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Density Functional Study of Geometry and Vibrational Spectra for the Isoelectronic $V(CO)_6^-$ and $Cr(CO)_6$ Molecules

Kenneth G. Spears

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

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We study the geometry and vibrational spectra obtained by density functional theoretical (DFT) methods for isoelectronic $V(CO)_6^-$ and $Cr(CO)_6$ molecules. We compare many Gaussian basis set options with the B3P86 method for the anion, and we systematically investigate results for both species with the SVWN, B3P86, BP86, and B3LYP methods and fewer basis sets. In general the gradient-corrected methods give good agreement for both geometry and vibrational frequencies, where the method variations are greater than effects of small basis set improvements. We note interesting differences between DFT methods for the isoelectronic neutral and anion species. The metal−carbon distance is sensitive to the method, and this distance increases in the anion by 0.025−0.03 Å for all DFT methods compared with the experimental increase of 0.02 Å. The absolute distance is closest to experiment for the neutral with B3LYP (+0.006 Å) and for the anion with B3P86 (+0.009 Å), where the anion results are too long by 0.009−0.033 Å and the neutral results range from −0.02 to 0.006 Å for the B3P86, BP86 and B3LYP methods. However, the B3P86 and B3LYP methods give good agreement for the C−O distance. The vibrational calculations show about 30 cm^{-1} random deviations for the metal−ligand modes while the CO stretching modes show 40−80 cm^{-1} deviations. The DFT trends for diatomic CO are maintained for the anion; however, the neutral with B3P86 gives frequencies that change from positive to negative deviations from experiment. The anion has its charge distributed over the whole molecule, but with oxygen and the vanadium having increased electron densities. We compare bonding charge distributions from natural population analysis and the long range interactions from electric moment values and electrostatic potential fitting of charges. The DFT calculations seem to be sufficiently good to allow their use in experimental interpretations involving geometry and vibrational frequencies. The isoelectronic comparison can be useful in testing various aspects of new DFT methods since the anion shows some subtle differences from the neutral molecule.

I. Introduction

The computation of molecular geometry and vibrational properties of transition metal complexes is of interest for theoretical and experimental reasons. The simplest metal carbonyl complexes have often been used to test theoretical methods, and many workers have concluded that electron correlation is very important for attaining a reasonable match to experiment. The density functional theoretical (DFT) method has been applied previously to $Cr(CO)_6$ with good results, and many such studies have been previously published.[1−9] Also, a wide variety of other *ab initio* calculation methods[10−12] have been used for $Cr(CO)_6$.

In this work we compare isoelectronic molecules, $V(CO)_6^-$ and $Cr(CO)_6$, in order to systematically explore the effects of DFT method and basis set on geometry and vibrational frequencies. The main motivation is to develop reliable models for experimental interpretations of electron transfer data involving the $V(CO)_6^-$ molecule and its neutral radical species.[13] The theoretical framework for interpreting such data requires geometries, vibrational frequencies, solvation effects, and cation-pairing effects so that the computational methods need to be characterized for different levels of basis set complexity to allow modeling more complex molecules in our future work. Calculations by SCF-Xα-DV methods[14] have been reported for $V(CO)_6$ and its anion in octahedral geometries.

II. Calculation Methods

The quantum calculations were done with Gaussian 94W programs[15] on a personal computer.[16] We compared DFT methods, especially the gradient-corrected methods, with exchange and correlation corrections developed by various authors. In this program package the methods of Becke[17] and Perdew[18] were used for exchange and correlation via the acronym of BP86 and a hybrid method[19] B3P86. We also studied a hybrid method[19] using the Lee−Yang−Parr correlation functional,[20,21] which is known as the B3LYP method. For some cases we studied the local density method using Slater exchange[22] and the Vosko−Wilk−Nusair[23] correlation functional, which is known as the SVWN method. We performed one reference calculation with HF and MP2 correlation[24] corrections.

The literature results for the chromium hexacarbonyl molecule provide guidance for our study. Geometric and vibrational results[1,4,6,7] from the BP86 method show good agreement with experiment, while dissociation energies[1−5] have provided another type of test for this method. The prior basis set comparisons[1,2,5] showed that d polarization functions on C and O are necessary and that 4f basis functions make minor improvements. The basis sets with triple-ζ complexity provide better dissociation energies when compared with double-ζ, but the smaller sets may be correctable for basis set superposition effects.[5] Prior literature emphasizes the BP86 method, but local density methods[8] have also been applied to $Cr(CO)_6$ as well as other *ab initio* methods such as multireference configuration interaction.[10−12] For single carbonyl bonds to metals, hybrid DFT methods such as B3LYP have been studied and judged to be satisfactory.[25−28]

