

A qualitatively correct description of the spectra of substituted benzene is achieved when $\bar{u}_1 \sim 0.1$ and $\tau \sim (2-4) \cdot 10^{-13}$ sec. In this time period, the molecule executes ≥ 4 oscillations about the time equilibrium position. Since $\sigma_1 > 1/\tau$, from (5) it follows that the spectrum can be approximated by superposition of three (and in the case of $I_1 \cong I_2$, two) Gaussians, and with an increase in ω the Gaussian with the smallest moment of inertia of the molecule makes an increasingly weighty contribution.

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PRELIMINARY TREATMENT OF XPS SPECTRA

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UDC 535.33

Contemporary program suites for treating experimental data are, as a rule, organized along a modular principle. A module is an autonomous program which solves a particular stage of the data analysis problem. The advantage of a modular system lies in the fact that it permits the researcher to process experimental data according to any scenario, although this requires a correct selection of the elementary means (phases) of treatment which when acting in concert insure the stability of the results.

In this study a number of problems of preliminary XPS processing have been examined, namely the suppression of anomalous spikes, smoothing, removal of noise from inelastic scattering of electrons in the medium, and compensation for the effect of satellites in the spectrum of the x-ray source. The latter of these problems will be analyzed in greater detail within the framework of a method proposed in this paper. Attention given to the enumerated problems is explained in the first place by their independent relevance in treating spectra, and in the second by the fact that the quality of the solution of the inverse (often unstable) problems of the subsequent stage of analysis of spectroscopic data depends in many respects on the quality of their solutions.

The methods set forth are realized in the form of individual blocks in the interactive suite of programs "Spectra-Dialog."

1. Suppression of Anomalous Spikes. Spikes are the rare anomalous values of spectral points which arise as a consequence of uncontrollable malfunctions of the apparatus. The goal of treatment is the suppression of spikes, for which the method proposed below guarantees stability of the results of further processing.

Consider a linear model for the measurement

$$g = Kf + v + \delta, \quad (1)$$

Institute of Chemistry, Far Eastern Division, Academy of Sciences of the USSR, Vladivostok. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 54, No. 1, pp. 40-45, January, 1991. Original article submitted January 22, 1990.

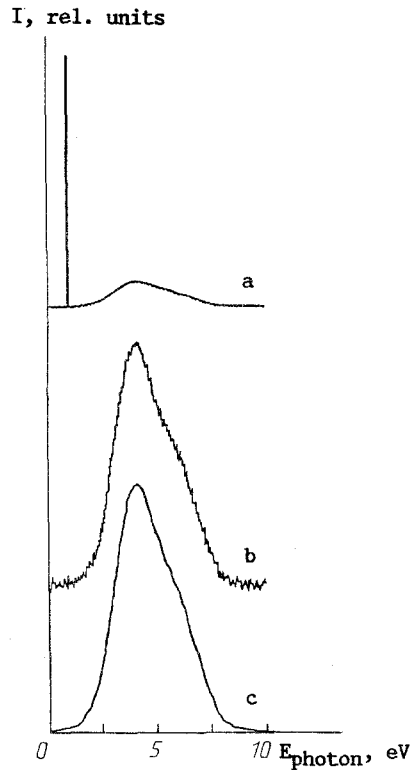


Fig. 1. A model spectrum - the sum of the unresolved doublet, random noise, and spikes (a); result of suppression of spikes (b); subsequent suppression of noise (smoothing) (c).

where g is the result of the measurement of an ideal spectrum f , obtained on the instrument according to some given operator K ; v is random noise, δ are possible spikes (vectors $g = (g_1 \dots g_N)$, $f = (f_1 \dots f_N)$, $v = (v_1 \dots v_N)$, etc.

