field. For molecules for which the formation of the quasicontinuum involves the participation of not less than four degrees of freedom, further accumulation of energy is described by the kinetic equation. The rate at which the energy accumulates is very dependent both on the density of vibrational states in the neighborhood of the excited levels and on the magnitudes of the dipole moments of the corresponding transitions. The removal of degeneracy and Fermi resonances lead to the formation of bands of relatively well-allowed transitions in the quasicontinuum. Efficient accumulation of energy in the quasicontinuum requires a large red shift of the laser field frequency relative to the resonance 0–1 transition.

We note in conclusion that the above analysis refers to two stages of collisionless dissociation of molecules, namely, traversal of the low-lying levels and the accumulation of energy in the band structure of the quasicontinuum of high-lying vibrational states. The process of only the dissociation of highly excited polyatomic molecules requires a separate analysis.

We also note that problems connected with the effect of laser radiation on the vibrational degrees of freedom of molecules were first discussed by Askar'yan[16] and Bunkin et al.[17]

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Resonance fluorescence in x-ray *K* spectra

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An analysis is made of the special features of the characteristic *K* x-ray fluorescence spectrum when the excitation is provided by an emission line of some element B, and the energy of this line coincides with the *K* absorption edge (lies within the natural width of the edge) of the investigated element A. It is shown that the *K* x-ray emission lines of the elements A are shifted toward lower energies and have profiles different from the usual Breit–Wigner shape. This effect has to be allowed for in precision measurements of the x-ray line energies and in studies of other effects associated with small line shifts (such as the chemical and isotopic shifts).

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INTRODUCTION

The processes associated with the excitation of an atom by electromagnetic radiation of frequency close to the resonance frequency of the atom and with the sub- sequent emission of light are well known in optics and are called resonance fluorescence.[1] A characteristic feature of these processes is that the profile and width of the emission (fluorescence) line depend strongly on the distribution of the primary radiation.

Conditions may be established also for the observation of a similar effect in the x-ray range if the energy of the excitation line coincides with the energy of the absorption edge within the natural width of the latter. We can easily see that such cases are not rare. Table I gives examples of coincidences within two natural widths of the K level taken from Bearden's table.[2][1]

We shall now consider the changes which occur under these conditions in the x-ray emission spectra. The distribution of the intensity $I(E)$ in the x-ray line providing the excitation and the distribution of the probability of states of the K level being excited $P(E)$ will be approximated by the Breit-Wigner formula:

$$I(E) = I_0 \frac{\Gamma_1}{2\pi} \frac{\hbar^2}{(E-E_X)^2 + \Gamma_1^2/4}, \tag{1}$$

$$P(E) = P \frac{\Gamma_2}{2\pi} \frac{\hbar^2}{(E-E_K)^2 + \Gamma_2^2/4}, \tag{2}$$

where Γ_1, Γ_2 and E_X, E_K are the natural widths and the most probable energies of the x-ray excitation line and of the K level.

We shall assume that when atomic levels are excited in a solid, the density of the final electron states is independent of the energy (in the range of interest to us) and there is no upper limit to the free-states band. Then, the initial excited state with a hole in the K shell and, consequently, the profile of the K x-ray lines (neglecting the width of the $2p$, $3p$, etc. states) can be written in the form

$$
\begin{aligned}
I'(E) &= P_0 \frac{\Gamma_2}{2\pi} \frac{\hbar^2}{(E-E_K)^2 + \Gamma_2^2/4} \int_E^{\infty} I_0 \frac{\Gamma_1}{2\pi} \frac{\hbar^2}{(E-E_X)^2 + \Gamma_1^2/4} dE \\
&= C \frac{\Gamma_2}{(E-E_K)^2 + \Gamma_2^2/4} \left[\frac{\pi}{2} - \text{arctg} \frac{(E-E_X)}{\Gamma_1/2} \right] = \\
&= C \frac{\Gamma_2}{(E-E_K)^2 + \Gamma_2^2/4} \left[\frac{\pi}{2} - \text{arctg} \frac{(E-E_K-\Delta)}{\Gamma_1/2} \right],
\end{aligned}
\tag{3}
$$

where $\Delta \equiv E_X - E_K$.

These lines are shown in Fig. 1 for various values of the parameter $\Delta (\Gamma_1 \approx \Gamma_2 \equiv \Gamma)$. Far from resonance $(\Delta \gg \Gamma)$ the profile of the emission lines does not differ from the usual Breit-Wigner form. However, on approach to resonance $(|\Delta| \lesssim \Gamma)$ the lines become deformed and shift toward lower energies.

