

TmS is examined as a case in which this method is used. It is concluded from comparison of the experimental and calculated shifts of the $K_{\alpha 1}$, $K_{\beta 1}$, and $K_{\beta 2}$,⁴ lines that the thulium ion in TmTe is basically in the bivalent state; an admixture of the bivalent state of thulium was observed for the first time in TmSe. The compound TmS is trivalent, with the structure $S = \text{Tm} - \text{Tm} = \text{S}$, the metal-metal bond apparently formed by the 5d electron.

The typical instrument for measurement of small x-ray line shifts in heavy atoms is a special Cauchois crystal diffraction spectrometer with two-meter focal length and a scintillation counter as a detector. The shift range that can be measured is 0.05 to 1.0 eV, and the relative error of the measurements $\sigma(\Delta E)/E \approx 10^{-7}$, where $\sigma(\Delta E)$ is the rms error. It should also be noted that another experimental technique based on silicon or germanium semiconductor detectors can also be used. Such instruments now deliver accuracies $\sigma(\Delta E)/E \approx 10^{-6}$.

The basic results have been published in the papers: Zh. Eksp. Teor. Fiz. 48, 445 (1965) [Sov. Phys.-JETP 21, 295 (1965)]; 50, 861 (1966) [23, 572 (1966)]; 53, 796 (1967) [26, 489 (1968)]; 54, 1352 (1968) [27, 724 (1968)]; 55, 745 (1968) [28, 385 (1969)]; 56, 536 (1969) [29, 296 (1969)]; 57, 1139, 1716 (1969) [30, 622, 927 (1970)]; 61, 1756 (1971) [34, 935 (1972)]; 65, 1157 (1973) [38, 573 (1974)].

Yu. S. Grushko, L. I. Molkanov, I. M. Band, and A. V. Olef'nik. Combination of the X-Ray Chemical Shift Method and the Mossbauer Effect in Study of Electron Valence Structure. A new experimental method has been developed successfully in recent years for study of electronic valence structure—the x-ray-line chemical-shift method^[1]. Similar information can be obtained from the Mossbauer effect.

The present paper is devoted to a comparison of the results obtained for various iodine compounds by these two methods. The chemical shifts of the $K_{\alpha 1}$, $K_{\beta 1}$, and $K_{\beta 2}$,⁴ lines were measured for a considerable number of iodine compounds. In addition, self-consistent Dirac-Slater calculations were made for 22 different electron configurations of the iodine ion, and the chemical shifts of the x-ray lines with respect to the $5s^2p^5$ configuration and the electron densities at the nucleus were computed.

Figure 1 shows the calculated results for the $K_{\alpha 1}$ line shift. A similar picture is observed for the $K_{\beta 1}$ line. It is seen that a certain permissible set of configurations corresponds to a given experimental shift and can be represented as a practically straight line with the numbers of 5s and 5p electrons as coordinates; we shall call this line the configurational trajectory. The same can be said of the $K_{\beta 1}$ line. The results of calculation of the electron density at zero can be represented graphically in much the same way as was done for the x-ray chemical shift, and the experimental isomeric shifts can be compared, by appropriate calibration, to the electron density at the nucleus and, as in the case of the x-ray chemical shifts, the configurational trajectories can be obtained from the Mossbauer effect. Obviously, all trajectories should intersect at the same point, whose coordinates correspond to the 5s and 5p populations that satisfy the entire aggregate of data analyzed. We should note that the presence of 5d elec-

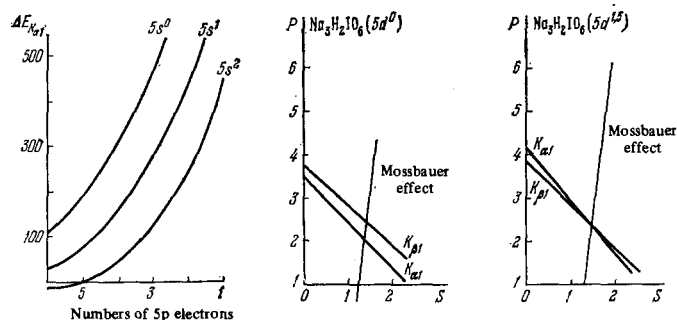


FIG. 1. ($\Delta E - \bar{I}$ meV).

FIG. 2

trons in the valence configuration substantially alters the coordinates of the trajectory intersection point, and that the change can be taken into account quantitatively with the aid of the results of the self-consistent calculation. Figure 2 gives an example of this analysis for sodium paraperiodate. It is seen that if we assume participation of only s and p electrons in the valence configuration, it is impossible to obtain a consistent configuration for the $K_{\alpha 1}$ and $K_{\beta 1}$ lines and the isomeric shift in $\text{Na}_3\text{H}_2\text{IO}_6$. But the assumption that 1.5 5d electrons participate in the configuration yields a single consistent configuration. The same analysis for KICl_2 and KICl_4 indicates that the experimental results agree satisfactorily without participation of 5s and 5d electrons in the configuration. This last result is consistent with the now generally accepted notion that the bonds in integraloid compounds are of pure p character. This configurational analysis, which was carried out for all of the compounds studied, indicated that it is necessary to assume participation of 5d electrons in the valence configuration for oxygen compounds of iodine.

The idea that d electrons participate in the chemical bonds of high-valence compounds of nontransition elements has been suggested by many authors, but we have apparently obtained the first quantitative data. For some of the compounds, the configurations obtained were used to calculate the quadrupole splitting constants of the ground state of the iodine-127 nucleus, which were then compared with the experimental values from the Mossbauer effect and NQR. The experimental and calculated values agree satisfactorily within the limits of error.

It can be stated in conclusion that combination of the x-ray chemical shift and Mossbauer effect methods enables us to acquire additional information on electron valence structure that does not follow from either of the methods taken alone.

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G. M. Drabkin, A. I. Sibilev, V. V. Klyubin, T. G. Braginskaya, and G. E. Shmelev. Spatial Correlation Effects of Fluctuations in a Liquid Binary Mixture and its Electrical Conductivity Near a Phase-Transition Point. The sensitivity of the spatial coherence modulus of light scattered at small angles to changes in the fluctuation dispersion of the triethylamine-water system under phase-transition conditions has been demonstrated experimentally. The spatial coherence modulus of the scattered light increases with increasing optical thickness of the sample, a fact explained by the

increase in the spatial correlation of concentration fluctuations with the approach to the phase separation temperature^[1]. This behavior of the spatial coherence modulus is qualitatively the opposite of that observed in small-angle scattering of light on a system of independent scatterers^[2].

The enthalpy and entropy of the triethylamine-water interaction were determined spectroscopically in the three-molecule complex. Substantial steric stresses in the complex are apparently one of the basic causes of phase separation in this system as the temperature rises^[3].

The usefulness of comparing the temperature curves of conductivity of systems with limited component solubility with other physicochemical characteristics under near-critical conditions has been demonstrated experimentally^[4]. The importance of studying conductivity in water-nonelectrolyte solutions as a parameter related to changes in associative equilibria and the need

to investigate spatial structure in these solutions have been discussed.

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