An interference effect in x-ray fluorescence spectra

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We consider theoretically the influence of interference effects on the shape of x-ray fluorescence spectra in symmetrical or nearly symmetrical molecules. We observe a strong dependence of the shape of the spectral band on the scattering angle and on the frequency of the exciting photon near the ionization threshold or the corresponding inner level. We use a diatomic molecule as an example to show how this effect can be used to classify molecular levels experimentally with respect to symmetry types.

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1. INTRODUCTION

Although it is clear that in general fluorescence should be considered as a process in which a photon (electron, ion) is scattered inelastically by the system, when studying x-ray fluorescence of molecules one usually neglects the process which produces the excited x-ray state. As the excited x-ray states (EXS) are in this process the intermediate states, interference between them is possible if the energy gap between EXS is less than or of the order of the natural linewidth of the x-ray line.[1] In the fluorescence damping law the interference term leads to beats.[2] In view of the short lifetime of EXS ($\tau \sim 10^{-5}$ s) it is difficult to check this experimentally. However, we shall show in what follows that one can study the interference through the characteristic dependence of the spectral band shape on the frequency of the exciting photon.

In the present paper we consider the interference between EXS and holes localized in different atoms of the molecule. In that case the amplitudes of the inelastic photon scattering channels (in what follows we consider x-ray fluorescence excited by a photon collision) will qualitatively differ from one another by phase factors of the form $e^{i\mathbf{k}\cdot\mathbf{R}}$, where **k** and **R** are the momentum of the ejected electron and the interatomic radius vector. The interference occurring as a result of this leads to a dependence of the shape of the valence band spectrum on the frequency of the exciting photon.

2. $L_{II,III}$-SPECTRUM

We consider a diatomic homonuclear cluster A-A′ which is a constituent part of a molecule. In the general case the atoms A and A′ have different immediate surroundings and due to that their inner levels have different ionization potentials. The process in which a photon γ is inelastically scattered by the cluster can proceed along the following two channels:

$$\begin{tikzcd}[column sep=small, row sep=small] & A_+ - A' + e^- \arrow[dr] & \\ \gamma + A - A' \arrow[ur] \arrow[dr] & & (A - A')_\Psi + e^- + \gamma'. \\ & A - A_+' + e^- \arrow[ur] & \end{tikzcd} \tag{1}$$

Here A_+-A′ and $(A\text{-}A')_\Psi$ correspond to molecular ions with a hole in the $L_{II,III}$ shell of atom A and a hole in the valence shell Ψ of the cluster A-A′.

In what follows we restrict ourselves to the case of molecules which are randomly orientated in the sample. We neglect for the sake of simplicity the spin-orbit splitting of the $L_{II,III}$ level.[1] The inelastic scattering of a photon into a solid angle do′ is described by the Kramers-Heisenberg formula.[3] In the one-particle approximation we have the following expression for the cross-section for process (1) ($\hbar = m = e = 1$):

$$\frac{d\sigma}{do'} = \frac{N\alpha^4}{4\pi^3}\omega\omega'^3 k \int d\hat{k}\bar{I}(\hat{k}), \tag{2}$$

$$I(\hat{k}) = \left| \sum_{\alpha=1,2} \sum_{m=-1} \frac{\langle \Psi_{1m}{}^\alpha | \mathbf{r}_\alpha \cdot \mathbf{e}'^* | \Psi \rangle \langle \Psi_{\mathbf{k}}{}^- | \mathbf{r}_\alpha \mathbf{e} | \Psi_{1m}{}^\alpha \rangle}{Z_\alpha} \right|^2;$$

$$\Psi_{1m}{}^\alpha = R_{2p}{}^\alpha(r_\alpha) Y_{1m}(\hat{r}_\alpha), \quad Z_\alpha = \omega' - \omega_\alpha + i\Gamma_\alpha/2, \tag{3}$$
$$\mathbf{r}_\alpha = \mathbf{r} - \mathbf{R}_\alpha, \quad \hat{k} = \mathbf{k}/k;$$

where N is the number of electrons in the shell Ψ; ω, **e** and ω', **e′** are, respectively, the frequencies and polarization vectors of the incoming and the scattered photons; ω_α is the frequency of the transition from the valence level Ψ to the $L_{II,III}$ level of atom α; R_{2p}^α is the radial part of the wavefunction of the $L_{II,III}$ shell of atom α; $\bar{I}(\hat{k})$ describes the averaging of $I/\hat{k})$ over the polarizations and orientations of the cluster.