Thus, the effect may be manifested by a long-wavelength shift of the x-ray emission lines and by a change in their profile. The purpose of our investigation is to

FIG. 1. Profile of a resonantly excited emission line plotted for different values of the parameter Δ (I is in units of $2C\pi/\Gamma$).

observe experimentally the energy shifts of the K x-ray lines under resonance fluorescence conditions.

EXPERIMENTS AND THEIR RESULTS

We determined the differences between the energies of the K x-ray lines ($K_{\alpha2}$, $K_{\alpha1}$, and $K_{\beta1}$) of an element A in two samples: in one sample the conditions were favorable for partial resonance excitation of the K level of the element $A(|\Delta| \approx \Gamma)$, but in the other (control) sample the conditions were not favorable for such excitation $(\Delta \gg \Gamma)$. This could be achieved experimentally in a number of ways.

In one of the ways used by us a sample consisting of a mechanical mixture of compounds of the elements A and B was irradiated with the bremsstrahlung from an x-ray tube. Each of the K x-ray lines of the element A was then a superposition of two lines: the normal (unshifted) line excited by the continuous spectrum from the x-ray tube and the shifted line due to the resonance excitation by the appropriate x-ray line of the element B. The resultant shift of such a composite line was governed by the contribution δ of the resonantly excited line to the total intensity of the measured line I_{tot} and by the value of $\Delta \equiv E_X - E_K$.

The energy shifts of the K x-ray lines ($K_{\alpha2}$, $K_{\alpha1}$, and $K_{\beta1}$) were determined by the well-known (see, for example, Sumbaev and Mezentsev[5]) method for determining small energy shifts of x-ray lines with a special diffraction spectrometer. The control sample was also a mechanical mixture (with the same composition) of compounds of two elements: the element A and an element C whose atomic number Z was close to B but whose fluorescence spectrum had no lines of energy close to the K edge of the element A.

Table II gives the experimental values of the shifts of the K lines ($K_{\alpha2}$, $K_{\alpha1}$, and $K_{\beta1}$) of some compounds of Tm and Te mixed with the compounds of Yb and Ba, respectively (the resonance excitation lines were then $K_{\beta1}$

TABLE I. Examples of coincidence of x-ray energies and K absorption edges within two natural K-level widths.

Element	E_K, keV	Resonantly excited x-ray line	E_X, keV	$E_X - E_K$ eV	in terms of Γ of K level
Se	12.6545	$L_{\alpha1}$-Ac	12.652	−2.5	−1.06
Nb	18.9869	L_{γ}-Th	18.9825	−4.4	−1.05
Te	31.8114	$K_{\alpha1}$-Ba	31.8171	+5.7	+0.57
Eu	48.519	$K_{\beta1}$-Gd	48.555	+36.0	+1.74
Gd	50.233	$K_{\beta1}$-Tb	50.229	−4.0	−0.18
Tb	52.002	$K_{\beta1}$-Dy	51.957	−45.0	−1.91
Er	57.487	$K_{\beta1}$-Tm	57.517	+30.0	+1.06
		$K_{\alpha1}$-Ta	57.532	+45.0	+1.6
Tm	59.380	$K_{\beta1}$-Yb	59.370	−10.0	−0.34
Yb	61.30	$K_{\beta1}$-Lu	61.283	−17.0	−0.54
Lu	63.31	$K_{\alpha1}$-Ir	63.2867	−23.3	−0.7

TABLE II. Energy shifts of K x-ray lines of some compounds of Tm and Te due to resonance fluorescence effect.

Samples compared		$E = E_{AB} - E_{AC}$, meV		
$A + B$	$A + C$	$K_{\alpha2}$	$K_{\alpha1}$	$K_{\beta1}$
10% Tm$_2$O$_3$ + 90% Yb$_2$O$_3$	10% Tm$_2$O$_3$ + 90% Lu$_2$O$_3$	−457±75	−713±92	−540±126
10% H$_6$TeO$_6$ + 90% BaCO$_3$	10% H$_6$TeO$_6$ + 90% CeO$_2$	−365±17	−365±20	−434±29
10% TeO$_3$ + 90% BaCO$_3$	10% TeO$_3$ + 90% CeO$_2$		−372±13	
10% TeO$_2$ + 90% BaCO$_3$	10% TeO$_2$ + 90% CeO$_2$		−278±14	
10% Te$_{\text{met}}$+ 90% BaCO$_3$	10% Te$_{\text{met}}$+ 90% CeO$_2$		−234±12	

of Yb and K_{α_2} of Ba) (see Table I). It is evident from Table II that all the investigated lines are shifted toward lower energies. The shifts are approximately the same for all the investigated K lines (K_{α_2}, K_{α_1}, and K_{β_1}) but depend on the chemical composition of the substance.