Huber (Ref. 1) proposed the following iterative algorithm for suppressing δ :

$$\tilde{g}_i = \begin{cases} g_i, & \text{if } |r_i| \leq \omega \varepsilon_i, \\ \xi_i - \omega \varepsilon_i, & \text{if } r_i < -\omega \varepsilon_i, \\ \xi_i + \omega \varepsilon_i, & \text{if } r_i > \omega \varepsilon_i. \end{cases} \quad (2)$$

Here ω is a parameter (usually chosen to be 1.5), ξ is the result of smoothing of the spectrum g for the purpose of obtaining an estimate of the vector Kf ; $r = g - \xi$ is the remainder vector; ε_i is the dispersion of the i -th component of the v vector. In actuality, (2) is only the first step of the iterative process under consideration, succeeding steps differ from it by exchange of \tilde{g}_i for g_i . In [1], the convergence of such a method was shown. Note that if $\delta = 0$ (no spikes), the data remain virtually unchanged, and consequently, algorithm (2) can be recommended for application in all cases as a preventive measure.

2. Smoothing. Recently, matrix formulated approaches have been increasingly successfully employed in place of heuristic smoothing algorithms [2] which permit the suppression of noise v on the basis of a priori information about v and f and when controlling distortion of the useful part of Kf . We examine one of these approaches, based on methods for solving the inverse problem [3].

Let $\xi = KK^-g$, where $K^- = \lim_{\omega \rightarrow 0} K^*(KK^* + \omega I)^{-1}$ is the pseudo-inverse operator. According to properties of $KK^-K = K$ we find that $\xi = Kf + KK^-v$, and hence, the filter KK^- from one side does not distort the useful signal Kf , while from the other side suppresses part of the noise $(I - KK^-)v$.

In practice, a priori information concerning the noise v and the ideal spectrum f is frequently accessible. Let the random vector v be controlled by the multidimensional normal distribution vector with zero average and the covariant matrix Σ , i.e., $v \sim N(0, \Sigma)$. Data on f is formulated analogously in the form of a statistical model $f \sim N(f_0, F)$. In this case an estimate

$$\xi = KFK^*(KFK^* + \Sigma)^{-1}(g - Kf_0) + Kf_0 \quad (3)$$

describes the vector Kf in the best form (optimal in the sense of the root mean square) [3].

The effectiveness of the described procedure for spike suppression and smoothing may be estimated by the results of their successive application to the model spectrum depicted in Fig. 1.

It is frequently reasonable to thin out the smoothed spectrum without leading to a substantial loss of information. The combination of smoothing and thinning out is termed aggregate, permitting not only suppression of noise, but also a substantial reduction in the time for further processing of the spectrum, this being very relevant to express analysis of spectroscopic data.

3. Removal of Inelastic Scattering Noise. As a result of inelastic electron scattering processes in the medium a noise component appears in the XPS, whose removal requires a correct account for the physical processes giving rise to it. In practice, however, it is usually sufficient to employ the simple approach of Shirley [4] or a modification of it [5]

$$f_i^{[n+1]} = g_i - b \sum_{j=1}^{i-1} [1 - m(i-j-1)] f_j^{[n]}, \quad (4)$$

where the initial spectrum is chosen as a zeroth order approximation of the iterative process.

In contrast to [5], in this paper only the measured spectroscopic material was directly used to determine parameters of the slope noise component. Calculation of the parameters were included in the iterative process in such a way that the high energy, sloped, linear part of the spectrum starting at the point p with energy E_p , was described by the linear approximation using the least squares method $g'_i = a - k_i$ ($i > p$). Assume, naturally, that in this region the useful component is absent and hence

$$b^{[n]} = \frac{a}{\alpha^{[n]}} - k \frac{\beta^{[n]}}{(\alpha^{[n]})^2},$$

$$(bm)^{[n]} = \frac{k}{\alpha^{[n]}}. \quad (5)$$

Here

$$\alpha^{[n]} = \sum_{j=1}^p f_j^{[n]} \text{ and } \beta^{[n]} = \sum_{j=1}^p (j+1) f_j^{[n]}.$$

Despite the fact that use of the operation of noise subtraction requires particular care, it is suitable for applications if this is necessary for procedures of subsequent treatment of data. In particular, it is useful for compensation procedures involving the satellite structure of the spectra of the x-ray source.