As the integral (2) over the direction of the ejection of the electron is invariant under the transformation $\mathbf{k} \to -\mathbf{k}$ we replace in Eq. (3) $\Psi_{\mathbf{k}}^-$ by $\Psi_{\mathbf{k}}^- = (\Psi_{\mathbf{k}}^+)^*$. The solution of the Lippmann-Schwinger (LS) equation for $\Psi_{\mathbf{k}}^+$ near the nucleus of atom α which gives the main contribution to the transition matrix element has the form[4]

$$\Psi_{\mathbf{k}}{}^+ = \sum_{lm} A_{lm}{}^\alpha R_l{}^\alpha(k, r_\alpha) Y_{lm}(\hat{r}_\alpha), \tag{4}$$

where R_l^α is the solution of the radial Schrödinger equation inside the (muffin tin or MT) sphere of radius b_α.

We write the wavefunction of the valence shell in the molecular orbital approximation neglecting the 3d atomic orbits:

$$\Psi = \sum_{\alpha=1,2} C_\alpha R_{3s}{}^\alpha Y_{00} + \ldots \tag{5}$$

Noting that the averaging over the orientations of the cluster is equivalent to averaging over the direction of the photon propagation and using the relation (i,j, . . . = x, y, z)

$$\overline{e_i{}'e_j{}'^* e_k e_n{}^*} = {}^1/_{60}[\delta_{ij}\delta_{kn}(7 - \cos^2\theta) + {}^1/_2(\delta_{ik}\delta_{jn} + \delta_{in}\delta_{jk})(3\cos^2\theta - 1)],$$

we get

$$\bar{I}(\hat{k}) = \sum_{\alpha=1,2} I_{\alpha\alpha}(\hat{k}) + 2I_{12}(\hat{k}), \tag{6}$$

$$I_{\alpha\beta}(\hat{k}) = \frac{C_\alpha C_\beta}{360} P^{(\alpha)} P^{(\beta)} \operatorname{Re}\left\{ \frac{1}{Z_\alpha Z_\beta^*} \left[(13 + \cos^2\theta) \left(P_0^{(\alpha)} P_0^{(\beta)} A_{00}{}^\alpha A_{00}{}^{\beta*} \right.\right.\right.$$
$$\left.\left.\left. + \frac{2}{5} P_2^{(\alpha)} P_2^{(\beta)} \sum_{m=-2}^{2} A_{2m}{}^\alpha A_{2m}{}^{\beta*} \right) + 3(3\cos^2\theta - 1) P_0^{(\alpha)} P_0^{(\beta)} A_{00}^{(\alpha)} A_{00}^{(\beta)*} \right] \right\}, \tag{7}$$

$$P^{(\alpha)} = \int_0^\infty dr\, r^3 R_{2p}{}^\alpha R_{3s}{}^\alpha, \quad P_l^{(\alpha)} = \int_0^{b_\alpha} dr\, r^3 R_{2p}{}^\alpha R_l{}^\alpha,$$

where θ is the angle between the directions of propagation of the initial and final photons, and I_{12} is the interference term.

We perform the subsequent calculations neglecting the long-range part of the Coulomb hole. As the interference is important when $|\omega_1 - \omega_2| \leqslant \Gamma$, i.e., when the distortion of the symmetry of the cluster is sufficiently small, we take the difference between the atoms A and A′ only into account in the transition frequencies. In this connection we drop in the appropriate places the indexes α.

We consider two limiting cases:

$$\omega > E(L_{\text{II, III}}) \quad (kR \gg 1),$$
$$\omega \sim E(L_{\text{II, III}}) \quad (kR \ll 1).$$

Here $E(L_{\text{II,III}})$ is the ionization potential of the $L_{\text{II,III}}$ level;

$$k = [2(\omega - E(L_{\text{II, III}}))]^{1/2}$$

A. High-energy limit, kR≫1

In this limit the ejected electron has a large kinetic energy and in the solution of the LS equation it is sufficient to restrict oneself to the first Born approximation:[4]

$$A_{lm}{}^{\alpha} = \frac{4\pi i^{l+1}}{kb^2[R_l, h_l^{(1)}]} Y_{lm}{}^{*}(\hat{k}) \exp(i\mathbf{kR}_{\alpha}), \tag{8}$$

where $h_l^{(1)}$ is a spherical Hankel function; the square brackets indicate the Wronskian in the point $r_\alpha = b$.