The Gaussian 94 program computes the optimum geometry by analytic methods and also performs analytic second deriva-

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TABLE 1: Computations for Diatomic CO

method	basis[a]	R(C−O) (Å)	μ (D)	ω (cm^{-1})	$\Delta\omega$ (cm^{-1})
BP86	Z	1.1374	0.184	2118	−52
BP86	R	1.1398	0.156	2122	−48
BP86	G	1.1392	0.202	2128	−42
BP86	D	1.1498	0.148	2118	−52
B3P86	Z	1.1244	0.118	2220	50
B3P86	R	1.1268	0.088	2226	56
B3P86	G	1.1262	0.126	2232	62
B3P86	D	1.1364	0.060	2225	55
B3LYP	Z	1.1253	0.097	2208	38
B3LYP	R	1.1277	0.072	2213	43
B3LYP	G	1.127	0.121	2221	51
B3LYP	D	1.1377	0.064	2212	42
exptl		1.1283	0.112	2170	

[a] Basis D, 6-31G(d); G, 6-311G(d); R, 6-311+G(d); Z, 6-311+G(3d).

tives to find the vibrational frequencies. We used the default methods of performing the DFT numerical integration according to the FineGrid option and a frozen core option for correlation calculations. Other Gaussian basis sets in the literature were also compared with the internal basis sets, which were specified for each atom. We did not study effective core potential basis sets since for a first row transition basis sets with all electrons were efficient.

III. Results and Discussion

A. Diatomic CO. The computation of CO defines how well the basis set and method might perform on properties such as vibrational frequencies when CO is bonded to a central metal atom. A number of studies of CO have been done with various DFT methods.[1,25,29] We present our results for the BP86, B3P86, and B3LYP methods with four basis sets in Table 1 and also compare with experiment.[30] These basis sets are 6-31G(d), 6-311G(d), 6-311+G(d), and 6-311+G(3d), where the polarization functions of d type are indicated in parentheses and diffuse functions of sp type are indicated by the plus sign.[15] The BP86 method behaves differently from the others in that the bond length is too long and the vibrational frequency is too low for all basis sets. The lowest level basis set shown here; the 6-31G(d) has a longer bond length by 0.01 Å for all methods although the vibrational frequencies are similar to a better basis. We can conclude that a simple triple-ζ basis such as 6-311G(d) can give reasonable results for the B3P86 and B3LYP methods. We might expect that the CO vibrational modes of a metal complex may be offset in similar directions and magnitudes as the diatomic results of 40−60 cm^{-1}.

B. Molecular Structures. *B.1. Experimental Data on V(CO)$_6^-$ and Cr(CO)$_6$.* The computations on V(CO)$_6^-$ can be compared with experimental data for geometry based on X-ray structures. Unfortunately, only a few compounds have been studied, and the anion structure can depend on the cation bonding and crystal disorder as well as the effort used to provide thermal corrections. In a study of [(Ph$_3$P)$_2$$^+$|V(CO)$_6^-$] the anion was octahedral with an R(V−C) of 1.931(9) Å and R(C−O) of 1.146(11) Å, but thermal corrections were not applied to these room temperature data.[31] If we use thermal corrections from Cr(CO)$_6$, these values can be approximately corrected by analogy. The neutron diffraction data[32] for Cr(CO)$_6$ at 78 K provided an estimate of room temperature thermal corrections for previously published X-ray data.[33] While the values are only estimates, increases in the Cr−C bond length of 0.007 Å and the C−O bond length of 0.01 Å were used to reevaluate the X-ray data. If we apply these thermal corrections to our case, we have R(V−C) of 1.938 Å and R(C−O) of 1.156 Å with errors of about 0.01 Å.

The pyridinium cation salt [C$_5$H$_5$NH$^+$|V(CO)$_6^-$] has been analyzed[34] with thermal corrections, and the V(CO)$_6^-$ shows two axial carbonyls with π bonding to the aromatic system of pyridinium and the four near-planar CO molecules with oxygen binding to the NH+ part of the pyridinium. The axial/planar values of R(V−C) are 1.934(9)/1.926(14) in Å, while for R(C−O) the axial/planar values are 1.137(11)/1.165(21). In this case the expected octahedral geometry is slightly distorted. The two values of R(V−C) are not significantly different, but there are larger errors in the R(C−O) due to disorder corrections. In this case the bonding effects of the cation seem to provide a major perturbation of the intrinsic structure so that the previously discussed compound with more symmetric bonding to the cation is probably preferred as a source of bond lengths. The mean values of R(V−C) of 1.930 Å and R(C−O) of 1.151 Å are consistent with the preferred values of 1.938 and 1.156 discussed in the prior paragraph.

