Title
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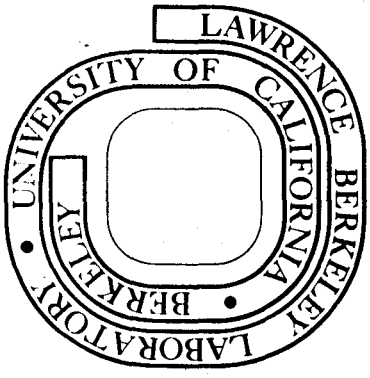

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The Use of Oxygen 1s Binding Energies and Multiplicity-Weighted C-O Stretching Frequencies to Measure Back-Bonding in Transition Metal Carbonyl Complexes

William L. Jolly*, Steven C. Avanzino and Richard R. Rietz

Back-bonding in a transition metal carbonyl involves a decrease in the C-O bond order of the carbon monoxide ligand:

$$^{-}M-C\equiv O^{+} \longleftrightarrow M=C=O$$

Because a decrease of bond order corresponds to a decrease of bond strength, the C-O stretching frequencies (or the derived force constants) of transition metal carbonyls have commonly been used to measure the degree of back-bonding. Unfortunately there are very few other physical properties which can be used to measure back-bonding and which are correlated with the stretching frequencies or force constants. Carbon-13 nmr chemical shifts have been shown to be related to the degree of back-bonding in carbonyls,[1] but good correlations with C-O stretching frequencies have been obtained only for restricted sets of compounds, in which the structures are very similar.[2]

Because back-bonding in a carbonyl involves a shift of negative charge from the metal atom to the oxygen atoms of the CO ligands, we anticipated that O 1s binding energies would be closely correlated with back-bonding. During the last few years we have measured these binding energies for a wide variety of transition metal carbonyl complexes in which the CO ligands are terminally bound.[3-5] The data are given in Table I. One would expect a correlation of the O 1s binding energies with the corresponding C-O stretching force constants. Unfortunately the force constants have not been calculated for all the molecules in Table I and could not be readily calculated without making some rather poor approximations. As an alternative to the use of force constants, we have used the multiplicity-weighted averages of the C-O stretching

Table I.

Correlation of Oxygen 1s Binding Energies of Carbonyl Complexes with Back-Bonding

Carbonyl Cpd.	E_B(O 1s), eV	ν_{CO} ; cm^{-1}	$(n_V + n_{CO})$	ν_{CO} Ref.
$C_6H_6Cr(CO)_3$	538.23	1938	10	6
$C_7H_7V(CO)_3$	538.6	1935	10	7
$C_5H_5V(CO)_4$	538.7	1963	10	8
$C_5H_5(CH_3)Mo(CO)_3$	538.8	1971	10	9
$C_5H_5Mn(CO)_3$	538.85	1974	11	10
$Mn_2(CO)_{10}$	538.89	2017	12	10
$C_7H_8Fe(CO)_3$	539.09	2004	12	11
$CH_3(OCH_3)CCr(CO)_5$	539.1	1984	12	12
$C_4H_6Fe(CO)_3$	539.29	2005	12	13
$W(CO)_6$	539.52	2017	12	10
$Mo(CO)_6$	539.61	2021	12	10
$CH_3Re(CO)_5$	539.64	2033	12	14
$Cr(CO)_6$	539.66	2018	12	10
$HMn(CO)_5$	539.84	2039	12	15
$CH_3Mn(CO)_5$	539.87	2032	12	16
$V(CO)_6$	539.9		11	
$CH_3COMn(CO)_5$	539.92	2038	12.5	17
$Fe(CO)_5$	540.00	2035	13	10
$Ni(CO)_4$	540.11	2066	14	10
$Cl_3SiMn(CO)_5$	540.31	2058	13	18

frequencies,[6-18] $\langle \nu_{CO} \rangle$. These values, also listed in Table I, were calculated from literature assignments of the frequencies by giving a weight of 1 to those of A or B symmetry, a weight of 2 to those of E symmetry, and a weight of 3 to those of T symmetry. A plot of E_B(O 1s) vs $\langle \nu_{CO} \rangle$, given in Figure 1, shows that these quantities are closely correlated.[19] The straight line through the points corresponds to the equation $E_B(O\ 1s) = 0.0146 \langle \nu_{CO} \rangle + 510.00$. We believe that this correlation is strong evidence that both E_B(O 1s) and $\langle \nu_{CO} \rangle$ can be used to measure back-bonding in carbonyl complexes.