Using Eqs. (2), (7), and (8) and

$$\int d\hat{k}\, e^{i\mathbf{kR}} \Phi(\hat{k}) \underset{kR\gg 1}{\approx} \frac{2\pi}{ikR} [\Phi(\hat{R}) e^{ikR} - \Phi(-\hat{R}) e^{-ikR}],$$

we get

$$\frac{d\sigma}{do'} = Q_{\infty} \Big[\sum_{\alpha=1,2} \frac{C_\alpha{}^2}{|Z_\alpha|^2} + 2C_1C_2\chi_{\infty} \operatorname{Re}\Big(\frac{1}{Z_1Z_2^{*}}\Big)\Big], \tag{9}$$

where

$$\chi_{\infty} = \frac{\sin(kR)}{kR},$$

$$Q_{\infty} = \frac{N\alpha^4}{90\pi} \omega\omega'^3 kP^2[(13+\cos^2\theta)(|\tilde{P}_0|^2 + 2|\tilde{P}_2|^2) + 3(3\cos^2\theta - 1)|\tilde{P}_0|^2],$$

$$\tilde{P}_l = P_l / kb^2[R_l, h_l^{(1)}]. \tag{10}$$

It is clear from Eq. (10) that the interference term tends to zero as kR → ∞.

B. Low-energy limit, kR≪1

We write down the solution of the LS equation in the MT potential approximation (see, e.g.,[4]

$$A_{lm}{}^{\alpha} = \frac{i}{kb_\alpha{}^2[R_l{}^\alpha, h_l^{(1)}]} B_{lm}{}^{\alpha}, \tag{11}$$

$$B_{lm}{}^{\alpha} - \sum_{\beta(\neq\alpha)} \sum_{l'm'} G^{\alpha\beta}_{lml'm'} t_{l'}{}^{\beta} B^{\beta}_{l'm'} = 4\pi i^l Y_{lm}{}^{*}(\hat{k}) \exp(i\mathbf{kR}_\alpha), \tag{12}$$

where

$$G^{\alpha\beta}_{lml'm'} = 4\pi \sum_{L} i^{L+l-l'} h_L^{(1)}(kR_{\beta\alpha}) Y^{*}_{L,m-m'}(\hat{R}_{\beta\alpha}) \int Y_{lm}{}^{*} Y_{l'm'} Y_{L,m-m'} do.$$

In what follows we need the matrix representation of the solution of the set of Eqs. (12):

$$\mathbf{B} = U\mathbf{Y}, \quad U = (I - Gt)^{-1} = I + \sum_{n=1}^{\infty} (Gt)^n. \tag{13}$$

Here t_l^α is the partial matrix for the scattering of an electron by atom α; I is the unit matrix;

$$\mathbf{Y} = \{4\pi i^l Y_{lm}{}^{*}(\hat{k}) \exp(i\mathbf{kR}_\alpha)\}.$$

When kR ≪ 1 the matrix elements of the Green function G and of the scattering matrix t behave as

$$G^{\alpha\beta}_{lml'm'} \sim (kR)^{-(l+l'+1)}, \quad t_l{}^{\alpha} \sim \Big(\frac{kb}{l+1/2}\Big)^{2l+1}. \tag{14}$$

Using these relations we get

$$[(Gt)^n]^{\alpha\beta}_{lml'm'} \sim (kb)^{l'-l} (b/R)^{l'+l+n} (l'+1/2)^{-(2l'+1)}.$$

Substituting this expression into Eq. (13) we have

$$B_{lm}{}^{\alpha} \sim \begin{cases} 1 & \text{for } l=0 \\ (kb)^{-l}(b/R)^{l+1} & \text{for } l \neq 0 \end{cases}. \tag{15}$$

The estimates we have obtained enable us to simplify Eqs. (12) when kR ≪ 1 and b < R (usually $b \leqslant \frac{1}{2}R$). Indeed, using (14) and (15) we find that

$$G^{\alpha\beta}_{lml'm'} t_{l'}{}^{\beta} B^{\beta}_{l'm'} \sim B_{lm}{}^{\alpha} \begin{cases} 1 & \text{for } l'=0. \\ \Big(\dfrac{b}{R(l'+1/2)}\Big)^{2l'+1} & \text{for } l' \neq 0. \end{cases} \tag{16}$$