The geometry of Cr(CO)$_6$ is well studied by neutron[32] and X-ray diffraction[33] methods where the neutron studies give values of 1.918(2) Å for R(Cr−O) and 1.141(2) Å for R(C−O). These are thermally corrected values for 78 K data. These values are reported in the original abstract and the text, and they are based on a model for corrections; these are not the values of their Table 5, which have been quoted previously in theoretical comparisons.[1] The X-ray data are consistent with the neutron data, but they probably have greater uncertainty so they are not used in our comparisons.

Interestingly, the Cr−C distance and C−O distances are significantly smaller than for V(CO)$_6^-$. One expects this qualitative effect for isoelectronic bonding in the presence of greater nuclear charge in Cr. For V(CO)$_6^-$ we find the metal−carbon distance for the anion to increase by 0.02 Å and the carbon−oxygen to increase by 0.015 Å, with uncertainties on the order of 0.01 Å due to the thermal corrections and crystal perturbation effects. The absolute values of bond distance and the relative changes with nuclear charge are both of interest in comparing methods of computation.

B.2. Geometry and Energy Computations for V(CO)$_6^-$. For this molecule we have performed extensive comparisons of basis set and DFT method. Our ultimate objective is to perform experimental spectroscopic interpretations with solvation effects and cation interaction effects. Therefore one of our goals is to ascertain the smallest basis set capable of giving reasonable geometries and vibrational frequencies.

The basis set comparisons were mostly done with the B3P86 method, and Table 2 has the results of these calculations. The basis set code has the first letter for the metal basis set and the second for the C,O basis set. The number of basis functions and corresponding primitive Gaussians are shown for the various basis set choices. All distances in this article are in angstroms (Å), where 1 Å = 0.1 nm or 100 pm. Selected values from Table 2 are plotted in Figure 1, where the V basis is the 6-311G basis[35] and the basis set on C and O is varied to examine the effects on geometry. The arbitrary zero of energy is for the DH basis set, the lowest energy of the built-in G94 basis sets with moderate size. We see from Figure 1 that polarization functions of d character (AD, AG) are essential to reduce the energy and narrow the deviation from experiment (AD vs AC and AG vs AE). The triple-ζ basis (AG) makes a large improvement (AG vs AD), while adding diffuse functions only makes a small improvement (AH vs AG). Other basis sets (AW, AX, AY) can be compared with the standard sets from Gaussian 94. We see that the double-ζ (AW) basis set cc-pVDZ,[36] which has large numbers of Gaussian functions, is of higher energy than the 6-311G(d) basis (AG). The AX triple-ζ basis

TABLE 2: Computations for V(CO

method	basis (code)	basis (metal)	basis (C,O)	energy (au)	R(V−C) (Å)	R(C−O) (Å)	No. basis (B) Gaussians (G)
exptl					1.938	1.156	
B3P86	AC	6-311G	6-31G	−1625.8529	1.9271	1.1844	147 B 330G
B3P86	AD	6-311G	6-31G(d)	−1626.0916	1.9411	1.1648	207 B 398G
B3P86	AE	6-311G	6-311G	−1626.0428	1.9324	1.181	195 B 378G
B3P86	AG	6-311G	6-311G(d)	−1626.2953	1.9467	1.1567	255 B 438G
B3P86	AH	6-311G	6-311+G(d)	−1626.3174	1.9461	1.1572	303 B 486G
B3P86	BH	6-311+G	6-311+G(d)	−1626.3206	1.9496	1.1572	315 B 498G
B3P86	CG	6-311G(d)	6-311G(d)	−1626.2981	1.9449	1.1568	262 B 445G
B3P86	DG	6-311+G(d)	6-311G(d)	−1626.3034	1.9485	1.1565	274 B 457G
B3P86	DH	6-311+G(d)	6-311+G(d)	−1626.3234	1.9477	1.1571	322 B 505G
B3P86	AV	6-311G	6-311G(2d)	−1626.3165	1.9503	1.1546	315 B 498G
B3P86	AW	6-311G	cc-pVDZ	−1626.1671	1.9464	1.163	207 B 534 G
B3P86	XG	AHL-PVTZ	6-311G(d)	−1626.3147	1.9481	1.1567	257 B 441 G
B3P86	XX	AHL-PVTZ	AHL-PVTZ	−1626.379	1.9454	1.1559	281 B 465 G
B3P86	AX	6-311G	AHL-PVTZ	−1626.3578	1.9451	1.1556	279 B 462 G
B3P86	DX	6-311+G(d)	AHL-PVTZ	−1626.3703	1.9473	1.1557	298 B 481 G
B3P86	BX	6-311+G	AHL-PVTZ	−1626.3675	1.9481	1.1559	291 B 474 G
B3P86	XY	AHL-PVTZ	TZVP-DGAUSS	−1626.3336	1.9436	1.1625	257 B 465 G
B3P86	BY	6-311+G	TZVP-DGAUSS	−1626.3234	1.9456	1.1622	267 B 474 G
B3P86	DY	6-311+G(d)	TZVP-DGAUSS	−1626.3269	1.9431	1.1623	274 B 481 G
B3P86	AY	6-311G	TZVP-DGAUSS	−1626.3143	1.9413	1.1626	255 B 462 G
B3P86	BD	6-311+G	6-31G(d)	−1626.1066	1.9502	1.1644	219 B 402 G
B3P86	BG	6-311+G	6-311G(d)	−1626.3004	1.9513	1.1565	267 B 450 G
BP86	AD	6-311G	6-31G(d)	−1624.3205	1.9554	1.18	
BP86	AG	6-311G	6-311G(d)	−1624.5355	1.9617	1.1717	
BP86	DH	6-311+G(d)	6-311+G(d)	−1624.5662	1.9623	1.1723	
B3LYP	AD	6-311G	6-31G(d)	−1624.1249	1.9611	1.1659	
B3LYP	AG	6-311G	6-311G(d)	−1624.3414	1.9708	1.1578	
B3LYP	DH	6-311+G(d)	6-311+G(d)	−1624.3743	1.9708	1.1587	
SVWN	AD	6-311G	6-31G(d)	−1618.9644	1.9111	1.1702	
SVWN	AG	6-311G	6-311G(d)	−1619.2085	1.9166	1.1607	
MP2	AD	6-311G	6-31G(d)	−1621.3512	1.9597	1.1806	

