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THE CORRELATION OF VIBRATIONAL BROADENING OF CORE LINES IN X-RAY PHOTOELECTRON SPECTRA WITH VALENCE BOND RESONANCE STRUCTURES

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Abstract:

When core ionization of an atom in a molecule causes significant changes in bond orders, the core-hole ion is formed in a strained configuration. This strain causes vibrational broadening of the core line. The core-hole ion can be represented as an ordinary chemical species by applying the equivalent cores approximation. Then simple rules of classical valence bond theory can be used to predict changes in the weighting of resonance structures and corresponding changes in bond orders. Thus qualitative changes in relative line widths can be predicted.

It has recently been shown that Franck-Condon vibrational excitation contributes importantly to core photoline broadening in molecules [1,2]. In general, the photoelectric process yields a molecule-ion in which the nuclei are not in their equilibrium positions. The more strained the geometry of the core-hole ion, the broader the photoline.

In the absence of other effects, the core ionization of an atom in a molecule causes a contraction of the valence electron cloud in the immediate vicinity of the atom, corresponding to a reduction of both the atomic size and the equilibrium bond distances. This contraction of the equilibrium distances is most pronounced when the atom is initially negatively charged and hence has an easily contracted electron cloud. In such cases the core-hole molecule-ion is formed in a highly strained configuration and the photoline is relatively broad. This generalization accounts for the fact that the carbon 1s line of CH_4 is broader than that of CF_4 [1], that the sulfur 2p line of the terminal sulfur atom in the $S_2O_3^{2-}$ ion is broader than that of the central sulfur atom in that ion [3-5], and that the nitrogen 1s line of NH_4^+ is broader than that of NO_3^- [1,5].

However, it is important to recognize that the correlation of atomic charge with line width is valid only when the formal bond orders of all the bonds in the molecule are unchanged upon ionization of the core. When ionization produces relatively large changes in bond order, the line width is broad regardless of the initial charge on the atom. In cases where ionization of a negatively charged atom causes a decrease in the order of the bonds to that atom, a cancellation of effects can occur, resulting in an unbroadened line. Significant changes in bond

order accompany the core ionizations of some of the molecules listed in Table 1, and we shall show that the relative line widths can be rationalized by the use of simple valence bond resonance concepts and the equivalent cores approximation [6,7].

The carbon 1s line of the outer carbon atoms of C_3O_2 is broader than that of the middle carbon atom in spite of the fact that the middle carbon atom is more negatively charged [8]. The ground state of the molecule can be represented by the valence bond structure O=C=C=C=O, with small contributions from the following resonance structures

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

The ion formed by core ionization of the middle carbon atom can be represented, using the equivalent cores approximation, by the structure $O{=}C{=}N^{+}{=}C{=}O$. Because the electronegativity of nitrogen is greater than that of carbon, the contribution of the resonance structures

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

is somewhat greater than the contribution of the analogous structures in the ground-state C_3O_2 molecule. This change in the weighting of the resonance structures tends to increase the C-C bond lengths, in opposition to the tendency for the middle carbon atom to contract and for the C-C bond lengths to shorten. The result is essentially no change in the equilibrium C-C bond lengths and a slight shortening of the equilibrium C-O bond lengths. Consequently a relatively narrow line is obtained for the middle carbon atom. The ion formed by ionization of an outer carbon atom can be represented by the structure $O{=}C{=}C{=}N^{+}{=}O$.

Table 1

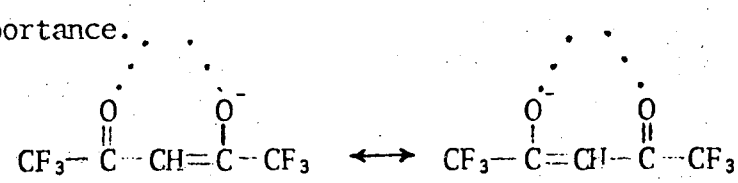
Core Line Width Data for Molecules

Molecule	Core Level	FWHM, eV[a)]
C_3O_2[b)]	C 1s (outer C)	1.11
	C 1s (inner C)	0.97
$Al[CH(COCF_3)_2]_3$[c)]	C 1s (CO)	1.31
	C 1s (CF_3)	1.13
$(CF_3)_2CO$[c)]	C 1s (CO)	1.01
	C 1s (CF_3)	1.05
N_2O[d)]	N 1s (outer N)	0.70
	N 1s (inner N)	0.59
$(CH_3O)_2CO$[c)]	O 1s (C=O)	1.37
COF_2[c)]	O 1s	1.44
$COCl_2$[c)]	O 1s	1.15
$CO(CH_3)_2$[c)]	O 1s	1.09
CF_4[e)]	F 1s	1.83
CH_3F[e)]	F 1s	1.36

a) Because of differing instrumental contributions to the line widths, FWHM values from different laboratories cannot be compared. b) Ref. [8]. c) T. Schaaf, unpublished data. d) Ref. [1]. e) T. D. Thomas, J. Amer. Chem. Soc. 92 (1970) 4184.

