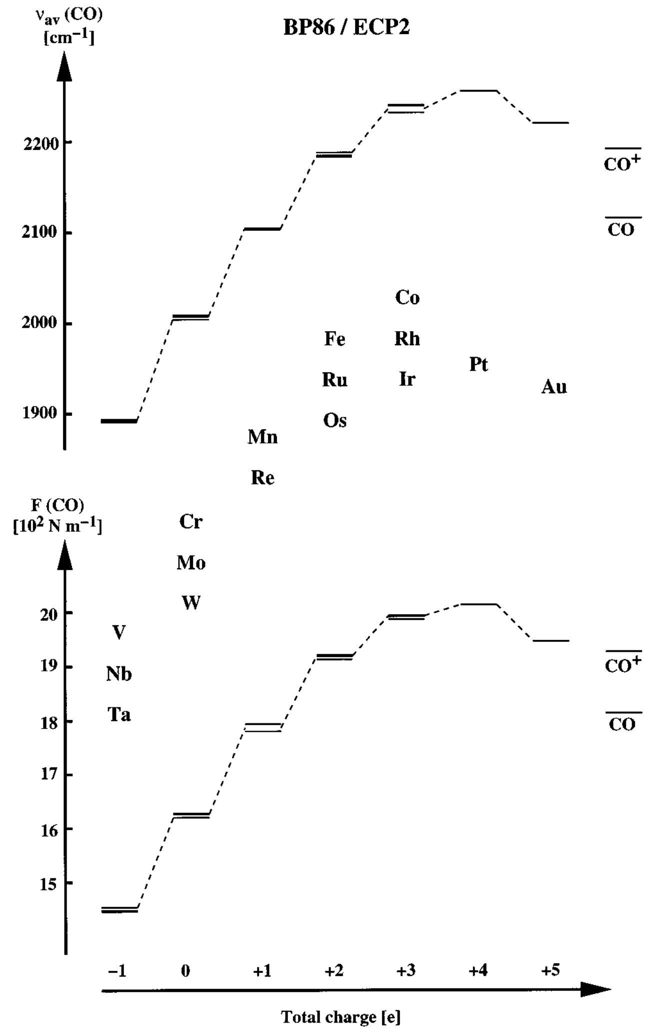

Figure 4. Average CO stretching frequencies $\nu_{av}(CO)$ and CO stretching force constants $F(CO)$ as a function of the total molecular charge (see Tables 1, 3−8, and S1).

4. Discussion

In this section, we discuss the variation of the computational results (BP86/ECP2) within the hexacarbonyl series $[M(CO)_6]^n$ (16 molecules, total charge n between −1 and +5).

In the vibrational spectra of transition-metal carbonyls, the CO stretching bands are normally the dominant features. Figure 4 shows the changes in the degeneracy-weighted average CO stretching frequencies $\nu_{av}(CO)$ and in the CO stretching force constants $F(CO)$ as a function of n (based on the BP86/ECP2 results in Tables 1, 3−8, and S1). On the chosen scale, the entries for different hexacarbonyls with the same charge nearly coincide. Both $\nu_{av}(CO)$ and $F(CO)$ increase significantly with increasing n up to $n = 4$ (M = Pt) before they start to decrease (toward M = Au). An analogous inverse trend is seen in the CO bond lengths (see Table 2), which gradually diminish from 1.170 Å for M = V, Ta to a minimum of 1.122 Å for M = Pt and then rise again to 1.125 Å for M = Au.

In the neutral hexacarbonyls, the Dewar−Chatt−Duncanson model[22,23] rationalizes the observed CO stretching frequencies in terms of synergic σ donation and π back-donation: the π effect dominates so that the frequencies are lower than in free CO. In the highly

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[52] Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333.

charged hexacarbonyl cations, however, the CO stretching frequencies are higher than in free CO. According to the Dewar−Chatt−Duncanson model, this could happen if π back-donation is suppressed and if σ donation strengthens the CO bond by removing electrons from the (formally antibonding) σ lone pair of CO. Free CO^+ should then provide an upper limit for these effects because there is no π back-donation (by definition) and because one electron is fully removed (i.e. more than is removed from the CO ligand in any of the hexacarbonyls; see the NPA charges in Table 10). Thus, the model cannot explain ν_{av}(CO) and F(CO) values higher than in free CO^+, as found for example for $[Ir(CO)_6]^{3+}$. In such cases, electrostatic effects[24] must be taken into account, i.e. the polarization of the electrons in the CO ligand by the positive charges in the $M(CO)_5$ moiety. This reduces the inherent $C^{\delta+}-O^{\delta-}$ polarity and leads to a more covalent "N_2-like" CO bond in the ligand.[24] From this point of view, the upper limit for the CO stretching force constant in the hexacarbonyls would not be given by CO^+ but by HCO^+ (experiment, 21.26 mdyn/Å; BP86/ECP2, 21.36 mdyn/Å; see Table 1).

