Lawrence Berkeley National Laboratory
Recent Work

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

**Permalink**
https://escholarship.org/uc/item/04q246gx

**Author**
Jolly, William L.

**Publication Date**
1975
THE CORRELATION OF VIBRATIONAL BROADENING OF
CORE LINES IN X-RAY PHOTOELECTRON SPECTRA
WITH VALENCE BOND RESONANCE STRUCTURES

William L. Jolly

January 1975

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

For Reference
Not to be taken from this room
THE CORRELATION OF VIBRATIONAL BROADENING OF
CORE LINES IN X-RAY PHOTOELECTRON SPECTRA
WITH VALENCE BOND RESONANCE STRUCTURES

William L. Jolly
Chemistry Department, University of California, and
Inorganic Materials Research Division,
Lawrence Berkeley Laboratory,
Berkeley, California 94720

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 CH₄ is broader than that of CF₄ [1], that the sulfur 2p line of the terminal sulfur atom in the S₂O₃²⁻ ion is broader than that of the central sulfur atom in that ion [3-5], and that the nitrogen 1s line of NH₄⁺ is broader than that of NO₃⁻ [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 \( \text{C}_3\text{O}_2 \) 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 \( \text{O}=\text{C}=:\text{C}=\text{O} \), with small contributions from the following resonance structures

\[ ^{+}\text{O}=\text{C}=\text{C}^-=\text{C}=\text{O} \leftrightarrow \text{O}=\text{C}^-=:\text{C}=\text{O}^+ \]

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

\[ ^{+}\text{O}=\text{C}^-=\text{N}=\text{C}=\text{O} \leftrightarrow \text{O}=\text{C}=\text{N}^-=:\text{C}=\text{O}^+ \]

is somewhat greater than the contribution of the analogous structures in the ground-state \( \text{C}_3\text{O}_2 \) 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 \( \text{O}=\text{C}=\text{C}=\text{N}^+=\text{O} \).
### Table 1

Core Line Width Data for Molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Core Level</th>
<th>FWHM, eV&lt;sup&gt;a)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C 1s (outer C)</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>C 1s (inner C)</td>
<td>0.97</td>
</tr>
<tr>
<td>Al[CH(COCF&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;c&lt;/sub&gt;</td>
<td>C 1s (CO)</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>C 1s (CF&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>1.13</td>
</tr>
<tr>
<td>(CF&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CO&lt;sup&gt;c&lt;/sup&gt;</td>
<td>C 1s (CO)</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>C 1s (CF&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>1.05</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;O&lt;sup&gt;d)&lt;/sup&gt;</td>
<td>N 1s (outer N)</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>N 1s (inner N)</td>
<td>0.59</td>
</tr>
<tr>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;O)&lt;sub&gt;2&lt;/sub&gt;CO&lt;sup&gt;c&lt;/sup&gt;</td>
<td>O 1s (C=O)</td>
<td>1.37</td>
</tr>
<tr>
<td>COF&lt;sub&gt;2&lt;/sub&gt; &lt;sup&gt;c&lt;/sup&gt;</td>
<td>O 1s</td>
<td>1.44</td>
</tr>
<tr>
<td>COCl&lt;sub&gt;2&lt;/sub&gt; &lt;sup&gt;c&lt;/sup&gt;</td>
<td>O 1s</td>
<td>1.15</td>
</tr>
<tr>
<td>CO(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; &lt;sup&gt;c&lt;/sup&gt;</td>
<td>O 1s</td>
<td>1.09</td>
</tr>
<tr>
<td>CF&lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;e)&lt;/sup&gt;</td>
<td>F 1s</td>
<td>1.83</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;F&lt;sup&gt;e)&lt;/sup&gt;</td>
<td>F 1s</td>
<td>1.36</td>
</tr>
</tbody>
</table>