It is of considerable interest to know what structural and electronic factors are important in determining that one carbonyl has a large amount of back-bonding and that another has a relatively small amount of back-bonding. One would expect, other things being equal,[20] that a low effective nuclear charge on the metal atom would be conducive to back bonding. The effective nuclear charge of the metal atoms in carbonyl complexes probably increases fairly regularly as the position of the metal in the periodic table moves from left to right. Hence we can use n_V, the number of valence electrons on the free metal atom, as a parameter linearly related to the effective nuclear charge of the metal in a carbonyl complex.

Another factor expected to influence the degree of back-bonding in a metal-carbon monoxide linkage is the competition for metal $d\pi$ electrons due to other carbonyl groups bonded to the metal, and due to other back-bonding ligands. The back-bonding in a carbonyl linkage should decrease with an increase in n_{CO}, defined as the total number of coordinated carbonyl groups and groups equivalent to carbonyl groups. In the case of carbonyl complexes containing ligands other than CO, we assume somewhat arbitrarily (although in fair agreement with prevailing opinions[21]

regarding the back-bonding abilities of ligands) that each of the following ligands is equivalent, as a π acceptor, to one CO group: C_7H_8 (tetrahapto), C_6H_6, C_5H_5, C_4H_6, $CH_3(OCH_3)C$, $SiCl_3$. We also assume that the C_7H_7 ligand is equivalent to two CO's, that the CH_3CO ligand is equivalent to one-half CO, and that the H atom and CH_3 group have no π acceptor character.

Back-bonding should decrease with an increase in either n_V or n_{CO}. Although it is not clear that the terms should be weighted equally, we have used the simple sum, $(n_V + n_{CO})$, as a parameter which is expected to correlate with E_B(O 1s) and $\langle \nu_{CO} \rangle$. The values of the parameter $(n_V + n_{CO})$ are given in Table I, and in Figure 2 is shown a plot of E_B(O 1s) vs $(n_V + n_{CO})$. The plot shows that there is a definite correlation[22] between these quantities, and, although the correlation is not as good as that of Figure 1, the plot indicates that our ideas regarding the fundamental nature of back-bonding are qualitatively sound. The poor fit of the point for $V(CO)_6$ is perhaps due to the fact that the vanadium atom in this compound is one electron short of the krypton effective atomic number. This electron deficiency would be expected to make the vanadium atom a relatively poor dπ donor.

When the appropriate XPS data become available, it will be of interest to test the correlations which we have observed with data for bridging carbonyl groups.

Experimental Section

All spectra were obtained with samples in the gas phase. Except in the case of $Fe(CO)_5$, the old Berkeley iron-free magnetic spectrometer and previously described procedures were used.[23,24] Differences between some of the data of Table I and previously published data are due to a spectrometer

recalibration and the present use of the value 248.62 eV for the Ar $2p_{3/2}$ reference.[25] The spectrum of $Fe(CO)_5$ was obtained using the Uppsala high resolution spectrometer;[26] the O 1s binding energy was measured relative to that for CO, 542.57 eV. The binding energies given to two decimal places have probable errors of ± 0.05 eV; those given to one decimal place have probable errors of ± 0.1 eV.

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Figure Captions

Figure 1. A plot of oxygen 1s binding energies for carbonyl complexes vs the multiplicity-weighted C-O stretching frequencies. Data given in Table I.

Figure 2. A plot of oxygen 1s binding energies for carbonyl complexes vs the parameter $(n_V + n_{CO})$. Data given in Table I.