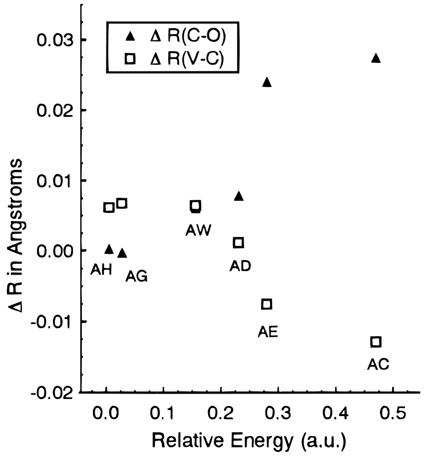

Figure 1. Bond lengths for $V(CO)_6^-$ with variation of the C,O basis set. The V basis is 6-311G, and the C,O basis is indicated by codes referenced to Table 2. The arbitrary energy zero is for basis set DH.

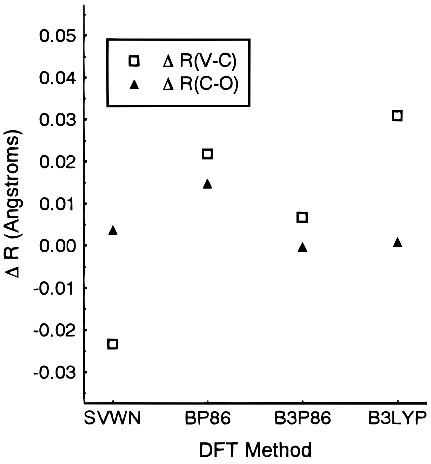

Figure 2. Bond lengths for $V(CO)_6^-$ with different DFT methods and a basis set AG in Table 2.

developed by Ahlrichs et al.[37,38] is of lower energy than AG, but the bond lengths are very similar. The AY triple-ζ basis[37,39] known as TZVP is similar to AG in energy but slightly increases the CO bond distance and decreases the V−C bond distance.

If we vary the vanadium basis set there is relatively little effect on AG from adding diffuse functions (BG) or adding f orbitals (CG) or adding both (DG).[35,40−42] The use of both f orbitals and diffuse functions on V and d orbitals and diffuse functions on C and O provides the lowest energy (DH) for the standard basis sets in Gaussian 94. The vanadium basis defined by Ahlrichs et al.[37,38] without f orbitals reduces the energy slightly compared with the other cases (XX vs DX) and provides the lowest total energy (XX).

The results (AD and AG) suggest that the simplest basis (AD) likely to provide useful experimental results is with 6-31G(d) on C and O, although there is an improvement of geometry by using triple-ζ (AG) with polarization 6-311G(d) for C and O. More complete basis sets (DH) appear to provide a marginal improvement in geometric parameters.