The constancy of the shifts for the different (K_{α_2}, K_{α_1}, and K_{β_1}) K lines is characteristic of the effect due to the special features of the excitation of the common (to all of them) initial state with a hole in the K shell. However, when the chemical composition is altered, the energy of the K edge changes (see, for example, Siegbahn's book[6]) and also, of course, the value of Δ which governs the measured effect. We can find Δ experimentally by recording simultaneously the K absorption edges of the investigated compounds and the profiles of the resonantly excited x-ray lines.

The method of determination of Δ is demonstrated in Fig. 2 which gives, by way of example, the K absorption edges of metallic tellurium Te$_{met}$ and of TeO$_3$, as well as the profile of the K_{α_2} line of Ba. We used similar graphs to determine the values of Δ assuming that the K-edge energy corresponded to half the total change in the absorption in the K edge.

Figure 3 gives the dependence of the experimental shifts of the K_{α_1} lines of Te (points) in some compounds (TeO$_3$, H$_6$TeO$_6$, TeO$_2$, and Te$_{met}$) on Δ. The continuous curve in Fig. 3 gives the same dependence obtained by the following calculation procedure. A line with the Breit-Wigner profile and of width Γ equal to the natural width of the K_{α_1} line of Te is combined with a fraction δ of a line whose position and profile are given by Eq. (3) for a particular value of Δ. Then, the usual program for the calculation of small energy shifts of x-ray lines (see, for example, Sumbaev and Mezentsev[7]) is used to find the shift ΔE of the new composite line relative to the initial Breit-Wigner line. The value of δ is deduced from the condition for the agreement between the calculated and experimental shifts in the case of TeO$_3$. For TeO$_3$ this quantity is 0.045. It is clear from Fig. 3 that the experimental dependence is in good agreement with the calculations.

In the resonance excitation of the K spectrum described above the contribution of the resonantly excited lines to the total intensity of the K lines represents a few percent and the K-line shifts are correspondingly small. Much greater shifts result in a different method
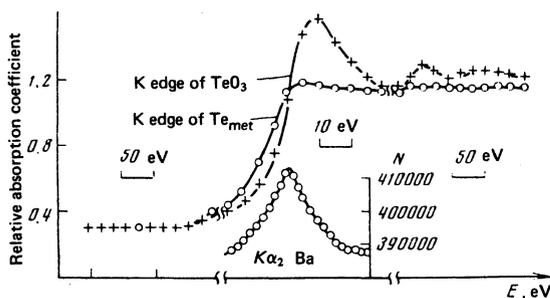
FIG. 3. Dependences of the energy shifts of the K_{α_1} line of Te on the parameter Δ. The continuous curve represents calculations and the points are the experimental values.

which we used for the resonance excitation of the K spectrum of Tm (Fig. 4).

Radiation emitted by the anticathode of an x-ray tube A reached a thick (~3 mm) plate of metallic Yb oriented at an angle ~45° in a lead collimator. The fluorescence of Yb passed through an aperture in this collimator and reached the investigated Tm sample (Tm$_2$O$_3$ or TmCl$_2$), exciting the fluorescence spectrum of Tm. A crystal diffraction spectrometer was used to measure the difference[2] between the energies of the K_{α_1} line of Tm excited in this way and the K_{α_2} line of Yb used as the control. This difference $\Delta E_1 = E^*_{K_{\alpha_1}-Tm} - E_{K_{\alpha_2}-Yb}$ was compared with a similar difference $\Delta E_2 = E_{K_{\alpha_1}-TM} - E_{K_{\alpha_2}-Yb}$, obtained as a result of excitation of the K_{α_1} line of Tm by the usual nonresonance method (employing bremsstrahlung from an x-ray tube). Hence, we found the energy shift of the K_{α_1} line of Tm, $\Delta E_{K_{\alpha_1}-Tm}$, in the case of partial resonant excitation:

$$\Delta E_{K_{\alpha_1}-Tm} = E^*_{K_{\alpha_1}-Tm} - E_{K_{\alpha_1}-Tm} = \Delta E_1 - \Delta E_2. \quad (4)$$

The experimental value of $\Delta E_{K_{\alpha_1}-Tm}$ was found to be -5.9 ± 1.0 eV for TmCl$_2$ and -8.1 ± 1.4 eV for Tm$_2$O$_3$.