It follows from this equation that when we sum the harmonics in Eq. (12) we need consider only the terms with $l' = 0$. Moreover, retaining in (12) only terms of order $(kb)^{-1}$ we get finally the following set of equations:

$$Q_\alpha - \sum_{\beta(\neq\alpha)} Q_\beta \frac{f_\beta}{R_{\alpha\beta}} \exp(i\mathbf{kR}_{\alpha\beta}) = \exp(i\mathbf{kR}_\alpha), \tag{17}$$

$$B_{lm}{}^{\alpha} = 4\pi ik \sum_{\beta(\neq\alpha)} h_l^{(1)}(\mathbf{kR}_{\alpha\beta}) Y_{lm}{}^{*}(\hat{R}_{\alpha\beta}) f_\beta Q_\beta, \quad l \neq 0, \tag{18}$$

where

$$Q_\alpha = (4\pi)^{-1/2} B_{00}{}^{\alpha}, \quad f_\alpha = \frac{1}{ik} t_0{}^{\alpha},$$

f_α is the s-wave scattering amplitude.

Equations (17) are well known as the equations for the multiple scattering in the s-wave approximation.[5] One should note that when one evaluates the intensity of p → s, d transition in the low-energy limit, we can not restrict the calculation to merely the p → s transition, as $B^\alpha_{2m} \sim B^\alpha_{00}(kb)^{-2}$. The contribution from the d-states can easily be evaluated, by using Eq. (18).

We turn to the diatomic cluster A-A′. As before we shall take the difference between the atoms A and A′ into account solely in the transition frequencies. The solution of the set of Eqs. (17) for the cluster has the following form:

$$Q_\alpha = \frac{1}{\Delta} \Big(\exp(i\mathbf{kR}_\alpha) + \frac{f}{R} \exp(ikR + i\mathbf{kR}_\beta) \Big), \tag{19}$$

$$\Delta = 1 - f_+ f e^{2ikR}/R^2.$$

Here f and f_+ are the s-wave scattering amplitudes for scattering by atom A in the ground state of the cluster and by atom A with a hole in the $L_{\text{II,III}}$ shell (or the K shell in the case of the K spectrum).

Using Eqs. (2), (7), (11), (18), and (19), we get

$$\frac{d\sigma}{do'} = Q_0 \Big[\sum_{\alpha=1,2} \frac{C_\alpha{}^2}{|Z_\alpha|^2} + 2C_1C_2\chi_0 \operatorname{Re}\Big(\frac{1}{Z_1Z_2^{*}}\Big)\Big], \tag{20}$$

where

$$\chi_0 = \Big[\frac{\sin(kR)}{kR} \Big(1 + \Big|\frac{f}{R}\Big|^2\Big) \tag{21}$$
$$+ 2\operatorname{Re}\Big(f\frac{e^{ikR}}{R}\Big)\Big]\Big[1 + \Big|\frac{f}{R}\Big|^2 + 2\frac{\sin(kR)}{kR} \operatorname{Re}\Big(f\frac{e^{ikR}}{R}\Big)\Big]^{-1},$$

$$Q_0=\frac{N\alpha^4\omega\omega'^3kP^2}{90\pi|\Delta|^2}[(13+\cos^2\theta)(|\tilde{P}_0|^2+2|\tilde{P}_2kfh_2^{(1)}(kR)|^2)$$
$$+3(3\cos^2\theta-1)|\tilde{P}_0|^2]\left[1+\left|\frac{f}{R}\right|^2+\frac{2\sin(kR)}{kR}\operatorname{Re}\left(\frac{fe^{ikR}}{R}\right)\right].$$

It is clear from Eq. (21) that $\chi_0 \to 1$ as $kR \to 0$. Therefore, if a photon with a frequency close to the ionization threshold of the $L_{II,III}$ level is scattered by the cluster the interference term becomes of the same order of magnitude as the contributions from the various scattering channels. The shape of the emission band will in that case no longer be described by the sum of the dispersion curves. In the fluorescence damping law the interference term leads to beats[2]

$$\sim e^{-\Gamma t}\cos[(\omega_1-\omega_2)t+\delta],$$

which in the optical band are an effective method for measuring the energy gap between levels which lie close to one another.

