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Two-Photon X-Ray Emission from Inner-Shell Transitions

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(Received 1 July 1982)

Two-photon emission of x-rays from inner-shell transitions has been observed for the first time. The continuous $K^{-1} \to L^{-1}$ two-photon spectrum of Mo appears to be in excellent agreement with a detailed theoretical analysis. This is not the case for transitions from higher shells.

PACS numbers: 32.80.Kf, 32.30.Rj

The lifetimes of metastable hydrogenic and heliumlike systems have been studied extensively, especially since the pioneering work of Lipeles, Novick, and Tolk[1] and the classic studies of Marrus and Schmieder.[2] Such metastable states decay either by two-photon electric dipole or by one-photon magnetic dipole or magnetic quadruple transitions. Here, we report the first measurements of two-photon x-ray emission from one-electron inner-shell transitions. In a many-electron atom, K-shell hole states are, of course, not metastable, and are filled almost immediately ($< 10^{-15}$ sec) by strong one-photon or Auger transitions. With much smaller probability, a K-shell vacancy may also be filled by a one-electron two-photon process, and the study of such transitions yields a new, rich, multiphoton inner-shell spectroscopy.[3,4]

In examining metastable states in hydrogenic and heliumlike ionic beams,[1,2] the background due to strongly allowed one-photon transitions is easily eliminated, since the intensities of these decay almost immediately leaving a clean metastable system. In the study of two-photon inner-shell transitions in solids, however, such as in the present study of metallic Mo, no simple isolation of the desired process is possible, and the major experimental problem is suppression of spurious effects due to the intense one-photon $K\alpha$ and $K\beta$ background.

As in previous studies,[1,2] we detect both emitted photons in fast time coincidence. For a pair of identical detectors, the expected ratio of the two-photon to the one-photon count rate may be written $N^{(2)}/N^{(1)} \sim 10^{-8} Z^2 (\Delta\Omega/4\pi)$, where $\Delta\Omega$ is the collection solid angle, and hydrogenic results[5] for the $2p \to 1s$ one-photon and the $2s \to 1s$ two-photon transitions have been employed. Although we use a moderately heavy element ($Z = 42$) and employ large-area, nearly 100% efficient Si(Li) energy-dispersive detectors for which $\Delta\Omega > 1$ sr, nonetheless, $N^{(2)}/N^{(1)}$ is still only $\sim 2 \times 10^{-6}$. Under such circumstances great care must be exercised if artifacts are to be avoided.

We have found that when the detectors are illuminated by the large one-photon K-line flux of Mo, they will, if permitted, talk to each other via a mechanism in which an electron freed in one detector crystal by the primary photoionization event of the detection process generates bremsstrahlung which reaches the second detector. This produces a coincidence event which closely mimics a true two-photon process in that the resulting energy spectrum is continuous and nearly flat, and the energies from the two detectors sum to the expected $K^{-1} \to L^{-1}$ transition energy. This problem was avoided by a proper choice of experimental geometry and the insertion of appropriate masks, the efficacy of which was directly verified by exhaustive experimental tests.

Our samples are measured in vacuum, and take the form of ~100-nm Mo films supported by minimal-area 6-μm Mylar foils. This results in very small losses due to self-absorption in the sample, an important consideration since both emitted photons must be detected for a two-photon event to be recorded. The use of these very thin samples also yields the following important additional advantages. (i) The detectors are effectively prevented from talking to each other *indirectly* via Compton scattering in the sample. (ii) Double Compton scattering[6] of the incident Ag $K\alpha$ radiation employed for K-shell vacancy production is reduced to negligible proportions. (iii) Bremsstrahlung cascades due to photoionized electrons are effectively eliminated. All of the above was verified by extensive experimental tests and supported by detailed theoretical analysis.