A comparison of DFT methods is done in Table 2 and Figure 2. In Figure 2 we plot the results for the AG basis set calculations, where the V basis is 6-311G and C,O are 6-311G-(d). We see from Figure 2 that BP86 gives bond lengths for both V−C and C−O that are longer than the good results of B3P86. The B3LYP method has a good C−O distance but has lengthened the V−C bond compared with the B3P86 method. The SVWN method also gives good C−O bond lengths but shortens the V−C bond. These results suggest that the V−C bond distance is most sensitive to method and that B3P86 is

TABLE 3: Calculations for Cr(CO)$_6$

method	basis (code)	basis (metal)	basis (C,O)	energy (au)	R(Cr−C) (Å)	R(C−O) (Å)
exptl					1.918	1.141
B3P86	AD	6-311G	6-31G(d)	−1726.499	1.8943	1.1488
B3P86	AG	6-311G	6-311G(d)	−1726.6984	1.8980	1.1401
B3P86	DH	6-311+G(d)	6-311+G(d)	−1726.7212	1.9012	1.1405
BP86	AD	6-311G	6-31G(d)	−1724.7417	1.9039	1.1640
BP86	AG	6-311G	6-311G(d)	−1724.9507	1.9077	1.1553
BP86	DH	6-311+G(d)	6-311+G(d)	−1724.9746	1.9106	1.1556
B3LYP	AD	6-311G	6-31G(d)	−1724.5267	1.9185	1.1499
B3LYP	AG	6-311G	6-311G(d)	−1724.7379	1.9236	1.1409
B3LYP	DH	6-311+G(d)	6-311+G(d)	−1724.7633	1.9273	1.1416
SVWN	AD	6-311G	6-31G(d)	−1719.2755	1.8597	1.1551
SVWN	AG	6-311G	6-311G(d)	−1719.5126	1.8629	1.1451
SVWN	DH	6-311+G(d)	6-311+G(d)	−1719.5368	1.8645	1.1454

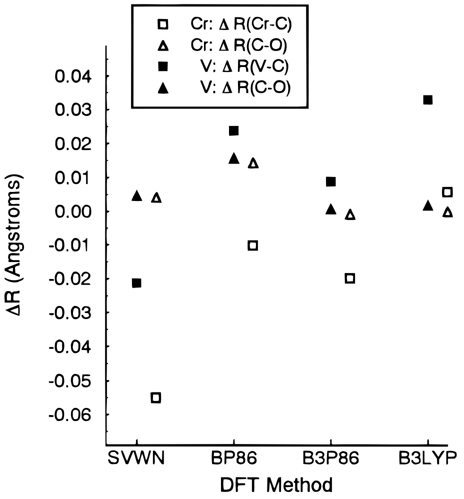

Figure 3. Bond lengths for Cr(CO)$_6$ and V(CO)$_6^-$ with different DFT methods and a basis set AG in Table 2.

the best overall method for the anion where the V−C distances for BP86, B3P86, and B3LYP are 0.024, 0.009, and 0.033 Å longer, respectively, than experiment. However, we will see below that the situation is different for the neutral isoelectronic Cr(CO)$_6$.

B.3. Geometry and Energy Computations for Cr(CO)$_6$. The results are presented in Table 3 and are combined with the V(CO)$_6^-$ in Figure 3 to demonstrate the geometry effects for the AG basis. For Cr(CO)$_6$ the B3LYP method has the best agreement with experiment with the Cr−C distance as 0.006 Å too long, while the B3P86 method has a Cr−C distance that is too small, but with a similar C−O distance. If we examine the data plotted in Figure 3, it is clear that the metal−carbon bond distance is affected the most by the DFT method. Clearly, the greater positive charge of Cr reduces the M−C (M is metal) distance in all methods while hardly affecting the C−O distance. The overall conclusion is that B3P86 and B3LYP give good results for the C−O distance but the M−C bond seems to be sensitive to nuclear charge. Interestingly, there is an offset between the M−C distance that that is independent of DFT method where the anion is about 0.025−0.03 Å longer than the neutral versus the experimental value of 0.02 Å. The quality of the basis set on the metal has little effect on the deviations of geometry from experiment. The question of how these bond length deviations are correlated with vibrational frequencies is discussed in the next sections.

C. Vibrational Frequencies. *C.1. V(CO)$_6^-$.* The vibrational frequencies of V(CO)$_6^-$ have been studied by Raman and IR spectroscopies,[43,44] and most frequencies have been assigned for the solution phase. The comparisons with theory are best done with gas phase harmonic potentials, but these are not available for this molecule. We have taken the approach of estimating both a solution frequency shift and anharmonic corrections for the high-frequency carbonyl modes and the metal carbon stretch modes. The anharmonic correction for one high-frequency CO mode is estimated from experiments with transient infrared spectroscopy,[13] and these are assumed to be the same for all CO modes. The solution shift is estimated by analogy with Cr(CO)$_6$, and no special correction is applied for the anionic solvent interactions. The estimated harmonic frequencies are shown in Table 4.