A control experiment in which the Yb plate was replaced with a plate of Lu, whose fluorescence spectrum did not have any line in resonance with the K spectrum of Tm, gave $\Delta E_{K_{\alpha_1}-Tm} = +1.6 \pm 0.8$ eV.

The expected value of the shift of the K_{α_1} line of Tm could be calculated when the values of δ and Δ were known (see above). The method for the determination of Δ was the same as in the preceding experiment. The value of δ was found semiempirically. In fact, in this method of excitation the K_{α_1} line of Tm was a superposition of two lines: the shifted line due to the reso-

FIG. 2. Profiles of the K absorption edge of Te$_{met}$ and TeO$_3$ and of the K_{α_2} line of Ba.
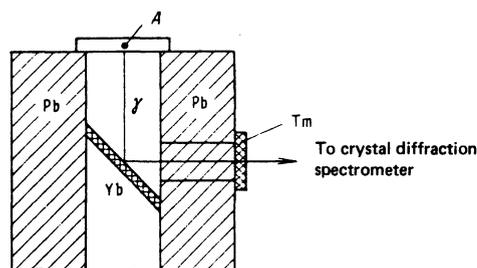
FIG. 4. Arrangement used in the second experiment on detection of resonance fluorescence in the K spectrum of Tm.

nant excitation of the K_{β_1} line of Yb and the normal unshifted line excited by the hard scattered radiation and by the $K_{\beta_{2,4}}$ and K_{β_5} lines of Yb. The proportion of the K_{α_1} line of Tm excited by the scattered radiation was determined experimentally: for this purpose a Yb plate was replaced with a Gd plate and the intensity of the K_{α_1} line of Tm was determined without a change in geometry. Since the fluorescence spectrum of Gd did not have any lines capable of exciting the K spectrum of Tm, the intensity of the K_{α_1} line of Tm could be attributed entirely to the excitation by the scattered radiation. The proportion of the intensity of the K_{α_1} line of Tm due to the excitation by the $K_{\beta_{2,4}}$ and K_{β_5} lines was calculated using the relative intensities of the $K_{\beta_{2,3}}$, K_{β_5}, and K_{β_1} lines of Yb. The value of δ obtained in this way was 0.27 ± 0.09. Then, Eq. (3) was used to calculate the profile of the resonantly excited line. This line was combined with a nonresonantly excited line with the Breit-Wigner profile in the experimentally determined ratio δ and the shift[3] of such a composite line relative to the nonresonance line was determined. The calculated shift was -4.9 eV for $TmCl_2$ and -5.3 eV for Tm_2O_3, which was in satisfactory agreement with the experimental results bearing in mind the experimental error and inaccuracy in the determination of δ.

CONCLUSIONS

The resonance fluorescence in the K x-ray emission spectra described above may result in considerable shifts of the x-ray lines.

The phenomenon of resonance fluorescence has to be allowed for in precision measurements of the x-ray line energies. In fact, the fluorescence spectrum of the anticathode material is always present in the excitation spectrum provided by an x-ray tube. If the energy of one of the lines in the fluorescence spectrum is close to the energy of the corresponding absorption edge of the investigated x-ray transitions, the x-ray lines become shifted toward lower energies. For example, if we consider the most widely used anticathode materials, we find that the K_{α_1} line of W can excite resonantly the K edge of Tm, and there are similar situations for other materials: L_{α_2} line of W and K edge of Ni, K_{α_1} line of Ag and K edge of Ru, K_{α_1} line of Cu and L_1 edge of Eu, $K_{\beta_{1,3}}$ line of Cu and L_{II} edge of Ho, $K_{\beta_{1,3}}$ line of Ni and

L_{II} edge of Tb, and so on.

The x-ray line energies are known to depend on the crystallochemical composition of a given substance (chemical shift) and on the isotropic composition (isotopic shift). Investigations of the x-ray line shifts give important information on the electron structure of solids and the charge radii of nuclei (see, for example, Boehm's review[8]). When systems formed from two or more elements are investigated by this method, allowance has to be made for the possibility of resonance fluorescence, which may result in apparent line shifts fully comparable with those being investigated.

Finally, a very similar shift may occur also in the case of accidental coincidence with the K-edge energy of one of the intense γ lines in a radioactive isotope.

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1) The natural widths of the K levels were deduced from the calculated total radiative widths [3] and the fluorescence yields for the K shell.[4]

2) The line position was in this case regarded as the midpoint of the line width at midamplitude.

3) See footnote 2.

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