The arguments concerning the importance of electrostatic effects[24] in highly charged hexacarbonyl cations are confirmed by our computational results. The calculated CO stretching force constants remain lower than the limiting value of HCO^+, whereas they may exceed the value for CO^+ (see Table 8). With increasing charge (up to $n = 4$), both ν_{av}(CO) and F(CO) increase while the polarity $q_C - q_O$ of the CO bond decreases (see Table 10). To be more specific, ν_{av}(CO) and F(CO) surpass the reference values for CO (see Figure 4) when the polarity $q_C - q_O$ drops below the value for CO (i.e. $n \geq 2$; see Table 10). The maximum strength of the CO bond is reached for $n = 4$, $[Pt(CO)_6]^{4+}$, where its polarity is lowest according to the GAPT charges (as evidenced by the low ν_6 infrared intensity; see section 3f). Finally, the electrostatic arguments imply that very high positive charges in the $[M(CO)_5]$ moiety might cause an inverse $C^{\delta-}-O^{\delta+}$ polarization and thereby weaken the CO bond in the ligand again. According to the calculations, this extreme situation is realized in $[Au(CO)_6]^{5+}$ (see Figure 4 and the GAPT charges in section 3f).

In the vibrational spectra of the hexacarbonyls, there are three CO stretching vibrations whose frequencies satisfy ν_1 (A_{1g}) > ν_3 (E_g) > ν_6 (T_{1u}). The corresponding splittings generally decrease with increasing n. For example, the difference $\nu_1 - \nu_6$ (BP86/ECP2) lies in the range between 125 and 127, 108 and 118, 82 and 98, 48 and 71, and 22 and 44 cm^{-1} for $n = -1$, 0, 1, 2, and 3, respectively, and is further reduced to 24 cm^{-1} for $n = 4$ (M = Pt) and 11 cm^{-1} for $n = 5$ (M = Au). According to the simplified Cotton−Kraihanzel approach,[49] these splittings are essentially determined by the interaction force constant F(CO,CO), which is qualitatively related to the strength of the M−CO π interactions.[49] Hence, the reduced splittings indicate that π back-donation becomes progressively less important with increasing n.

Analogous evidence comes from the δ(MCO) bending vibrations (ν_5, ν_7, ν_{10}, ν_{12}). π Back-donation is expected to stiffen the MCO angles, thus leading to higher frequencies. In contrast, the calculated bending frequencies (BP86/ECP2) decrease with increasing n in each transition-metal series (3d, 4d, 5d), typically by 10−20% when going from the Cr group ($n = 0$) to the Co group ($n = 3$) and even more for M = Pt ($n = 4$) and M = Au ($n = 5$). These changes are another indication for the diminishing π back-donation.

The MC stretching vibrations (ν_2, ν_4, ν_8) show similar trends within each transition-metal series, with reductions of the corresponding degeneracy-weighted average frequencies of 22% (3d), 16% (4d), and 12% (5d) between $n = 0$ and $n = 3$, which become even more pronounced in the 5d series for $n = 4$ and $n = 5$ (20% and 40%, respectively, relative to $n = 0$). These trends are mirrored by a corresponding decrease in the MC stretching force constants (see Table 8). The weakening of the MC bonds with increasing n is partially caused by the reduced π interactions (see above), but the Coulomb repulsion between positively charged atoms M and C is also expected to contribute significantly for $n > 3$ (see Table 10). Considering the MC bond lengths (Table 2), the minimum BP86/ECP2 values within a given transition-metal series (3d, 4d, 5d) are found for M = Mn ($n = 1$, 1.892 Å), M = Ru ($n = 2$, 2.028 Å), and M = Os ($n = 2$, 2.045 Å), respectively. For the more highly charged cations, the weakening of the MC bonds with increasing n apparently overcompensates any trend to smaller MC distances due to smaller atomic radii.

Among the hexacarbonyl cations that are as yet unknown (M = Co, Rh, Pt, Au), it should be most difficult to detect $[Au(CO)_6]^{5+}$, which is predicted to have very weak AuC bonds ($R = 2.227$ Å, $F = 0.87$ mdyn/Å). The PtC bonds in $[Pt(CO)_6]^{4+}$ are significantly stronger ($R = 2.111$ Å, $F = 1.60$ mdyn/Å), while the CO bond strength reaches its maximum in this cation (see above). Hence, there would seem to be some hope for generating $[Pt(CO)_6]^{4+}$, but it may be hard to prepare thermally stable salts.[21] The intrinsic properties of $[Co(CO)_6]^{3+}$ and $[Rh(CO)_6]^{3+}$ are computed to be not too different from those of the known $[Ir(CO)_6]^{3+}$ trication,[10] even though their predicted MC force constants are somewhat lower (Table 8). $[Co(CO)_6]^{3+}$ and $[Rh(CO)_6]^{3+}$ are therefore the most promising candidates for experimental identification. It is hoped that our theoretical predictions will facilitate the spectroscopic detection of the hexacarbonyl cations that are as yet unknown.

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Supporting Information Available: Table S1, containing the results for the neutral compounds $[M(CO)_6]$ (M = Cr, Mo, W), and Figure S1, illustrating the correlation between the theoretical and experimental CO stretching frequencies in $[M(CO)_6]$ (M = Cr, Mo, W) and $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os) (2 pages). Ordering information is given on any current masthead page.

Note Added in Proof: Three other relevant theoretical papers have appeared recently.[53−55]

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