Although the two-photon spectrum falls in an intrinsically empty spectral window, incomplete collection of the charge produced in the detectors by the large one-photon K-line flux yields a spurious background which is about four orders of magnitude larger than the two-photon signal. This background is largely eliminated by the coincidence electronics which yields, *inter alia*, the apparent two-photon energies, E_1 and E_2, of each near coincidence as well as the time separation Δt of the signals from the two detectors. From these data, histograms as a function of Δt are prepared that contain all those events for which the sum $E_1 + E_2$ falls within some narrow energy window centered at a predetermined value. When $E_1 + E_2$ is larger or smaller than a possible transition energy of Mo, then only random one-photon coincidences should be present. For these, all values of Δt are equally probable, implying that the resulting histograms should be flat. On the other hand, when $E_1 + E_2$ equals a possible transition energy, which falls in the 17–20-keV region, then true two-photon events should be present and a peak centered at $\Delta t = 0$ should appear.

In Fig. 1, we present data for a number of different values of $E_1 + E_2$ using a 1-keV energy window. The data clearly peak in the anticipated energy interval. In Fig. 2(a), we plot the area under the two-photon peaks of Fig. 1 as a function of $E_1 + E_2$. Here, the 17.1-keV peak corresponds to $K^{-1} \to L^{-1}$ two-photon transitions, whereas the 19.7-keV peak corresponds to transitions from higher shells.

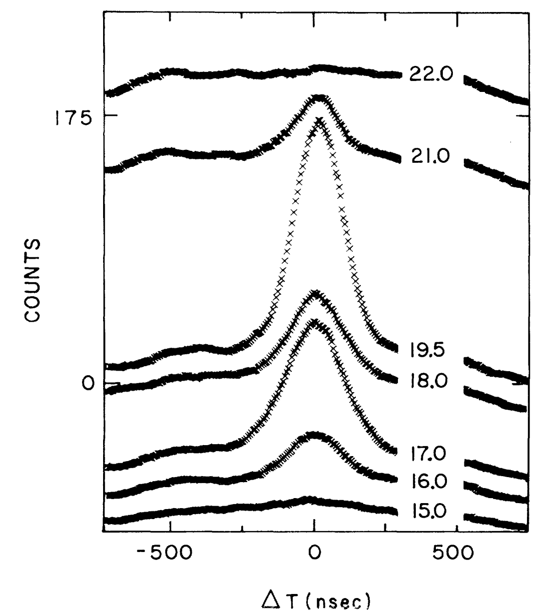

FIG. 1. Number of coincidence events vs Δt for different values of the energy sum $E_1 + E_2$ in the range 15.0–22.0 keV.

The two-photon spectral density may be written[7]

$$\frac{dW^{(2)}}{d\omega} = \frac{2r_0^2\omega_1\omega_2}{\pi c^2} |M(\omega_1,\omega_2)|^2 \left(\frac{\Delta\Omega}{4\pi}\right)^2, \tag{1}$$

where the ω are the photon frequencies, r_0 is the classical electron radius, and $M(\omega_1,\omega_2)$ is the appropriate (dimensionless) matrix element which determines the two-photon spectrum. In Fig. 2(b) we plot measured values of $|M(\omega_1,\omega_2)|$ vs E_1 for $K^{-1} \to L^{-1}$ two-photon transitions corresponding to the 17.1-keV peak of 2(a), and in 2(c) we plot the corresponding data for the 19.7-keV peak. In making these plots, the data were corrected for measured losses and were placed on an absolute intensity scale by normalizing to the measured Mo one-photon K-line flux.

We turn now to a comparison of these data with theory. The two-photon matrix element may be written $M(\omega_1,\omega_2) = M(A^2) + M(\vec{p}\cdot\vec{A})$. Since the product of the photon wave vector k and the K-shell orbital radius a is $ka \sim 0.15 \ll 1$, $M(A^2)$ contributes principally to $mp \rightarrow 1s$ two-photon transitions, while $M(\vec{p}\cdot\vec{A})$ contributes principally to $ms, md \rightarrow 1s$ transitions. In the present experiment, our energy resolution is insufficient to distinguish between transitions from sublevels of a given principal shell, so that only the dominant contribution of each shell need be calculated. The $M(A^2)$ term is easily evaluated and is found to be small both in comparison with experiment and with theoretical estimates of $M(\vec{p}\cdot\vec{A})$. In the "frozen orbital" approximation, $M(\vec{p}\cdot\vec{A})$ may be written for an initial $(1s)^{-1}$ state as[3,4]