The strong dependence of χ_0 on the frequency ω of the exciting photon leads to an ω-dependence of the shape of the spectrum. We consider this problem in more detail using the example of a symmetric diatomic molecule A-A ($\omega_1 = \omega_2$).

C. Dependence of the shape of the emission band on the frequency of the exciting photon

Two kinds of levels will show up in the $L_{II,III}$ spectrum of the A-A molecule: σ_g ($C_1 = C_2 = C_g$) and σ_u ($C_1 = -C_2 = C_u$) with, respectively, occupation numbers N_g and N_u. In general $C_g \neq C_u$. We note that strictly speaking one should write the wavefunction (5) of the valence shell in the form

$$\Psi_\alpha=\sum_{\beta=1,2}C_{\alpha\beta}R_{3s}^{\beta}Y_{00}+\ldots,$$

indicating by the index α the atom on which the hole is localized. In that case, in general, $|C_{\alpha 1}| \neq |C_{\alpha 2}|$ due to the relaxation of the wavefunction onto the hole on the atom α. However, only the diagonal components $C_{\alpha\alpha}$ enter into the transition matrix element (3) and they have the same symmetry properties as the coefficients C_α of the wavefunction of the ground state of the molecule. In what follows we shall therefore in order to simplify the notation use the ground state functions implying by C_α the coefficients $C_{\alpha\alpha}$.

Combining Eqs. (9), (10) and (20), (21) we get the following expression for the ratio of the intensities of the transitions $\sigma \to L_{II,III}$ and $\sigma_g \to L_{II,III}$:

$$\frac{I_u}{I_g}=\frac{N_u}{N_g}\left(\frac{C_u}{C_g}\right)^2\left(\frac{1-\chi}{1+\chi}\right), \tag{22}$$

$$\chi\to\begin{cases}\chi_0 & \text{for } kR\ll1\\ \chi_\infty & \text{for } kR\gg1\end{cases}. \tag{23}$$

Equation (23) is only in the limit as $kR \to \infty$ the same as the normally used formula

$$\frac{I_u}{I_g}=\frac{N_u}{N_g}\left(\frac{C_u}{C_g}\right)^2.$$

The interference leads to the fact that the intensity of the transition $\sigma_u \to L_{II,III}$ tends to zero as $\omega \to E(L_{II,III})$. The behavior of the function χ_∞ is qualitatively the same as that of the function χ_0 as $kR \to 0$. Bearing this in mind we used the function χ_∞ for estimating the frequency dependence of the factor $(1-\chi)/(1+\chi)$ (Fig. 1).

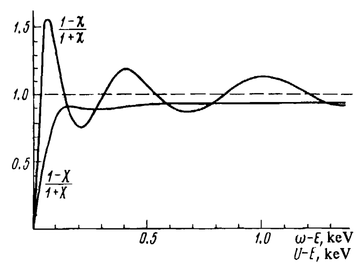

FIG. 1. The interference factor as function of the frequency ω of the incident photon when x-ray fluorescence is excited by a photon beam and as function of the potential U on the x-ray tube when the fluorescence is excited by a secondary method, R=2. The function $(1-X(U))/(1+X(U))$ was calculated for E=0.4 keV.

3. K SPECTRUM

We consider the process (1) in which the intermediate states are states of the cluster with holes in the K shells of the atoms A and A′. We write the wavefunction Ψ_m of the valence shell in the form

$$\Psi_m=\sum_{\alpha=1,2}C_m^{(\alpha)}3P_m^{(\alpha)}+\ldots;\quad m=x,y,z,$$

where we have retained only contributions from orbits which manifest themselves in the K spectrum; the z-axis is along the cluster axis.

Calculations like those for the $L_{II,III}$ spectrum lead to the following result:

$$\frac{d\sigma_m}{do'}=G_m\left[\sum_{\alpha=1,2}\left|\frac{C_m^{(\alpha)}}{Z_\alpha}\right|^2-2C_m^{(1)}C_m^{(2)}\operatorname{Re}\left(\frac{\gamma_m}{Z_1Z_2^*}\right)\right], \tag{24}$$

where

$$G_m=\frac{N_m\alpha^4\omega\omega'^3k}{270(2\pi)^3}(PP_1)^2\int d\hat{k}\Big[(7-\cos^2\theta)\sum_{m'}|A_{1m'}^1|^2$$
$$+(3\cos^2\theta-1)|A_{1m}^1|^2\Big],$$

