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Chemical Effects on the Lifetime of 1*s*-Hole States*

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The linewidths of 1*s* photoelectron energy spectra have been measured for carbon, nitrogen, and oxygen, each in a variety of molecules in the gas phase. The linewidths of a given element increase with decreasing binding energy of the 1*s* electron. We interpret these changes in linewidth to be due to changes in the lifetime of the 1*s* hole caused by changes in the chemical environment.

Relatively little is known about the lifetimes of atoms excited by removal of a 1*s* (core) electron. For elements heavier than sulfur, there are a few data on x-ray linewidths from which lifetimes can be inferred.[1] Even less is known about chemical effects on these lifetimes. We report here evidence to show that chemical effects may cause observable changes in the 1*s*-hole lifetime relative to that calculated for free atoms.[2]

When a photoelectron leaves an atom or molecule, the width of the corresponding line in the electron energy spectrum is due to (1) the intrinsic width of the exciting radiation, (2) the resolution of the electron spectrometer, (3) the lifetime of the excited ionic state, and (4) thermal broadening. The hole state may decay in a variety of ways; for 1*s* holes, however, the most important contributions to the de-excitation rate are from radiative and nonradiative Auger transitions from the *L* shell. For $Z<10$, radiative transitions are relatively slow, and the lifetime of 1*s* holes is primarily determined by *K-LL* Auger transition rates.

For the Auger transition, we may write the matrix element (ignoring antisymmetrization) as

$$\langle \Phi_f(\alpha)\Psi(\beta)| (|\vec{r}_\alpha - \vec{r}_\beta|^{-1})| \Phi_i(\alpha)\Phi_i(\beta)\rangle ,$$

where $\Phi_i(\alpha)$ and $\Phi_i(\beta)$ are initial quasibound[3] states for electrons α and β, and $\Phi_f(\alpha)$ and $\Psi(\beta)$ are a quasibound and a continuum state, respectively. We may expect that changes in the electron distribution due to chemical bonding will affect these transition matrix elements. In particular, the compounds formed by the elements lithium through neon should exhibit the strongest effects for transitions filling a *K* hole, since in these elements the *L* shell is the valence (bonding) shell.

To the simplest approximation we might expect that, given an atom with a *K* hole, the transition rate for filling the hole will increase with an increase in valence electron density in the vicinity of that atom. That such effects might be observable could be inferred from the observation that lines in the photoelectron energy spectrum due to the emission of fluorine 1*s* electrons and nitrogen 1*s* electrons have experimental widths that depend upon the chemical state.[4, 5] In addition, the fluorine 1*s* electron lines are as much as twice as broad as those of other first-row elements: C, N, O, and Ne. Because fluorine's atomic orbitals lie lower in energy than the other members of the first-row elements with which it bonds, electron densities in molecules containing

F tend to be concentrated nearer the F. Hence, one might expect that the lifetime of a molecular core hole localized at the F atomic core will be decreased relative to that of a core hole in a free F atom. We also note that the effects of chemical bonding on x-ray line shapes and fluorescence yields have been reported.[6]

In order to examine the approximate quantitative behavior of the Auger transition rates, we neglect antisymmetrization and expand the Auger interaction operator using a multipole expansion and the spherical-harmonic addition theorem. This leads to an expression for the Auger transition rate of the form

$$\sum_{l,m} \int \Phi_f^*(\alpha)\Phi_i(\alpha) r_\alpha^{\,l} Y_l^{m*}(\theta_\alpha \varphi_\alpha)\,d\tau \times \int \Psi^*(\beta)\Phi_i(\beta) r_\beta^{-(l+1)} Y_l^{m}(\theta_\beta \varphi_\beta)\,d\tau .$$

The radial part of the first term in the expansion is

$$\int \Phi_f^*(\alpha)\Phi_i(\alpha) r_\alpha^{\,2}\,dr_\alpha \int \Psi^*(\beta)\Phi_i(\beta) r_\beta\,dr_\beta .$$

The first integral has the form of an overlap between the photohole and the initial state of the electron which fills that hole; it is this part of the expression for the transition rate which will increase with valence-electron density in the vicinity of a core-electron hole.

One may get a first-order approximation of the relative outer electron density associated with a given atomic core by measuring the binding energy of the core electrons. The greater the electron density near a given core, the less bound those electrons become. This effect is well known and is the basis for the chemical shift method of analysis in electron spectroscopy. The core-electron binding energies of the first-row elements have been measured in numerous compounds, and approximately linear relations between core-electron binding energy and charge at that core have been established both empirically and by model calculations.[5,7] To a first approximation, therefore, we expect a correlation between core-electron binding energies and linewidths.

To investigate the ideas expressed above, we have measured the 1s photoelectron spectra of several gaseous compounds of C, N, and O in our cylindrical-mirror electron spectrometer.[8] The compounds were chosen so as to cover as broad a range in 1s binding energy as possible for each element of interest. The linewidths were extracted from the spectra using a least-squares analysis.