$$M(\vec{p}\cdot\vec{A}) = (\hbar/m)(1+P_{1,2})\sum_n \langle ms,md|\hat{u}_1\cdot\nabla|np\rangle\langle np|\hat{u}_2\cdot\nabla|1s\rangle/(\Omega_{np,1s}-\omega_2), \tag{2}$$

where the $\hat{u}$ are unit photon polarization vectors, $\Omega_{np,1s}$ is the transition frequency from the intermediate np state to the $1s$ state, advantage has been taken of the fact that $ka \ll 1$, $P_{1,2}$ permutes the subscripts 1,2, and the final state is either $(ms)^{-1}$ or $(md)^{-1}$. Equation (2) is evaluated as follows: For $n=2$, 3, and 4, we calculate the matrix elements explicitly, using the wave functions of Clementi and Rosetti.[8] For the remaining bound states we make use of the fact that $\Omega_{np,1s}$ and $\Omega_{np,2s}$ are essentially independent of n and we use sum rules to obtain the required matrix elements.[3] For the continuum contribution we take advantage of the fact that the required matrix elements also appear in the expression for

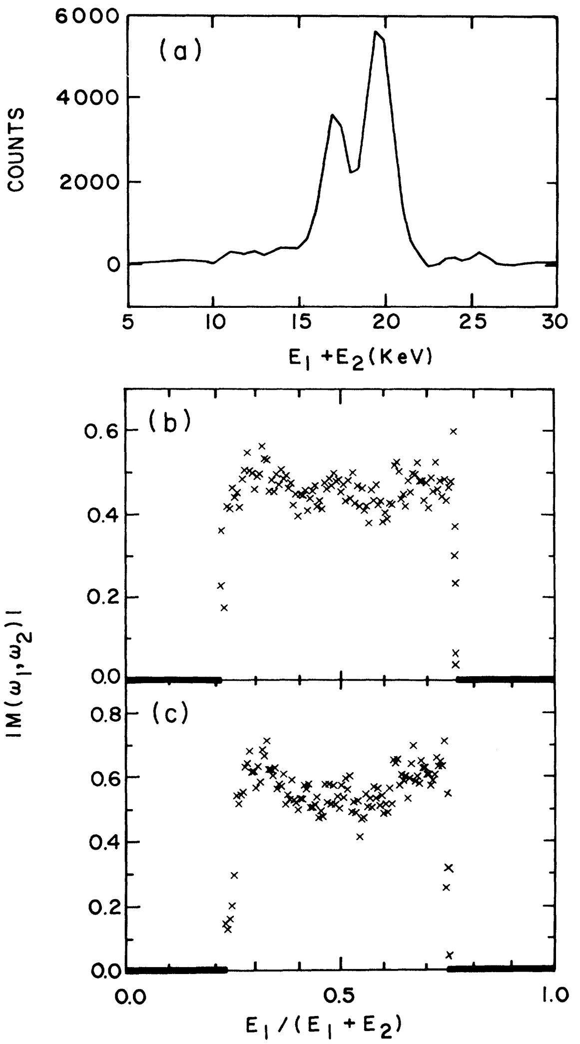

FIG. 2. (a) Total two-photon intensity vs energy sum E_1+E_2. After correction for various losses the 19.7-keV peak is estimated to be about two times the intensity of the 17.1-keV peak. $|M(\omega_1,\omega_2)|$ [Eq. (1)] vs E_1 for events comprising (b) the 17.1-keV and (c) the 19.7-keV peaks of (a). The data are restricted to an ~4–14-keV window by lower- and upper-level discriminators which cut off electronic noise and the Mo K-lines, respectively. Since the energies of the photon pairs are symmetrically distributed about $\frac{1}{2}(E_1+E_2)$ the effective windows are somewhat narrower.

