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ABSTRACT

The intensity distribution of K x-ray lines excited in ion-atom collisions is formulated for very asymmetric collisions. At high x-ray energies, the distribution falls off as the x-ray energy to the minus eleventh power while around the line center, it is approximately Lorentzian. For nearly symmetric collisions, our formula describes MO x-rays and no purely separated atom Lorentzian is present.

In Macek and Briggs' (1974) dynamical theory of molecular orbital (MO) x rays, the intensity of continuum x rays observed far from the separated atom (SA) lines, is shown to come from contributions from the natural Lorentzian line shape of the SA x rays and a part which is due to MO x rays. The problem with this theory is that in many cases, the natural Lorentzian gives a yield as large or larger than the yield of continuum x rays experimentally observed far from the line center. In this communication, we show that for symmetric collisions (where the atomic number of the projectile equals that of the target) the yield of continuum x rays comes from a part which is due to one-collision MO x rays and a part which is due to two-collision MO x rays. No SA Lorentzian contribution is present. Even in very asymmetric systems where no MO x rays are present, the distribution, though near Lorentzian at the line center, falls to zero much more rapidly at high photon energies.

Following Macek and Briggs (1974) and Weisskopf (1935), we find the line shape by Fourier analysis:

$$D_c(\omega_x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(t) D\big(R(t)\big)\, e^{i\int_0^t \omega_x - \omega_{KL}(t')dt'}\, dt \qquad (1)$$

where $D\big(R(t)\big)$ is the dipole velocity matrix element, $\omega_{KL}(t) = \omega_{KL}^0 + \Delta\omega(t)$ is the time dependent energy difference between the 2p and 1s (or $2p\pi$ and $1s\sigma$) states. In this paper we restrict ourselves to K and L transitions, but extension to other transitions is straightforward. The amplitude A(t) is for having excited a K electron into a higher bound or continuum state and the resulting frequency dependent dipole, abbreviated as $D_c(\omega)$, is a function of the higher state quantum numbers and energy, of impact parameter b, and ion energy E_1. The cross section in atomic units for x-ray emission is therefore the integral over impact parameter and sum over higher states:

$$\frac{d\sigma}{dE_x}(E_x,E_1) = \frac{4\alpha^3}{3}\,\omega_x\, S\int 2\pi b db\;|D_c(\omega_x)|^2 \qquad (2)$$

where $\alpha = 1/137$ and S stands for the sum over higher states. It is easy to show that a Lorentzian line shape is obtained when $\omega_{KL}(t)$ and $D(t)$ are time independent and:

$$A(t) = \begin{cases} 0 & t<0 \\ e^{-\lambda t/2} & t>0 \end{cases}$$

where λ is the total transition probability. To treat the more general case, we replace $A(t)$ by $a(t)\exp(-\lambda t/2)$ where $a(t)$ expresses the amplitude for having excited a K electron through some collision process, and $\exp(-\lambda t/2)$ expresses the decay of the vacancy by radiation and emission of Auger electrons. In a two state, weak coupling approximation, $a(t)$ is written:

$$a_3(t) = \int_{-\infty}^{t} V_{K3}(t)\; e^{-i\int_{-\infty}^{t}\omega_K(t')-\omega_3(t')dt'}\,dt \qquad (3)$$

where $V_{K3}(t)$ couples the 1s state to a continuum or some other state denoted 3. To evaluate (1) we consider $t=0$ to be the time at the distance of closest approach in the first collision. Prior to $t=0$, no other collisions have occurred (the ion has just entered the target), but for $t>0$, we recognize that further collisions having non-zero $A(t)$ from the first collision can occur. We integrate from $-\infty$ to T and from T to ∞ where T is some time after the first collision when $V(T)$ and $\Delta\omega(T)$ can be considered negligibly small. Partially integrating, we obtain:

$$\sqrt{2\pi}\,D_c(\omega_x) = [i(\omega_x-\omega_{KL}^0)-\lambda/2]^{-1}\times\left[\int_{-\infty}^{T}(\dot{a}D+\dot{D}a-i\Delta\omega aD)\,e^{i\int_0^t(\omega_x-\omega_{KL}^0-\Delta\omega(t')+i\lambda/2)dt'}\,dt\right.$$