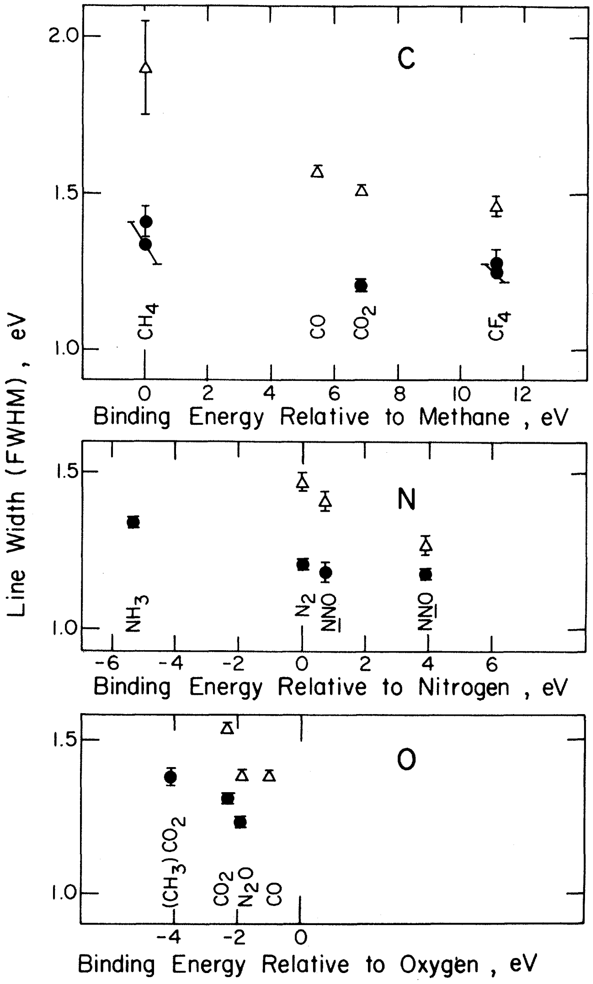

FIG. 1. Linewidths (full width at half-maximum) of carbon, nitrogen, and oxygen 1s photoelectron energy spectra extracted using a Gaussian filling function. Data marked with closed circles, taken using Mg $K\alpha$ x rays; those marked with open triangles, using Al $K\alpha$. Error bars indicate that value of the linewidth required to increase the reduced χ^2 by 1.

The results of the measurements and width analysis for C, N, and O are shown in Fig. 1, where we have plotted linewidth versus binding energy for a number of compounds. Although the effect is small (of the order of 0.1 eV), there is clearly a systematic trend of increasing width with decreasing binding energy, or, equivalently, decreasing lifetime with increasing electron density in the vicinity of the photohole. This trend is observed both for Gaussian and Lorentzian fitting functions. We have repeated these measurements several times and have used both Al $K\alpha$ and Mg $K\alpha$ exciting radiation. The same trend is always observed.

In order to extract more quantitative information from these data, one must deconvolute the line into its constituents. In order to do this, one requires an accurate knowledge of the profile of the exciting radiation and the spectrometer function. Unfortunately, neither of these is very well known to us at present. If, however, we approximate the profile of the exciting radiation as Lorentzian and assume that the spectrometer resolution function is also Lorentzian, we find, for example, that the contribution to the width of the carbon 1*s* photopeak from the 1*s* hole lifetime is 0.17 eV greater in CH_4 than in CF_4. This may be compared with lifetimes of 0.06 eV for 1*s* holes in free C atoms calculated by Walters and Bhalla.[9] Chemical effects on the linewidths of the 1*s* photoelectron spectra in the other elements—nitrogen and oxygen—are of the same order of magnitude as those seen in carbon.

In the above discussion, we have associated the binding energy of the 1*s* electrons with the local valence electron density. It is important to note, however, that the 1*s* electron binding energy and the Auger transition rate (as we have expressed it) depend on different moments of the valence-electron distribution. For spherical valence-electron distributions, the relation between rate and binding energy is monotonic; for valence-electron distributions of more complex symmetry, this monotonic relation may not hold. A proper analysis must take the detailed shape of the valence charge distribution into account in calculating the Auger transition rate.[10]