$$\gamma_m=-\left\{\int d\hat{k}\Big[(7-\cos^2\theta)\sum_{m'}A_{1m'}^1A_{1m'}^{2*}+(3\cos^2\theta-1)A_{1m}^1A_{1m}^{2*}\Big]\right\}$$
$$\times\left\{\int d\hat{k}\Big[(7-\cos^2\theta)\sum_{m'}|A_{1m'}^1|^2+(3\cos^2\theta-1)|A_{1m}^1|^2\right\}^{-1},$$

$$P=\int_0^\infty dr\,r^3R_{1s}R_{3p},\quad P_1=\int_0^b dr\,r^3R_{1s}R_1.$$

In the limiting cases $kR \ll 1$ and $kR \gg 1$ the parameters G_m take on the following values:

$$G_m\to\frac{4N_m}{27\pi}\alpha^4\omega\omega'^3k^3|P\tilde{P}_1fh_1^{(1)}(kR)|^2\eta_m(\theta)\cdot$$
$$\times\left[1+\left|\frac{f}{R}\right|^2+2\frac{\sin(kR)}{kR}\operatorname{Re}\left(f\frac{e^{ikR}}{R}\right)\right]\quad\text{when}\quad kR\ll1,$$
$$G_m\to\frac{4N_m}{27\pi}\alpha^4\omega\omega'^3k|P\tilde{P}_1|^2\qquad\text{when}\quad kR\gg1, \tag{25}$$

and for γ_m we have

$$\gamma_m\to\begin{cases}\chi_0 & \text{when } kR\ll1\\ -\eta_m(\theta)\chi_\infty & \text{when } kR\gg1,\end{cases}$$

$$\eta_m(\theta)=\frac{3}{20}[(7-\cos^2\theta)+\delta_{m,z}(3\cos^2\theta-1)].$$

Here $\tilde{P}_1 = P_1/kb^2[R_1, h_1^{(1)}]$; R_{1s}, R_{3p}, and R_1 are the radial parts of the 1s, 3p, and Ψ_k^+ (see (4)) wavefunctions in which we have dropped the indexes α, as stipulated above; N_m is the number of electrons in the valence shell Ψ_m.

As in the $L_{II,III}$ spectrum the interference becomes important near the ionization threshold of the K level ($\gamma_m \to 1$) and it can be neglected as $kR \to \infty$ ($\gamma_m \to 0$). It is clear from Eqs. (24) and (25) that in contrast to $L_{II,III}$ fluorescence the shape of the K spectrum depends not only on the frequency of the incident photon, but also on the angle θ. This is connected with the different angular dependence of the intensities of the transitions from valence levels with σ- and π-symmetries.

We consider the particular case of a symmetrical molecule A-A which has the levels: σ_g, σ_u, π_g, and π_u. We determine the wavefunctions of these levels by the equations:

$$\sigma_i: \ C(\sigma_i)=C_z^{(1)}=\delta_i C_z^{(2)}; \qquad N(\sigma_i)=0\div 2,$$

$$\pi_i: \ C(\pi_i)=C_{x(y)}^{(1)}=\delta_i C_{x(y)}^{(2)}; \qquad N(\pi_i)=0\div 4;$$

$$\delta_i=\begin{cases} -1, \text{ if } & i=g \\ +1, \text{ if } & i=u. \end{cases}$$

Using Eqs. (24) and (25) we get the following expressions for the relative intensities of the K spectrum

$$\frac{I(\sigma_u)}{I(\sigma_g)}=\frac{N(\sigma_u)}{N(\sigma_g)}\left(\frac{C(\sigma_u)}{C(\sigma_g)}\right)^2\left(\frac{1-\gamma_\sigma}{1+\gamma_\sigma}\right). \tag{26}$$

We obtain the ratio $I(\pi_u)/I(\pi_g)$ from (26) by the substitution $\sigma \to \pi$ (here and henceforth $\gamma_\sigma \equiv \gamma_z$, $\gamma_\pi \equiv \gamma_{x(y)}$, see (25)):

$$I(\pi_i)/I(\sigma_j)=\Lambda(\theta)\xi_{i,j}, \tag{27}$$

$$\Lambda(\theta)\to 2\left(\frac{3+\cos^2\theta}{7-\cos^2\theta}\right) \text{ when } kR\ll 1,$$

$$\Lambda(\theta)\to 1 \text{ when } kR\gg 1,$$

$$\xi_{i,j}=\frac{N(\pi_i)}{N(\sigma_j)}\left(\frac{C(\pi_i)}{C(\sigma_j)}\right)^2\left(\frac{1-\delta_i\gamma_\pi}{1-\delta_j\gamma_\sigma}\right).$$

