1 (1969).

[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.

[12] M. O. Krause, T. A. Carlson, and R. D. Dismukes, Phys. Rev. 170, 37 (1968).

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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

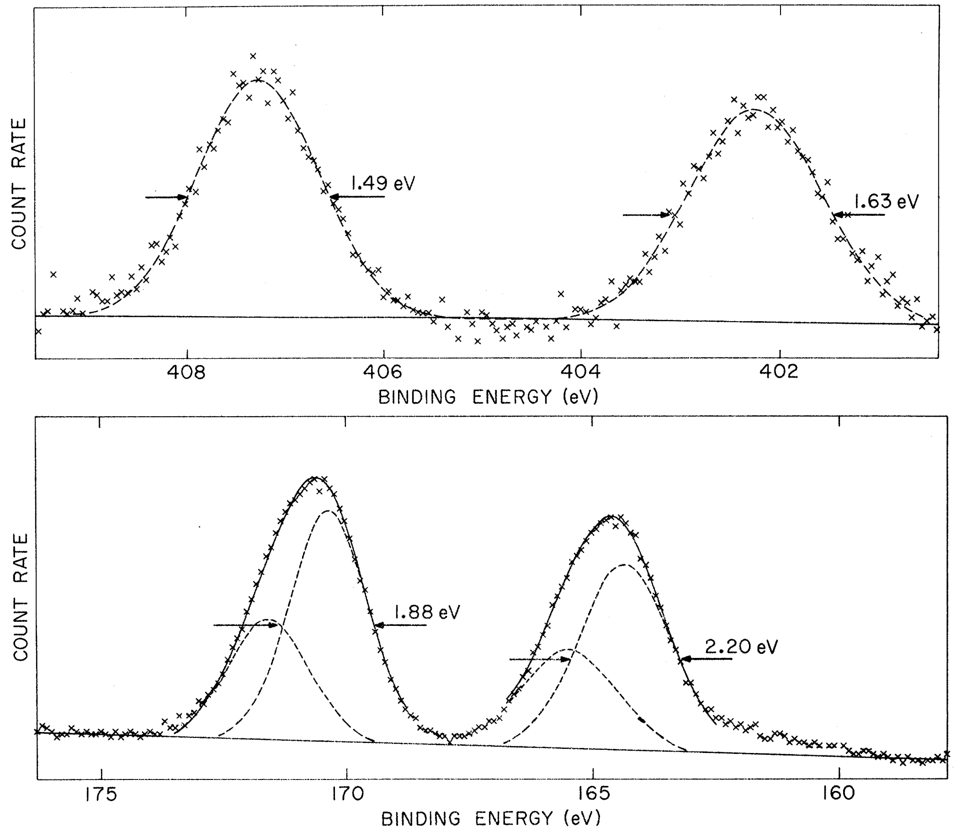
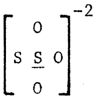
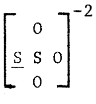


FIG. 1. Photoelectron spectra of N 1*s* lines from $NH_4NO_3$ (upper) and S 2*p* lines from $Na_2S_2O_3$ (lower). The lines from the nitrogen in $NO_3^-$ and from the central sulfur atom in $S_2O_3^{-2}$ are on the left. Shown are measurements (crosses), computer-fitted background (solid sloping line), and sum of fitted Gaussian peaks and background (solid curve). Sums of background and individual components of computer-resolved doublets are shown for S 2*p* (dashed curves).