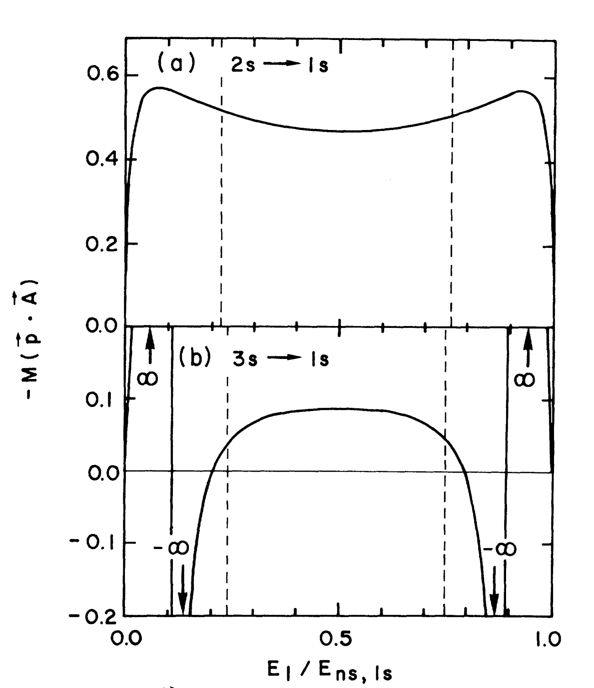

FIG. 3. $M(\vec{p}\cdot\vec{A})$ according to Eq. (2) calculated for (a) the $2s \rightarrow 1s$ and (b) the $3s \rightarrow 1s$ two-photon transitions of Mo. (The broken vertical lines define the ~4–14-keV energy window of Fig. 2.) Note that the calculations in (a) are in excellent quantitative agreement with the measured data [Fig. 2(b)]. The strong peaks in (b) are due to the intermediate $2p$ resonance.

the x-ray photoabsorption coefficients. For these we use experimentally derived empirical formulas.[9] The relative signs of the different terms, when not determinable directly, are obtained from appropriate sum rules.[3] Finally, we test the self-consistency of these procedures with the aid of additional sum rules and find them to be good to ~(5–10)%.

In Fig. 3(a), we plot calculated values of $M(\vec{p}\cdot\vec{A})$ for the $2s \to 1s$ two-photon transition. Since theory and experiment [Fig. 2(b)] are in excellent agreement, the $K^{-1} \to L^{-1}$ two-photon spectrum appears to be well understood. In Fig. 3(b), we plot $M(\vec{p}\cdot\vec{A})$ for the $3s \to 1s$ transition. Note that at the spectral midpoint, $\omega_1 = \omega_2$, the intensity of this transition is calculated to be only 3.5% that of the $2s \to 1s$ transition, so that it makes an apparently negligible contribution to the 19.7-keV peak of Fig. 2(a).

The method described above is not easily implemented for $3d \to 1s$ transitions, for example, principally because of the difficulty in separating out the $3d$ contribution to the x-ray photoabsorption coefficient. Accordingly, we attempt here only an approximate estimate of $M(\vec{p}\cdot\vec{A})$ for this and other higher levels: We note that at the spectral midpoint ω is about half the *smallest* $\Omega_{np,1s}$ of Eq. (2), so that the approximation $\Omega_{np,1s} - \omega \simeq \Omega_{np,1s}$ appears reasonable. Then

$$M(\vec{p}\cdot\vec{A}) \simeq \langle ms, md|(\hat{u}_1\cdot\nabla)(\hat{u}_2\cdot\vec{r}) + (\hat{u}_2\cdot\nabla)(\hat{u}_1\cdot\vec{r})|1s\rangle . \quad (3)$$

This result yields 0.34 and 0.12 for the spectral midpoint of the $2s \to 1s$ and $3s \to 1s$ transitions respectively, while the "true" values (Fig. 3) are 0.47 and 0.088. Thus, Eq. (3) appears to be reliable to better than ± 50%. The only other transition with appreciable intensity is, on this basis, $3d \to 1s$, for which the root square sum over the various d states is 0.20. Accordingly, the intensity of the 19.7-keV peak of Fig. 2(a) is predicted to be about $\frac{1}{4}$ that of the 17.1-keV peak, in contrast to the measured factor of ~2. Whether this large discrepancy is simply due to the inadequacies of our approximations or to some more fundamental cause is presently uncertain.

In summary, we have presented the first measurements of two-photon x-ray emission from inner-shell transitions. For Mo, the $K^{-1} \to L^{-1}$ two-photon spectrum appears to be well understood, but this is not the case for transitions from higher shells. We anticipate that with further advances both in theory and experiment, two-photon x-ray emission measurements will provide a rich new source of information or inner-shell processes.

We are pleased to acknowledge important contributions by Professor Joel I. Gersten.

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