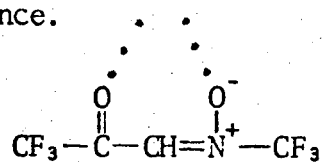
However, because of electrostatic interactions, the contributions of the resonance structures $^{+}O{\equiv}C\text{-}C{\equiv}N^{+}\text{-}O^{-}$ and $^{+}O{\equiv}C\text{-}C^{-}{=}N^{+}{=}O$ are probably greater, and that of the resonance structure $O{=}C{=}C^{-}\text{-}N^{+}{\equiv}O^{+}$ is probably less, than the contributions of the analogous structures in the ground state. (Note that the favored structures have the atoms with +1 formal charges widely separated, whereas the disfavored structure has these atoms adjacent to one another.) Inasmuch as the outer carbon atoms of C_3O_2 are positively charged, they have little tendency to contract upon core ionization. We conclude that, because of the changes in bond order, the core-hole ion of an outer carbon atom is formed in a fairly strained configuration, causing a vibrationally broadened line.

In the carbon 1s spectrum of the trishexafluoroacetylacetonate of aluminum, $Al[CH(COCF_3)_2]_3$, the carbonyl carbon atom line is considerably broader than the CF_3 carbon atom line. This result is remarkable in view of the fact that the line widths for the carbonyl and CF_3 carbon atoms in hexafluoroacetone (Table 1) and ethyl trifluoroacetate [4] are approximately the same. There seems to be no structural evidence that the broadening of the carbonyl carbon line might be due to the existence of nonequivalent carbonyl groups,* and so we believe the broadening of the carbonyl line is due to vibrational structure. In the ground-state chelate, the following resonance structures are of equal importance.



*Both X-ray diffraction [9] and infrared vibration [10] data indicate that chelating groups of this type are symmetric.

However, in the core-hole ion, the structure in which the oxygen atom bearing a negative formal charge is bonded to the ionized carbon atom is of principal importance.



Hence the ion is formed in a strained configuration.

The nitrogen 1s line of the outer nitrogen atom of N_2O is broader than that of the inner nitrogen atom [1]. This result is consistent with the rough rule that more negatively charged atoms have broader lines, but in this case the broadening is due to a lengthening, not a shortening, of the equilibrium bond to the outer nitrogen atom. In N_2O, the equilibrium bond distances are r_{N-N} = 1.129 Å and r_{N-O} = 1.187 Å, corresponding to the resonance structures

$$N{\equiv}N^{+}{-}O^{-} \longleftrightarrow N^{-}{=}N^{+}{=}O$$

Core-ionization of the outer nitrogen atom yields an ion which can be represented by $O{=}N^{+}{=}O$, which has the equilibrium bond distance r_{N-O} = 1.154 Å. Obviously the ion is formed in a strained configuration. Core ionization of the inner nitrogen atom yields an ion which can be represented by the resonance structures

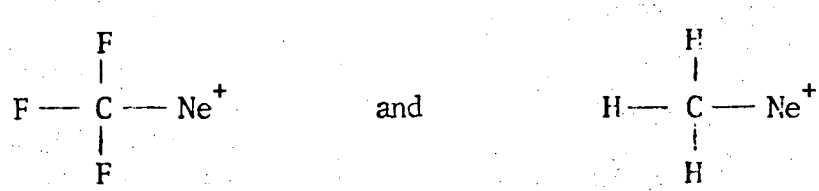
$$N{\equiv}O^{2+}{-}O^{-} \longleftrightarrow N^{-}{=}O^{2+}{=}O$$

The relative weighting of these structures is probably similar to that of the analogous structures of N_2O. For this reason, and because the inner nitrogen atom is positively charged and not subject to much contraction, the core-hole ion is produced in a relatively unstrained state and the line is not strongly vibrationally broadened.

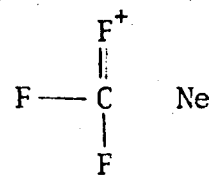
The oxygen 1s lines of the carbonyl oxygen atoms in $(CH_3O)_2CO$ and COF_2 are significantly broader than the corresponding lines of many other carbonyl compounds, such as $COCl_2$ and $CO(CH_3)_2$. This broadening is due to changes in the equilibrium distances of the bonds to the carbonyl carbon atom upon core ionization. The carbonyl C-O distance increases and the other distances decrease because of the contribution of resonance structures of the following type:

Structures like these are of less importance in the ions produced by the core ionization of the oxygen atoms in $COCl_2$ and $CO(CH_3)_2$ because of the reduced π donor characters of chlorine atoms and methyl groups.

The equivalent cores representations of the fluorine 1s hole states of CF_4 and CH_3F are, respectively,



In the case of CF_3Ne^+, one expects considerable π bonding in the C-F bonds, corresponding to significant contributions from "no-bond" resonance structures of the following type:



Inasmuch as the CF_3^+ ion would be expected to be a planar triangular species with relatively short C-F bonds, one predicts that the tetrahedral core-hole ion of CF_4, is formed in a highly strained state, yielding a broad line. In the case of CH_3Ne^+, no π bonding can occur and so the core-hole ion of CH_3F is not formed in as strained a configuration.

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