that the intensity ratio of the two components be 1:2 and that their widths be the same. Errors due to any inadequacy of this latter assumption tend to cancel in a ligand-atom–central-atom comparison. Deconvoluted peak area ratios for the chemically different atoms agree with abundances within errors. In Table I are presented results from these data analyses and information from the literature[3,4] on N 1*s* and C 1*s* linewidths measured with gases $N_2O$ and $C_3O_2$. The particular choice of S 2*p* and N 1*s* lines for investigation in this work was based on the fact that vacancies corresponding to these lines lie immediately below the valence shell and that the Auger processes, which are almost entirely responsible for filling these vacancies, necessarily involve two valence electrons. Variation in valence-shell electron density associated with bonding differences should be reflected in the Auger rates, and thus in the vacancy lifetimes and the photoelectron linewidths. A decrease in valence-shell population, which normally results in an increase of core electron binding energy, should then also result in lengthening the vacancy lifetime and decreasing the photoelectron linewidth. Inspection of the S 2*p* data and the N 1*s* data (Table I) shows that the anticipated correlations are present. In the case of $Na_2S_2O_3$ the S 2*p* line components of the ligand sulfur are 0.32 eV broader than those of the central sulfur, and the corresponding difference for the wider 2*s* lines is 0.17 eV. Vacancies in the S 2*s* level are filled almost entirely by relatively fast Coster-Kronig processes.[5] These involve only one valence electron, in contrast to the Auger filling processes for the 2*p* vacancy, which require two valence electrons. For this reason alone chemical effects on the 2*s* linewidth should be less than on the 2*p*. A possible second reason for the smaller sensitivity of the 2*s* width to chemical form may be seen in the *L*-shell Auger and Coster-Kronig rate calculations of McGuire.[2] These show[6] that while 2*s*

TABLE I. Photoelectron linewidths and binding energies for sulfur, nitrogen, and carbon in various chemical forms.

| Element | Compound | Reference | Atom Site | Designation | Level Binding Energy (eV)[a] | Width (eV) |
|---|---|---|---|---|---|---|
| S | $Na_2S_2O_3(s)$[b] | This work |  $\left[\begin{array}{ccc} & O & \\ S & \underline{S} & O \\ & O & \end{array}\right]^{-2}$ | $2\underline{p}_{1/2}$ | 171.61(2)[c] | [1.88][d] |
| | | | | $2\underline{p}_{3/2}$ | 170.32(1) | 1.88(2) |
| | | | | $2\underline{s}_{1/2}$ | 234.41(1) | 3.00(3) |
| | | |  $\left[\begin{array}{ccc} & O & \\ \underline{S} & S & O \\ & O & \end{array}\right]^{-2}$ | $2\underline{p}_{1/2}$ | 165.44(4) | [2.20][d] |
| | | | | $2\underline{p}_{3/2}$ | 164.28(1) | 2.20(4) |
| | | | | $2\underline{s}_{1/2}$ | 228.62(2) | 3.17(3) |
| N | $NH_4NO_3(s)$ | This work | $NH_4^+$ | $1\underline{s}_{1/2}$ | 407.24(1) | 1.49(2) |
| | | | $NO_3^-$ | $1\underline{s}_{1/2}$ | 402.19(1) | 1.63(3) |
| | $N_2O(g)$ | Siegbahn[e] | $N\underline{N}O$ | $1\underline{s}_{1/2}$ | 412.5 | 0.95 |
| | | | $\underline{N}NO$ | $1\underline{s}_{1/2}$ | 408.5 | 1.05 |
| C | $C_3O_2(g)$ | Gelius[f] | $O\underline{C}C\underline{C}O$ | $1\underline{s}_{1/2}$ | 294.9 | 1.11 |
| | | | $OC\underline{C}CO$ | $1\underline{s}_{1/2}$ | 291.5 | 0.97 |

[a] Binding-energy differences for a given compound are significant, but differences between compounds depend upon calibrations which do not necessarily correspond.

[b] In this column (s) and (g) denote solid- and gas-phase samples.

[c] The quantity in parentheses is the standard deviation of the computed parameter obtained from the variance-covariance matrix of the least-squares fit of the Gaussian line shape to the experimental data.

[d] $p_{1/2}$-$p_{3/2}$ components of the $p$ doublet are required to have the same width (see text).

[e] See Ref. 3.

[f] See Ref. 4.

vacancies are filled to a major extent by transitions involving 3*s* electrons, these electrons are involved only to a minor extent in 2*p* filling. Therefore, if the valence densities of the ligand and central sulfur atoms differ less in *s* character than in *p* character, the width effects on the S 2*s* line should be relatively small.