In Table 4 we show the basis set effect on vibrational frequency for the B3P86, BP86 and B3LYP methods where the C,O basis is either 6-31G(d) (AD) or 6-311G(d) (AG). The first observation is that the A$_{1g}$ mode, $\nu 1$, the totally symmetric C−O stretching mode, is offset from the expected value by an amount similar to diatomic CO. For the case of the 6-311G(d) basis, we find that B3P86 has +62 cm^{-1} for diatomic and +48 cm^{-1} for $\nu 1$, BP86 has −42 cm^{-1} for diatomic and −51 cm^{-1} for $\nu 1$, and B3LYP has +51 cm^{-1} for diatomic and +29 for $\nu 1$. These results suggest that the metal bonding maintains the CO bonding character as sensed by vibrational frequencies and that the BP86 method is consistently different from the other methods. The basis set effect is similar for all DFT methods in that the larger AG basis reduces the A$_{1g}$ C−O stretching mode, $\nu 1$, by about 12 cm^{-1} and reduces the A$_{1g}$ V−C stretching mode, $\nu 2$, by about 9 cm^{-1}. If we compare the bond length changes in Table 2 with these frequencies, we see that the reduced frequency of $\nu 1$ is accompanied by a shorter C−O bond length of about 0.008 Å but the reduced frequency of $\nu 2$ is accompanied by a longer V−C bond length of 0.006−0.009 Å. These results show that basis set effects on vibration and bond length are not simply related but are similar for all DFT methods.

A view of the frequency agreement is shown in Figure 4 for the AG basis. This graph shows that the C−O high-frequency modes are scaling as expected from diatomic results for all DFT methods. The spread of agreement across the $\nu 1$, $\nu 3$, and $\nu 6$ modes may be a result of our arbitrary application of various corrections to the solution data. The V−C stretching modes, $\nu 2$, $\nu 4$, and $\nu 8$, have smaller corrections from solution data. The graph shows that the B3P86 method, with good bond lengths, has V−C frequencies that are too high. The BP86 and B3LYP methods have similar scatter, and B3LYP has slightly smaller deviations, despite its worse agreement for the V−C bond length. While the deviations indicate a slightly better result for vibrations with B3LYP, the overall agreement seems to be reasonably good for all methods when the basis set bias is considered for the CO modes.

C.2. Cr(CO)$_6$. The experimental data for the Cr(CO)$_6$frequencies are more reliable than for V(CO)$_6^-$ because gas phase data is available and harmonic frequencies have been determined

TABLE 4: Vibrations for V(CO

symmetry	label	motion	exptl^a (cm^{-1})	harmonic^b (cm^{-1})	B3P86^c (AD)	B3P86^c (AG)	BP86^c (AD)	BP86^c (AG)	B3LYP^c (AD)	B3LYP^c (AG)
A1g	ν1	C−O	2020	2055	2115	2103	2015	2004	2097	2084
Eg	ν3	C−O	1894	1929	2010	1994	1917	1902	1992	1974
T1u	ν6	C−O	1858	1893	1990	1973	1901	1886	1973	1955
T1u	ν7	b-MCO	650	650	702	700	672	670	681	678
T2g	ν10	b-MCO	517	517	527	533	501	506	517	523
T2u	ν12	b-MCO			525	527	504	506	516	518
T1u	ν8	MC	460	464	487	484	469	466	468	462
Eg	ν4	MC	393	397	416	410	403	397	398	390
A1g	ν2	MC	374	378	407	399	397	388	393	382
T1g	ν5	b-MCO			369	375	355	361	358	365
T1u	ν9	b-CMC			98	95	94	91	99	96
T2g	ν11	b-CMC	84	84	91	90	87	86	90	89
T2u	ν13	b-CMC			56	53	53	50	57	54

[a] Experimental values in solutions from IR and Raman. See text. [b] Harmonic estimates from solution values. See text. [c] DFT method with basis set code. See Table 2.