4. Compensation for the Influence of Satellites of the Spectrum of the X-Ray Source. Along with random errors and inelastic scattering noise, spectra from XPS measured using traditional equipment contain apparatus distortions associated with the nonmonochromatic and multiple line characteristics of radiation of an x-ray source, which, besides the broadening effect on the structure of the recorded spectra, leads to the appearance of parasitic satellite lines in the spectra.

The action of the operator K on the ideal spectrum f in this case is described by the convolution integral

$$g(E) = f(E) * k(E), \quad (6)$$

where E is the binding energy of the electrons; $k(E)$ is the spectral function of the x-ray source. Solving the inverse problem, it is possible to recover the true spectrum, if the function $k(E)$ is known, in which event the solution is notably simplified if preliminarily the measured spectrum $g(E)$ is transformed into the form $\xi(E)$ which it would have been were

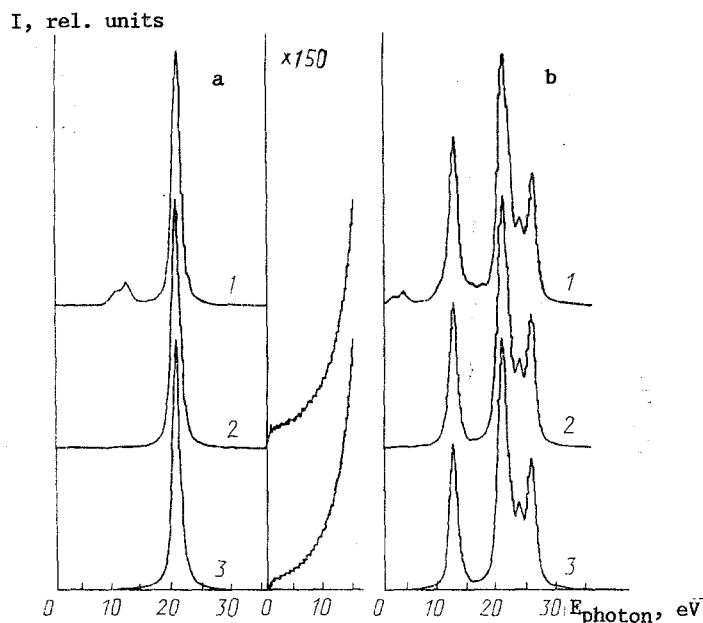


Fig. 2. Correctness and efficiency of satellite structure suppression in model spectra containing one (a) and five principle lines (b): model spectra with satellite structure (1), results of its treatment (2). For comparison, model spectra containing only principal lines are cited (3).

the spectral function a single line and symmetrical (the spectrum of the x-ray source contains only the $K\alpha_1$ line), that in fact, signifies the suppression of parasitic structures due to satellites of the source in the x-ray spectrum.

As a rule, to synthesize the spectral function of traditional Mg and Al sources, the Lorentzian line shape is used, limited to the most intense $K\alpha_1$, $K\alpha_2$, $K\alpha_3$, and $K\alpha_4$ components [6, 7]. The relative intensity of other lines in the spectra of these x-ray sources is so small [8], that their distorting effect on the XPS is usually not considered. Each of the four Lorentzian L_i is characterized by a half width at half maximum Γ_i , displacement along the energy scale δ_i , and integral intensity I_i , which are defined relative to the position and integral intensity of the primary L_1 line. For the principle $K\alpha_{1,2}$ doublet, owing to the $2p_{3/2,1/2} \rightarrow 1s$ transitions at singly ionized atoms, one may set $\Gamma_2 = \Gamma_1$ (components overlap) and $I_2 = 0.5$ (in accordance with the relation of the magnitudes $2s + 1$). The widths, though, of the lines owing to $2p \rightarrow 1s$ transitions in singly ionized atoms, are greater than the width of the principle $K\alpha_1$ line. Taking into account the fact that the convolution of two Lorentzian functions yields a Lorentzian function with a width equal to the sum of the widths of the displaced functions, one may represent L_3 and L_4 as a convolution of the main line L_1 with broadened Lorentzians L'_3 and L'_4 , respectively. Then the spectroscopic function may be put in the form