The chemical effects on natural linewidths are probably greater than the linewidth changes observed, because the measured widths include contributions from the width of the exciting radiation (~0.7 eV),[7] from spectrometer resolution (0.2 to ~1.0 eV), and from dispersion in charging effect along the powdered sample surface. Thus, the difference between the two N 1*s* natural widths in $NH_4NO_3$ is $\geq 0.14 \pm 0.04$ eV, an impressive figure relative to the 0.09 eV width calculated for the free nitrogen atoms.[8] In $N_2O$, the N 1*s* width difference is about 0.10 eV and, as expected, the line having higher binding energy is the narrower. In the case of $C_3O_2$, however, the width-binding energy correlation is the inverse of that holding for the other three compounds. Here it may be that the broader 1*s* line of the two outer carbons in this symmetrical linear molecule, OCCCO, is actually a composite of lines corresponding to different final states. Gelius *et al.*[4] have shown that the O 1*s* photoelectron line and the 1*s* line from the adjacent carbon atoms are accompanied by intense satellite lines corresponding to simultaneous excitation of an electron from the occupied $1\pi_g$ molecular orbital to the lowest unoccupied $2\pi_g$ orbital. This coupling between the 1*s* ionizations and the molecular orbitals may produce vibration or distortion in the ion. If the ions can be formed both with and without this vibration or distortion, or if the distortion is such as to remove the degeneracy of the levels assigned to the core orbitals of the outer carbon atoms, then multiple electron lines would appear having separations probably of the order of tenths of an eV. An effect of this magnitude would result in a broadening of the line observed.

In an accompanying paper Shaw and Thomas,[9] from a study of gases, present conclusions similar to those given here about chemical influence on linewidth.

In summary, the widths of photoelectron lines from core levels lying just below the valence levels are greatly affected by chemically associated valence level changes. Furthermore, as indicated by the sulfur results, comparison of width changes for core levels of different $l$ values may give information not only on the valence levels as a whole but specifically on components of the valence population. Measurements made at high resolution with improved spectrometers and narrow monochromatic photon lines should show these chemical effects dramatically.

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[3] Siegbahn *et al.*, Ref. 1, p. 15.

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[5] E. J. McGuire, Phys. Rev. A 3, 587 (1971).

[6] In Ref. 2 calculations are for $Z \geq 18$. Since the types of Auger processes energetically possible are essentially the same for Ar ($Z=18$) and S ($Z=16$), Auger rate ratios for Ar were used, appropriately corrected for the S-Ar valence-shell population difference following the procedure of E. J. McGuire, Phys. Rev. 185, 1 (1969).

[7] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, Nova Acta Regiae Soc. Sci. Upsal. 20, 173 (1967).

[8] E. J. McGuire, Phys. Rev. 185, 1 (1969).

[9] R. Shaw and T. D. Thomas, Phys. Rev. Lett.

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# Cascade Radio-Frequency Spectroscopy of Excited $S$ and $D$ States of Rubidium; Anomalous $D$-State Hyperfine Structure*

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We report the first successful measurements by cascade radio-frequency spectroscopy of the hyperfine structures of excited $S$ and $D$ states of rubidium. We obtain the following magnetic dipole coupling constants (in MHz): for $\mathrm{Rb}^{87}$, $A(7^2S_{1/2})=312.5\pm3.5$, $A(5^2D_{3/2})=14.1\pm0.5$, $A(5^2D_{5/2})=-8.0\pm1.5$; for $\mathrm{Rb}^{85}$, $A(7^2S_{1/2})=92.6\pm1.0$, $A(5^2D_{3/2})=4.1\pm0.5$. The anomalous, negative value of $A$ for the $5^2D_{5/2}$ state may be related to the anomalously small fine-structure interval of the $5D$ state of rubidium.

In spite of the fundamental interest in alkali atoms, there are serious gaps in our knowledge of the properties of excited states of these atoms. Relatively little is known about excited-state radiative lifetimes and hyperfine structures. Only the excited $P$ states, which can be produced by the absorption of resonance light, have been studied in any detail. A satisfactory picture of the alkali atoms cannot be gained without comparable experimental information about non-$P$ excited states. There is no reason to suppose that the properties of non-$P$ excited states are completely normal and predictable. For instance, the fine-structure intervals of the $D$ and $F$ states are known to be anomalously small and they are often inverted in all of the alkali atoms except lithium.[1] To lowest order, the hyperfine-structure intervals should be closely related to the fine-structure intervals, and it would be very interesting to measure the hyperfine structures of some non-$P$ excited states with anomalous fine-structure intervals.

To our knowledge, the only previous attempt to measure $D$-state hyperfine structures in alkali atoms was made by Archambault *et al.*,[2] who used radio-frequency spectroscopy with electron excitation to investigate excited states of sodium and cesium. They obtained $A<0.33$ MHz for the