$$\left.+\;a(\infty)\int_{T}^{\infty}(\dot{D}-i\Delta\omega D)\,e^{i\int_0^t(\omega_x-\omega_{KL}^0-\Delta\omega(t')+i\lambda/2)dt'}\,dt\right] \qquad (4)$$

where a, $\dot{a}$, D, $\dot{D} = dD/dt$, and $\Delta\omega$ are all functions of time. Unlike Macek and Briggs' analogous formula (Eq. 9, 1974) no pure Lorentzian contribution such as $D(0)[i(\omega_x - \omega_{KL}^0) - \lambda/2]^{-1}$ is apparent here. In the literature on MO x-rays (Meyerhof et al, 1974), one-collision (where vacancies are "created" and then radiate in the same collision) and two-collision mechanisms (where vacancies are brought into the collision having been formed in some prior encounter) for the formation of MO x rays have been theorized. The first term here gives one-collision MO x rays; the second effectively gives Macek and Briggs' expression for two-collision MO x rays multiplied by the amplitude for having created a vacancy.

The SA x ray line is in the $\dot{a}D$ term in this expression. To see this, let $\Delta\omega$ and $\dot{D}$ be zero which should be the case in systems where the projectile atomic number (Z_1) is much less than the target atomic number (Z_2). In such a system, only the SA line should appear. Equation (4) reduces to:

$$\sqrt{2\pi}\, D_c(\omega_x) = D[i(\omega_x - \omega_{KL}^0) - \lambda/2]^{-1} \int_{-\infty}^{T} V_{K3}\, e^{i(\omega_x + \omega_L - \omega_3)t - \lambda/2t}\, dt \qquad (5)$$

Over the range of integration -T to +T [since $V(t < -T)$ is zero], $\lambda t/2$ can be neglected. Now consider what happens when ω_x approaches ω_{KL}. We obtain:

$$\sqrt{2\pi}\, D_c(\omega_x) = D[i(\omega_x - \omega_{KL}^0) - \lambda/2]^{-1} \int_{-T}^{T} V_{K3}\, e^{i(\omega_K - \omega_3)t}\, dt \qquad (6)$$

where the integral is simply $a_3(\infty)$. The square of $D_c(\omega_x)$ summed over higher states gives a Lorentzian times the probability of creating a vacancy.

Far from the line center, however, this term does not predict a Lorentzian line shape. To see this for the case where $Z_1 << Z_2$ and no MO x rays are present, we can use the Semi-Classical Approximation (SCA) (Bang and Hansteen, 1959; Choi and Merzbacher, 1969) to evaluate (5). Again $\dot{D}$, $\Delta\omega$, and $\lambda t/2$ are neglected. Here we specialize state 3 to include only $L = 0$ states in the continuum. It is known that excitation to bound states is generally negligible when $Z_1 << Z_2$ (Merzbacher and Lewis, 1955). The probability of exciting $L = 1$ and 2 states becomes important at high v_1/v_K where v_1 is the projectile velocity and v_K is the K electron velocity, but since we will be calculating the x ray cross section per K vacancy (calculated making the same approximation), errors here will tend to cancel out. The cross section per K vacancy is defined as

$$\frac{1}{\sigma}\,\frac{d\sigma}{dE_x} = \frac{4/3\alpha^3\,\omega_x|D|^2/2\pi}{(\omega_x - \omega_{KL}^0)^2 + \lambda^2/4}\;\frac{\int_0^\infty 2\pi b db \int_0^\infty d\varepsilon |M_p(\omega_x + \omega_L - \varepsilon)|^2}{\int_0^\infty 2\pi b db \int_0^\infty d\varepsilon |M_p(\omega_K - \varepsilon)|^2} \qquad (7)$$

where ε is the continuum energy, α is the fine structure constant, and

$$M_p(\omega) = \int_{-\infty}^{\infty} V_{K\varepsilon}(t)\, e^{i\omega t}\, dt \quad \text{with} \quad V_{K\varepsilon}(t) = Z_1 e^2 \int d^3\vec{r}\; \psi_\varepsilon^* |\vec{r} - \vec{R}(t)|^{-1} \psi_{1s} \qquad (8)$$