$$k(E) = L_1(E, \Gamma_1) + 0.5 \cdot L_1(E - \delta_2, \Gamma_1) + L_1(E, \Gamma_1) * sat(E), \quad (7)$$

where $sat(E) = I_3 \cdot L'_3(E + \delta_3; \Gamma'_3) + I_4 \cdot L'_4(E + \delta_4, \Gamma'_4)$; $\Gamma'_3 = \Gamma_3 - \Gamma_1$; $\Gamma'_4 = \Gamma_4 - \Gamma_1$.

In consideration of (7), from (6) we obtain

$$\xi(E) + 0.5\xi(E - \delta_2) = g(E) - \xi(E) * sat(E). \quad (8)$$

Here $\xi(E) = f(E) * L_1(E, \Gamma_1)$, the satellite-free spectral structure being sought.†

Equation (8) is similar to the nonhomogeneous, linear, integral Fredholm equation of second order, differing from it by the presence in the left-hand part of a second term. To solve this equation one may, of course, directly organize an iterative loop relation

† $f * (L_1 * L'_{3,4}) = (f * L_1) * L'_{3,4}$ according to properties of convolutions.

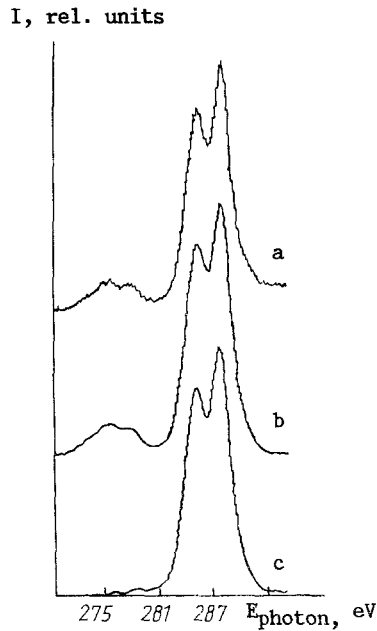


Fig. 3. Recovery treatment of the XPS spectra of carbon 1s electrons of graphite oxide: initial spectrum (a), smoothing with account for noise according to Shirley (b), results of suppression of satellite structure (c).

with respect to $\xi(E)$. However, so as to accelerate convergence, it turns out to be more effective to construct an iterative process with partition of each iteration step of the main loop (over the index n) into two stages of the following form:

$$\begin{cases} \theta^{[n]}(E) = g(E) - \xi^{[n-1]}(E) * sat(E), \\ \xi^{[n=0]}(E) = g(E). \end{cases} \quad (9)$$

Computation of the n -th approximation of the sought spectrum $\xi^{[n]}(E)$ occurs at a second stage by means of a procedure for removing one of the overlapping components of the doublet structure organized into an iterative subloop over the index k

$$\begin{cases} \xi^{[k]}(E) = \theta^{[n]}(E) - 0,5\xi^{[k-1]}(E - \delta_2), \\ \xi^{[k=0]}(E) = \theta^{[n]}(E). \end{cases} \quad (10)$$

Note, that for a discrete model spectrum the displacement δ_2 does not absolutely have to be a multiple step of the partition of the spectrum. In this event, the intensity in the channel with energy $E - \delta_2$ used in the procedure, may be approximated by means of a second order polynomial determined by the method of least squares for the neighboring four channels.