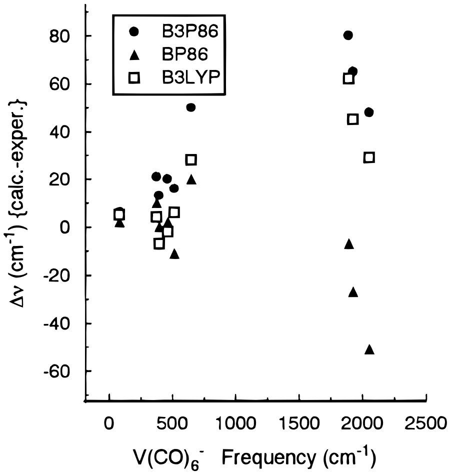

Figure 4. V(CO)$_6^-$ vibrational frequency deviations from experiment with different DFT methods. The basis set is AG in Table 4, and the experimental frequency is an estimated harmonic value.

for some modes. There is a body of transient infrared spectroscopy[45−48] that has been able to make good estimates for anharmonicity of the ν6 mode in Cr(CO)$_6$, Cr(CO)$_5$X, and W(CO)$_6$ to be about 15 cm^{-1} in solutions rather than the 43.3 cm^{-1} from spectral analysis. We have arbitrarily used 20 cm^{-1} for all C−O stretching modes and 4 cm^{-1} for the Cr−C modes as the harmonic correction in Table 5. Here we tabulate the deviations and do not show the basis set effects since they are similar to those of V(CO)$_6^-$ in magnitude and direction. A graph of deviations for the AG basis is shown in Figure 5, where we notice that the B3P86 method has high-frequency modes that do not scale similar to the diatomic frequency. This is an unusual change in correlation, which did not occur for the anion. The lower frequencies show scatter similar to Figure 4, with B3LYP providing a slightly better overall agreement.

D. Bonding and Charge Distributions. The comparison of these two molecules can demonstrate the effect of net charge for isoelectronic bonding in very similar molecular orbitals. While electron density plots could be informative, the assignment of charge distributions to each atom provides a quantitative, if arbitrary, representation. We have used the natural population analysis (NPA) method[49,50] rather than the Mulliken method[51] for assigning charge to atom centers. The NPA method finds charges associated with each atom from analysis of the density matrix, and this method has been shown to be reliable for many types of molecules.[52−55] Charge population analysis by the NPA method is a method of characterizing the bonding rather than assigning charges at specific atomic coordinates. An alternative method of atoms in molecules (AIM) works directly with charge density to define boundaries between atoms.[52,55−57] The AIM and NPA methods have been useful for characterizing bonding effects in polarized and ionic bonding situations because both the NPA and AIM methods account for asymmetrical bonding situations, but by different means.

The results of the NPA analysis for three DFT methods are shown in Table 6, where we also include a Mulliken analysis for one DFT method. From the NPA data we note that in proceeding from the neutral to the anion there is an increase in negative charge associated with the metal, but the oxygen atoms show a major increase of negative charge while the carbons become less positive. These values indicate that the molecular orbitals for the anion distribute the excess charge throughout the molecule, but with enhanced polarization on the metal and oxygen sites. All DFT methods show similar effects from forming the anion, but there appear to be differences in polarization for each method. The Mulliken analysis shows that both molecules are polarized, but that the anion has increased its negative charge on C,O and not V.

The electrostatic character of these two molecules also can be characterized by the quadrupole moment and hexadecapole moment. If we compare the quadrupole and diagonal hexadecapole moments, one finds an increase of about 20% by creating the anion; therefore the bonding for either molecule shows similar polarizations with an anion enhancement effect. For the B3LYP method the quadrupole moments of the neutral and anion are −83.1 and −98.9 D Å, respectively. The diagonal component of the hexadecapole moments are −979.5 and −1173.7 D Å^3, respectively.

An alternative scheme of electrostatic analysis is to consider the electrostatic potential created by the molecules as would be observed by a test charge outside the molecule. In this case a set of atom-based charges are created to fit the electrostatic potential at longer range distances. We note that unlike the NPA method, this method is not useful for characterizing bonding effects. We investigated two such schemes of assigning charges, the CHELPG[58,59] and Merz−Kollman−Singh (MKS)[60] methods. We found that the CHELPG method was much more sensitive to atom radii than the MKS method but that it became stable and more similar to MKS when radii were large enough. Table 6 shows the results for radii of 2.2 Å (1.8 was too small) for all atoms, and as expected the negative polarization of oxygen is enhanced for the anion. Interestingly, the electrostatic character of the long range interaction for either molecule can only be characterized by significant negative charge on the metal, which is consistent with the large multipole moments.