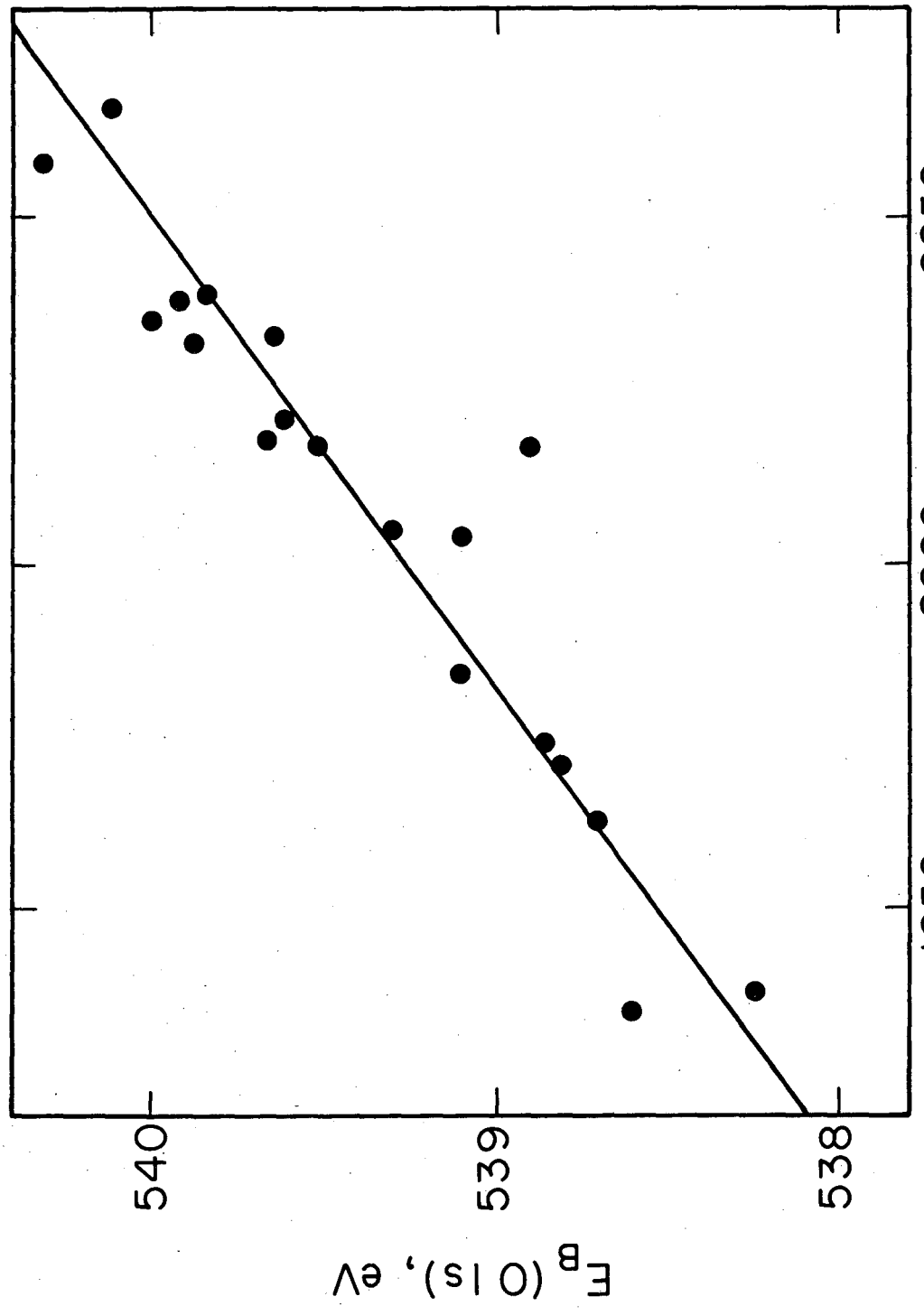

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Fig. 1