If the satellite structure contained in the measured spectrum is regarded as several distortions, then it turns out that after completing each two-step iterative pass, the distortion spectrum is displaced along the measured spectral region by a value $\delta_3 - \delta_2$ to the low energy side (in the process its form changes, while the intensity of the distortion signal changes in accordance with the values of I_3 and I_4). What is critical is the fact that the spectrum observed has a finite width for the measured spectral region, and consequently, the distortion spectrum has a high energy boundary, above which the signal intensity can be assumed to be zero. From what has been said it is clear that as a result of completion of a definite number of iterative passes, the distortion spectra associated with the x-ray $K\alpha_{2,3,4}$ satellites will be subtracted from the edges of the region of interest to the researcher.

It is obvious, however, that under conditions of realistic measurements prior to proceeding to suppression of satellite radiation, one must subtract the noise component from the spectrum. Indeed, in the described method the region lying higher than the limiting spectral point, by an indirect means, exerts an influence on the results of each iterative pass. In the event that zeroing of this region is not legitimate, application of the procedure we proposed may exert a distorting effect in recovery of the spectrum with its help.

In order to demonstrate the efficiency of the algorithm proposed a model spectrum is presented in Fig. 2 containing along with the primary lines, the $K\alpha_{2,3,4}$ satellites

corresponding to them, the results of treatment by means of the method presented, and model spectra containing only primary lines. The spectral lines were modeled by convolutions of Gaussians with Lorentzians, a model of the spectrum of the x-ray radiation being chosen from [6]. In Fig. 3 the subsequent results are depicted of the regeneration treatment of a realistic x-ray spectrum of the 1s electron of carbon of a sample of graphite oxide; measured on an ES-2401 spectrometer with a Mg K α source (the source spectrum was modeled also).

Of course, application of the proposed method is limited by the need to identify all peaks in the region of interest to the researcher, which may not have fundamental x-ray K $\alpha_{2,3,4}$ satellite lines (auger lines, satellites, and ghost peaks, distributed within this region), and to accurately account for their spectral role. However, in the majority of cases these limitations do not play a critical role. More important is the problem of determining the parameters of the spectral model of the x-ray spectrum of the equipment on which measurements are carried out. For its solution, it is proposed to use an optimization process based on the described procedure for suppression of K $\alpha_{2,3,4}$ satellites in which the width parameters of the Lorentzians are varied. The root mean square of the deviation from the average intensity in the region of the K $\alpha_{3,4}$ satellites of results of processing the main line of the measured standard spectrum may serve as minimum estimate criterion.

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FRANCK-CONDON FACTORS AND RELATIVE STRENGTHS OF THE $c^1\Sigma_u \rightarrow a^1\Delta_g$, $c^1\Sigma_u \rightarrow X^3\Sigma_g$ ELECTRONIC TRANSITIONS IN THE O₂ MOLECULE

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UDC 539.192

Franck-Condon (FC) factors are the squares of the overlap integrals of the vibrational wave functions $\Psi_{v'}$ (r) and $\Psi_{v''}$ (r) belonging to upper and lower electronic states of a molecule

$$q_{v'v''} = \left| \int \Psi_{v'}(r) \Psi_{v''}(r) dr \right|^2 \quad (1)$$

At present various methods for calculating $q_{v'v''}$ have been developed. A complete summary of FC factor data for 400 electronic transitions of 180 diatomic molecules as well as computational methods have been given in [1]. The most accurate FC factors are obtained using the Rydberg-Klein-Rees (RKR) method or its variants. However, use of RKR potentials has its own substantial difficulties owing to both the lack of a sufficient quantity of reliably measured spectroscopic data for constructing true RKR potentials, and the fact that using approximate methods for solving the Schrödinger equation based on RKR potentials leads to the necessity of controlling the accuracy of the wave function obtained. Both reasons limit application of the RKR method.

Hence, in [2, 3], exact potential curves for compound electronic states of the Cu₂ molecule were constructed on which basis FC factors were computed. The reliability of the

N. É. Bauman State Technical University, Moscow. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 54, No. 1, pp. 46-50, January, 1991. Original article submitted March 16, 1990.