<sup>a)</sup> Because of differing instrumental contributions to the line widths, FWHM values from different laboratories cannot be compared.  <sup>b)</sup> Ref. [8].  <sup>c)</sup> T. Schaaf, unpublished data.  <sup>d)</sup> Ref. [1].  <sup>e)</sup> T. D. Thomas, J. Amer. Chem. Soc. 92 (1970) 4184.
However, because of electrostatic interactions, the contributions of
the resonance structures $^+\text{O}=\text{C}^-\text{C}=\text{N}^+-\text{O}^-$ and $^+\text{O}=\text{C}^-\text{C}^-=\text{N}^+=\text{O}^+$ are probably
greater, and that of the resonance structure $\text{O}=\text{C}^-\text{C}^-=\text{N}^+=\text{O}^+$ 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
$\text{C}_3\text{O}_2$ 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 trishexafluoroacetylacetone of
aluminum, $\text{Al}[\text{CH(COCF}_3)_2]_3$, the carbonyl carbon atom line is considerably
broader than the $\text{CF}_3$ carbon atom line. This result is remarkable in
view of the fact that the line widths for the carbonyl and $\text{CF}_3$ 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.

$$
\text{CF}_3-\text{C}^-\text{CH}=\text{C}^-\text{CF}_3 \leftrightarrow \text{CF}_3-\text{C}^-\text{CH}!^-\text{C}^-\text{CF}_3
$$

*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.

$$\text{CF}_3-C-\text{CH}=\text{N}^+-\text{CF}_3$$

Hence the ion is formed in a strained configuration.

The nitrogen 1s line of the outer nitrogen atom of N$_2$O 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$_2$O, the equilibrium bond distances are r$_{N-N} = 1.129$ Å and r$_{N-O} = 1.187$ Å, corresponding to the resonance structures:

$$\text{N} \equiv \text{N}^+-\text{O}^- \leftrightarrow \text{N}^+-\text{N} = \text{O}$$

Core-ionization of the outer nitrogen atom yields an ion which can be represented by O=\text{N}^+=\text{O}, which has the equilibrium bond distance r$_{\text{N-O}} = 1.154$ 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:

$$\text{N} \equiv \text{O}^{2+}-\text{O}^- \leftrightarrow \text{N} = \text{O}^{2+} = \text{O}$$
The relative weighting of these structures is probably similar to that of the analogous structures of N₂O. 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 (CH₃O)₂CO and COF₂ are significantly broader than the corresponding lines of many other carbonyl compounds, such as COCl₂ and CO(CH₃)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:

\[
\begin{align*}
\text{CH}_3\text{O}^+ & \quad \text{and} \quad \text{F}^+ \\
\text{C} & \quad \text{C} & \quad \text{Ne}^+ \\
\text{F} & \quad \text{F} & \quad \\
\text{CH}_3\text{O} & \quad \text{F} & \quad \text{C} \quad \text{F} & \quad \text{F} \\
\end{align*}
\]

Structures like these are of less importance in the ions produced by the core ionization of the oxygen atoms in COCl₂ and CO(CH₃)₂ because of the reduced π donor characters of chlorine atoms and methyl groups.

The equivalent core representations of the fluorine 1s hole states of CF₄ and CH₃F are, respectively,

\[
\begin{align*}
\text{F} & \quad \text{H} \\
\text{C} & \quad \text{Ne}^+ & \quad \text{and} & \quad \text{H} & \quad \text{C} & \quad \text{Ne}^+ \\
\text{F} & \quad \text{H} & \quad \text{F} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]
In the case of CF$_3$Ne$^+$, one expects considerable $\pi$ bonding in the C-F bonds, corresponding to significant contributions from "no-bond" resonance structures of the following type:

\[
\begin{array}{c}
\text{F}^+ \\
\mid \\
\text{F}--\text{C} \quad \text{Ne} \\
\mid \\
\text{F}
\end{array}
\]

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$_3$ is formed in a highly strained state, yielding a broad line. In the case of CH$_3$Ne$^+$, no $\pi$ bonding can occur and so the core-hole ion of CH$_3$F is not formed in as strained a configuration.

This work was supported by the U. S. Atomic Energy Commission and the National Science Foundation (Grant GP-41661X).
References

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.