It is clear from Eqs. (26) and (27) that the effect of the frequency of the exciting photon on the shape of the K spectrum remains basically the same as for $L_{II,III}$ fluorescence. The dependence on the scattering angle is determined by two parameters: γ_m and $\Lambda(\theta)$ (Fig. 2). In contrast to γ_m the function $\Lambda(\theta)$ is not connected with interference. The angular dependence of the parameter $\Lambda(\theta)$ is caused by the non-sphericity of the solution Ψ_k^+ and the difference in symmetry of the σ- and π-levels. The asymmetry of Ψ_k^+ vanishes only in the high-energy limit, and as a result of this $\Lambda(\theta) \to 1$. In the general case (not only symmetrical molecules) there will also occur a connection between the shape of the emission spectrum and the scattering angle θ due to the nonsphericity of Ψ_k^+. One notes easily that close to the ionization threshold of the K or $L_{II,III}$ levels both the frequency- and the angular dependence of the relative intensities give direct information about the symmetry of the corresponding valence levels.

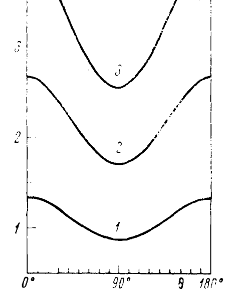

FIG. 2. The intensity ratio $I(\pi_i)/I(\sigma_j)$ as function of the scattering angle of the photon near the ionization threshold of the K level. Curves 1: $\xi_{i,j}=1$; 2: $\xi_{i,j}=2$; 3: $\xi_{i,j}=3$.

4. EXCITATION OF FLUORESCENCE BY A NONMONOCHROMATIC PHOTON BEAM

In the general case the intensity of the emission radiation is described by the formula

$$I(\omega')\sim\iint d\omega\, d^3r\frac{d\sigma}{do'}I_\omega \exp[-\sigma_{\text{abs}}(\omega)\rho h-\sigma_{\text{abs}}(\omega')\rho h'].$$

Here I_ω is the spectral intensity of the exciting radiation; σ_{abs} is the cross-section for the absorption of the photon by a sample of density ρ; h and h′ are the distances which the exciting photon traverses in the sample up to the point **r** and which the emitted photon traverses from the point **r**; $\int d^3r$ is an integral over the volume of the sample.

Neglecting absorption ($\sigma_{\text{abs}}\rho h \ll 1$) we get

$$I(\omega')\sim\int d\omega\frac{d\sigma}{do'}I_\omega.$$

For an x-ray tube with a thick anode we have the following empirical formula:[6]

$$I_\omega\sim[Z(U-\omega)+0.038Z^2],$$

where Z is the atomic number of the anode substance, U the potential on the tube in at.un.. Approximating the absorption cross-section of the nl subshell of an atom by the formula $\sigma_{nl} \sim \omega^{-(l+7/2)}$ we note that for a description of the shape of the spectrum it is sufficient to replace in Eqs. (22), (26), and (27) for the relative intensities χ by X(U), where

$$X(U)=\int_E^U d\omega\, I_\omega\omega^{-(l+7/2)}\chi \bigg/ \int_E^U d\omega\, I_\omega\omega^{-(l+7/2)},$$

U is the ionization threshold of the nl level.

To estimate the way the shape of the spectrum depends on the potential on the tube we take the function χ_∞ for the function χ. We give in Fig. 1 the U-dependence of the quantity $(1-X)/(1+X)$ for a copper anode. It is clear that the spectral intensity I_ω smoothes out the oscillations in the interference term.

The dependence of the shape of the spectrum on the way the excitation takes place can be studied not only through fluorescence, but also by primary methods, also varying the potential on the tube. For a direct verification of the effects considered in the present paper it is desirable to use a monochromatic photon beam. As monochromatization of the beam appreciably decreases the intensity of the exciting radiation it is necessary to have a sufficiently powerful source of x-rays. Charged particle accelerators are at present such sources.[7,8]

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