TABLE 5: Vibrations for $Cr(CO)_6$

symmetry	label	motion	exptl[a] (cm^{-1})	harmonic[b] (cm^{-1})	B3P86[c] (AD)	B3P86[c] (AG)	BP86[c] (AG)	B3LYP[c] (AG)
A1g	$\nu1$	C−O	2119	2139	2115	2103	2101	2185
Eg	$\nu3$	C−O	2027	2047	2010	1994	2013	2097
T1u	$\nu6$	C−O	2000	2020	1990	1973	1994	2078
T1u	$\nu7$	b-MCO	668	668	702	700	691	689
T2g	$\nu10$	b-MCO	532	532	527	533	529	540
T2u	$\nu12$	b-MCO	511	511	525	527	521	530
T1u	$\nu8$	MC	441	444	487	484	463	448
Eg	$\nu4$	MC	391	394	416	410	410	391
A1g	$\nu2$	MC	379	383	407	399	406	387
T1g	$\nu5$	b-MCO	364	364	369	375	361	357
T1u	$\nu9$	b-CMC	97	97	98	95	104	107
T2g	$\nu11$	b-CMC	90	90	91	90	94	96
T2u	$\nu13$	b-CMC	68	68	56	53	62	65

[a] Experimental values in gas phase. [b] Harmonic estimates from gas phase values. See text. [c] DFT method with basis set code. See Table 2.

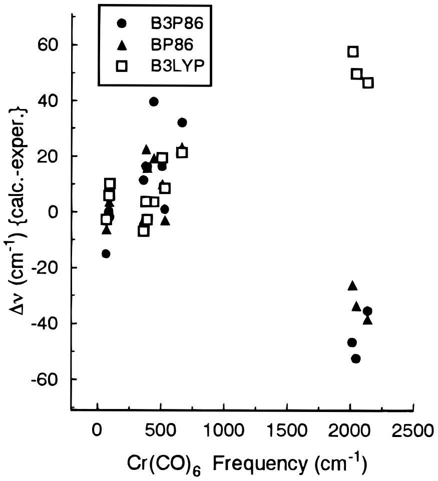

Figure 5. $Cr(CO)_6$ vibrational frequency deviations from experiment with different DFT methods. The basis set is AG in Table 5, and the experimental frequency is an estimated harmonic value.

TABLE 6: Comparison of Charges in Isoelectronic Metal Carbonyls

charge method[a]	DFT method[b]	molecule	charge metal	C	O
NPA	B3P86	$Cr(CO)_6$	−0.293	0.484	−0.435
NPA	B3P86	$V(CO)_6^-$	−0.431	0.432	−0.527
NPA	BP86	$Cr(CO)_6$	−0.200	0.441	−0.407
NPA	BP86	$V(CO)_6^-$	−0.311	0.384	−0.499
NPA	B3LYP	$Cr(CO)_6$	−0.171	0.467	−0.438
NPA	B3LYP	$V(CO)_6^-$	−0.302	0.413	−0.529
MUL	B3LYP	$Cr(CO)_6$	0.559	0.055	−0.149
MUL	B3LYP	$V(CO)_6^-$	0.629	−0.031	−0.241
CHELPG	B3LYP	$Cr(CO)_6$	−1.793	0.557	−0.258
CHELPG	B3LYP	$V(CO)_6^-$	−2.169	0.568	−0.373
MKS	B3LYP	$Cr(CO)_6$	−2.032	0.605	−0.266
MKS	B3LYP	$V(CO)_6^-$	−2.423	0.619	−0.382

[a] NPA is by natural population analysis; MUL is by Mulliken density analysis; CHELPG and MKS are by electrostatic potential matching. See text for references and discussion. [b] The calculation used basis set AG, see Table 2.

E. Conclusions

The comparison of isoelectronic $Cr(CO)_6$ and $V(CO)_6^-$ by DFT quantum calculation methods shows that the gradient-corrected methods known as B3P86, BP86, and B3LYP provide good geometries and good vibrational frequencies useful for experimental interpretation. The basis set for C and O needs to have polarization functions of d character, but simple all electron basis sets for the metals are adequate. The isoelectronic comparison, which has not been done previously, provides additional insight into DFT methods since some interesting differences are found between the neutral and ionic species.

The DFT method affects the predicted bond distances between the metal and carbon much more than the carbon−oxygen bond lengths; the metal−carbon distance increases in the anion by 0.025−0.03 Å for all DFT methods while the experimental increase is 0.02 Å. For the anion the B3P86 method has the best bond length for the metal−carbon distance, but the M−C bond lengths are too long by 0.009−0.033 Å for the B3P86, BP86, and B3LYP methods. For the neutral, the B3LYP method is best but the M−C bond length deviations range from −0.02 to 0.006 Å. For vibrations the B3LYP and B3P86 methods are similar for both species, and the high-frequency C−O vibrations scale similar to the diatomic deviations, except for the B3P86 method in the neutral, which switches from positive to negative deviations. The vibrational frequencies are in good overall agreement with experiment with about 30 cm^{-1} scatter for the non-C−O stretching modes and 40−80 cm^{-1} for the C−O modes. The bonds are very polarized in both species, and the anion has its charge distributed throughout the molecule. By NPA analysis the oxygen and metal are regions of negative charge in both the neutral and anion species, but the anion has slightly more charge at these sites.

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