T can be taken to be infinity because $V(t < T)$ and $V(t > T)$ is zero if only single collisions are considered. We restrict ourselves to low energy collisions where $(v_1/v_K)^2 << 1$. The integrals can be evaluated obtaining Huus' approximation (Bang and Hansteen, 1959)

$$\int_0^\infty 2\pi b db |M_p(\omega)|^2 = \frac{1}{Z_S^2 Ry}\,\frac{d\sigma}{dW} \cong \frac{2^{20}\pi}{5}\,\frac{Z_1^2 a_K^2}{Z_2^2}\left(\frac{v_1}{v_K}\right)^4 \frac{1}{W^{10}} \qquad (9)$$

where $W(\omega) = \hbar\omega/(Z_S^2 Ry)$, Z_S is the screened target charge, and a_K is the target

K shell radius. This is integrated over ε to obtain:

$$\frac{1}{\sigma}\frac{d\sigma}{dE_x} = \frac{\lambda_x/2\pi}{(\omega_x-\omega_{KL}^0)^2+\lambda^2/4}\left(\frac{\omega_K}{\omega_x+\omega_L}\right)^9 \tag{9}$$

where λ_x is the radiative transition probability. Very close to the line center, we again have a Lorentzian multiplied by the probability (or cross section) for making K vacancies. Far from the line center, at high x-ray energies, the intensity drops off as ω_x^{-11}. Note that in general (10) could also be written as:

$$\frac{1}{\sigma}\frac{d\sigma}{dE_x} = \frac{\lambda_x/2\pi}{(\omega_x-\omega_{KL}^{\circ})^2+\frac{\lambda^2}{4}}\;\frac{\sigma(E_1, U=E_x+U_L)}{\sigma(E_1, U=U_K)} \tag{11}$$

so scaling law curves (e.g., Merzbacher and Lewis, 1955) can be used to predict the entire spectral intensity.

In Fig. 1 we plot this intensity for 33 MeV O + Zr and compare with the experimental intensity (Anholt and Saylor) and a natural Lorentzian line shape. There, the SCA theory nearly holds; it predicts a K vacancy cross section of 160 barns compared to 130 ± 30 measured. It is not known whether the continuum intensity observed in this experiment is due to MO x rays ($\dot{D}$ and $\Delta\omega$ are not quite negligible), bremsstrahlung, or some other effect. Clearly our theory of the SA line lies much lower than experiment.

As ω_x approaches zero (10) predicts that the yield for 0 + Zr would approach the ratio of the Zr K to L binding energy raised to the ninth power. This large factor, 9^9, is an artifact of the neglect of $(v_1/v_K)^2$ terms in (9). When (11) is used, we obtain only about 10^3 times the Lorentzian intensity at $\omega_x = 0$, and the total area of this curve agrees with the area under a pure Lorentzian (unity) to within 3 parts per thousand. For low x-ray energies we have plotted the Eq. (11) results in Fig. 1 and not the results based on (10).

In near symmetric ion-atom collisions, $\Delta\omega$ and $\dot{D}$ are not negligible, and this distribution does not describe the x-ray yield. In those systems we cannot distinguish between the distribution coming from the SA x-rays and the one-collision MO x-ray yield. The continuous (though often oscillatory) buildup and decay of the amplitude governs the x-ray line shape, and in these low energy systems this slow buildup cannot be described by a step function.

In conclusion, it has been shown that while a nearly Lorentzian line shape is obtained around the center of x-ray lines coming from collisionally excited K vacancies, the distribution falls off much more rapidly than a Lorentzian in the high energy wings of the line. The Lorentzian line shape comes from the purely artificial assumption that vacancies can be instantaneously created at time $t = 0$. When both the creation and the decay of the vacancy is considered, the resulting photon distribution can be very different.

REFERENCES

R. Anholt and T. K. Saylor (to be published).

J. Bang and J. M. Hansteen, (1959) Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 31, #13, 1-42.

B. Choi and E. Merzbacher, (1969) Phys. Rev. 177, 233-239.

J. H. Macek and J. S. Briggs, (1974), J. Phys. B7, 1312-1322.

E. Merzbacher and H. W. Lewis, (1955) Encyclopedia of Physics, ed. by S. Flügge (Springer-Verlag, Berlin), 34, 166-192.

W. E. Meyerhof, T. K. Saylor, S. M. Lazarus, A. Little, B. B. Triplett, L. F. Chase, Jr., and R. Anholt, (1974) Phys. Rev. Letters 32, 1279.