In principle, the *K-LL* Auger electron energy spectrum is capable of giving detailed information about the relative contributions of various excited many-electron configurations to the filling of the *K* photohole. For Auger transitions, however, the linewidth information is complicated by the fact that the *K*-hole state is the initial state, and the final state is a complex valence-shell double-hole state. Hence, the linewidths also reflect the lifetime of this more complex state, which may itself decay by further autoionization, predissociation, etc. These other nonradiative modes may be very fast.[11] The photoelectron spectrum is unique in that the initial state is the ground state which has zero width, and the final state is the *K*-hole state; in this case, the only decay time contribution to the width of the hole state is from the decay of the *K* hole. Implicit in this argument is the assumption that the outer electrons are not strongly perturbed by the removal of the core electron. In fact, it has been well established that the "parent" 1*s* photopeak appearing at highest kinetic energy corresponds to the atomic or molecular ion with a *K* photohole and all other electrons with unchanged quantum numbers. Excitation of other electrons caused by photoionization of a 1*s* electron is well known and corresponds to satellite photopeaks lying at lower kinetic energies relative to the parent in the photoelectron spectrum.[12] It is, however, possible that the sudden photoemission of a 1*s* electron may generate a manifold of vibrationally excited states in the remaining molecular ion. If the equilibrium bond lengths of the molecule and the ion are significantly different, a series of vibrational states could be produced in the ion. These states would lie below the limits of our experimental resolution and would appear as a broadening of the linewidth. In general, such manifolds of vibrational states appear strongly only when the excited electron is a bonding electron and hardly at all when it is nonbonding. In the cases studied here, the ejected electrons are all nonbonding, and we would therefore expect no such problem.

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[10] The effect of the detailed shape of the valence-electron distribution on the Auger transition rate may explain the experimental observations of U. Gelius (see Ref. 7, p. 331) that in carbon suboxide (O-C-C-C-O), the widths of the carbon 1*s* photoelectron spectral lines increase with increasing binding energy. The peak due to the central carbon is significantly narrower (0.1 eV) than that of the other carbons. The $1\pi_g$ valence orbital, however, has a node at the central carbon and, therefore, the overlap between the valence orbital and a core photohole associated with that carbon is very small.

[11] The very high decay rate of valence-shell double-hole states is indicated by the breadth of the lines in Auger spectra. See Ref. 4, pp. 90, 103.

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Chemical Effects on Linewidths Observed in Photoelectron Spectroscopy*

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Widths of photoelectron lines associated with vacancies in core levels immediately below the valence shell are shown to depend on the chemical environment. The width variation is ascribed to change in vacancy lifetime. Valence electron density influences these lifetimes through its effect on Auger transition rates. Correlation of linewidth and chemical shift in electron binding energy is discussed.

It is well known that photoelectron lines associated with primary vacancies in different core levels of a given atomic species vary in width. In a given principal quantum level, for example, the width of the line arising from a sublevel generally decreases with increasing value of the azimuthal quantum number *l*; and this variation, which is easily as great as a factor of 5, has been ascribed to variation in the vacancy lifetime.[1] In core levels accessible for study with ≈ 1-keV photons, the Auger process is the predominant mechanism for vacancy filling. Coster-Kronig transitions, Auger processes in which one of the two final vacancies remains in the same principal quantum level as the primary vacancy, become increasingly important in shortening vacancy lifetime as the *l* value decreases. Thus the fact that the width of the 2*s* photoelectron line of Ar is broader than the $2p^1$ is probably due, in large part, to Coster-Kronig transitions.[2] Obviously this type of Auger process cannot occur for a primary vacancy corresponding to the least-bound electron in a principal level.

Much smaller width variations have been reported for photoelectron lines originating from a given level in chemically different forms of the same element. In N_2O the 1*s* lines from the two chemically distinct nitrogen atoms have been observed to have widths differing by about 10%, even though instrumental effects account for most of the measured linewidth.[3] Similar results have been obtained for the two types of carbon in C_3O_2.[4] Until now, no explanations for these effects have been offered; and it is the object of this paper to present some new data and an interpretation of this chemical influence on linewidth.

Measurements were made with the solids $Na_2S_2O_3$ and NH_4NO_3. In the first compound the ligand and central sulfur atoms are assigned formal charges − 2 and + 6, respectively; in NH_4NO_3 the nitrogen atoms have formal charges − 3 and + 5. It is advantageous in measurements made with solids to have the different chemical states of the element present in one compound so as to eliminate sample-to-sample width differences arising from instrumental effects. It may be feasible, however, to monitor and correct for such sample-dependent differences by measurement of linewidths from a simple, monatomic ion common to salts of the counterions of interest.

A Varian IEE-15 photoelectron spectrometer with a Mg x-ray anode was used for the measurements. Samples were cooled to about 0°C to prevent decomposition which had been observed at higher temperatures through changes in the electron spectra. In Fig. 1 are shown the S 2*p* lines from $Na_2S_2O_3$ and the N 1*s* lines from NH_4NO_3. Measurements were also made on the S 2*s* lines. Spectra were analyzed by computer fitting of Gaussian line shapes to the background-subtracted data, and the background functions were obtained as least-squares fits of polynomials to regions on both sides of the peaks. For the resolution of each S $2p_{1/2}$-$2p_{3/2}$ doublet, it was required