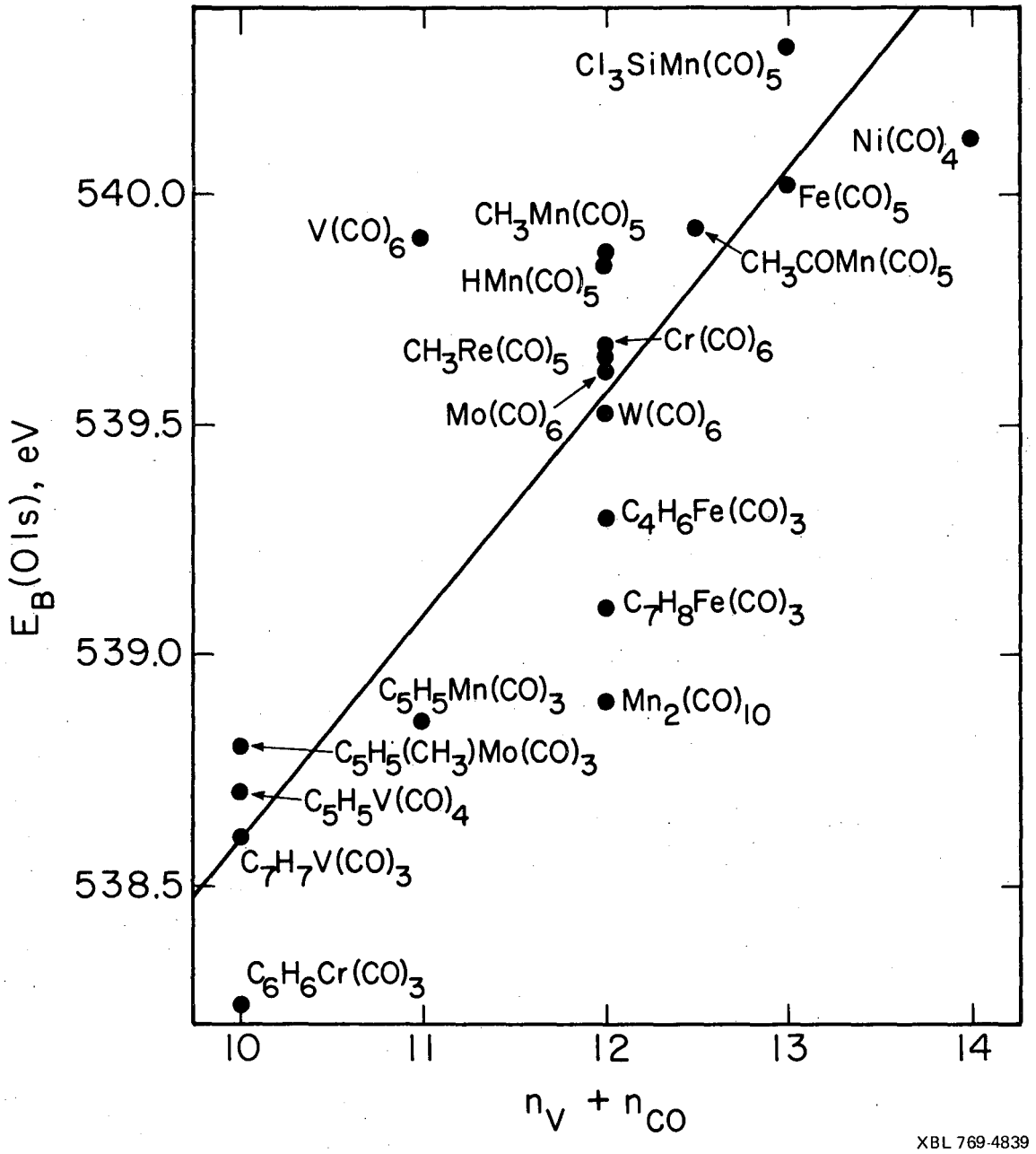

FIG. 2

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