V. Weisskopf, (1933) Phys. Zeit 34, 1-24.

FIGURE CAPTION

Fig. 1 Photons/keV/Zr K vacancy for 33 MeV O + Zr collisions. Dashed curve gives experimentally observed continuum yield. Dash-dot gives natural Lorentzian line shape; solid gives shape calculated in present work. We have ignored the Kβ lines here, and the Kα line has been shifted to an average energy.

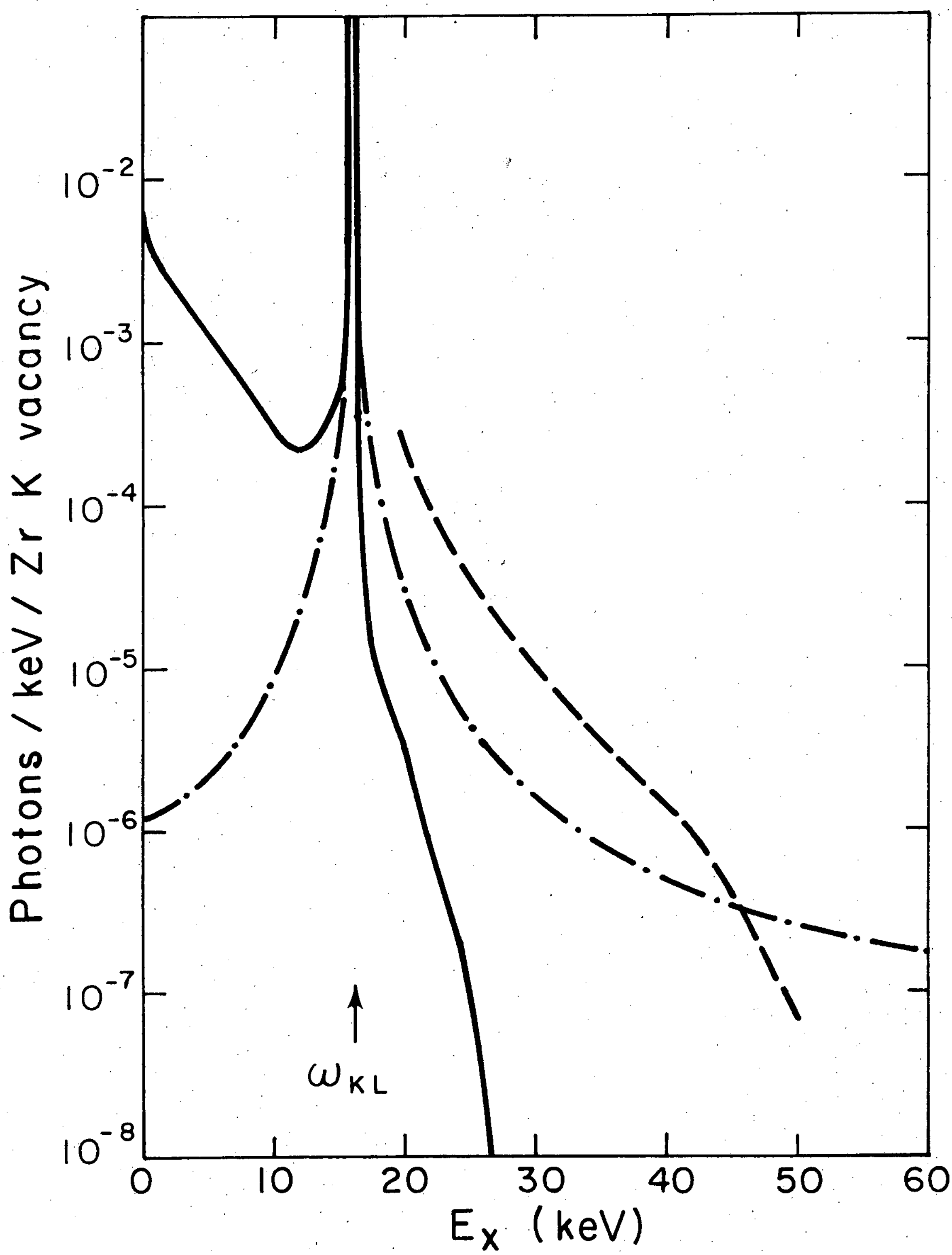

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Fig. 1