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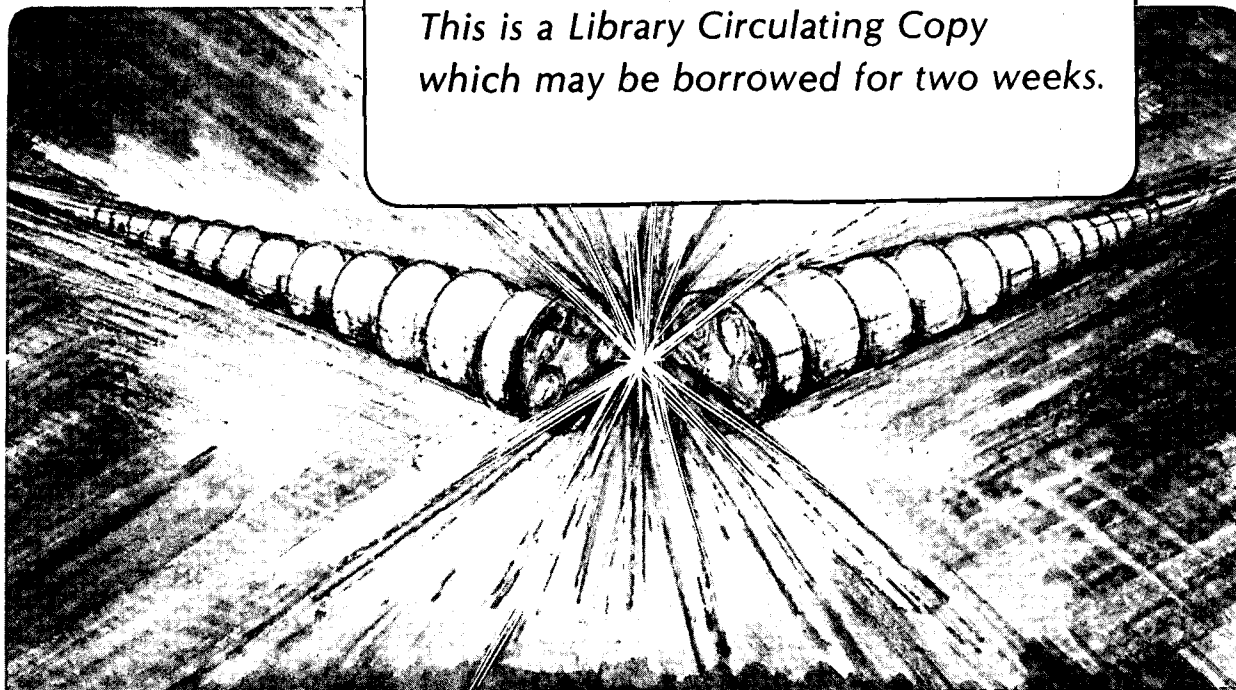
Center for X-Ray Optics

Sub-Threshold Excited Cl Kβ (K-V) X-Ray Fluorescence from CF$_3$Cl Molecule

R.C.C. Perera, P.L. Cowan, D.W. Lindle, and R.E. LaVilla

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DISCLAIMER

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SUB-THRESHOLD EXCITED Cl Kβ (K-V) X-RAY FLUORESCENCE FROM CF_3Cl MOLECULE

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ABSTRACT

With the availability of tuneable synchrotron radiation sources, unoccupied molecular orbits (below vacuum level) can be selectively populated producing highly excited neutral molecules. X-ray fluorescence spectra from molecules were obtained with excitation below the ionization threshold and were observed to have significant intensity changes, absolute and relative energy position shifts and line width changes as compared to fluorescence spectra excited above the threshold. As an example, the Cl Kβ (K-V) emission spectra from CF_3Cl vapor are presented. The energy shifts and intensity changes are explained in terms of perturbation effects due to the presence of an electron in an unoccupied molecular orbital. The narrow line widths obtained in the spectra excited below threshold are explained in terms of the "effective" hole production region in a core state limited by the broadening of the unoccupied level. The change in line widths as a function of below-threshold excitation energy is proposed as a novel technique to study the localized properties and reorganization effects of a hole in a core level.

In the present report, the Cl K absorption spectrum and Cl $K\beta$(K-V) fluorescent spectra of CF_3Cl vapor were measured using the monochromatic synchrotron radiation (band pass about 0.4 eV) from the NBS x-24A beam line [1] at Brookhaven's NSLS. The unoccupied molecular orbitals were selectively populated producing highly excited neutral molecules (i.e., exciton states), resulting in x-ray emission spectra from photon excitation below the ionization threshold [2]. A detailed description of the beamline [1] and the monochromator [3] is given elsewhere. The Cl $K\beta$ (K-V) fluorescent radiation was analyzed by a variable radius curved crystal spectrometer [4] consisting of a silicon (111) crystal of 2d = 6.271 and a linear position-sensitive gas proportional counter [5] filled with a gaseous mixture of Xe (90% vol) and CH_4 (10% vol) at a pressure of 1 atm. The sample gas contained in a cell by .001 in thick beryllium windows at a pressure of 100 torr was located inside the Rowland circle of the spectrometer. The Cl K absorption spectrum was obtained by measuring the incident and transmitted flux with helium-filled ion chambers.

The Cl K absorption spectrum CF_3Cl (gas) is shown in Fig. 1. The energy calibration of the absorption spectrum and, in turn, the monochromator calibration in this energy region were obtained using Cl K absorption of CF_3Cl measured with a laboratory spectrometer. The lowest unoccupied valence molecular orbitals (MOs) of CF_3Cl are $6a_1$, $7a_1$ and 6e in the order of decreasing binding energy (BE). The first discrete absorption maximum at 2823.1 eV results from transition of a chlorine 1s electron to the unoccupied $6a_1$ orbital. Using available Cl $K\beta$ (K-V) emission data [6] and UPS [7] BEs, the Cl 1s energy is estimated to be 2829.6 eV.

The Cl $K\beta$ (K-V) emission spectrum presented in Fig. 2 was excited at 2832.5 eV energy, which is about 3 eV above the Cl 1s ionization threshold energy (K + 3 eV), but below the double vacancy threshold energy. It was shown before [2,8] that such excitation produces no multiple vacancy satellite contributions in this spectral region. The energy calibration of the emission spectra was obtained using the position of the elastic peaks unaltered by self-absorption. Also shown in Fig. 1 are the deconvolved Voigt spectral components along with the sum of the components and experimental data. The Voigt spectral components were derived using a 1.0 eV Gaussian total instrumental broadening, estimated empirically by analyzing a series of x-ray spectra in this energy region. This is consistent with direct measurement of secondary spectrometer resolution. Presented in Table 1 are energies of the (K + 3eV) spectral components, full width at half maximum (FWHM) of the Voigt profile in eV, relative radiative yields (the areas under the Voigt components) and Lorentzian FWHM obtained by removing instrumental broadening from the Voigt width. Peaks 1 and 2 in Fig. 2 are assigned as dipole-allowed transitions from electrons in 5e and $5a_1$ valence MOs, whereas peak 3 is attributed to the overlapping transitions from the $3e+2e+4a_1$ valence MOs.

In Fig. 3, the Cl $K\beta$(K-V) spectrum excited with 2823.1 eV (K-6.5 eV) photon energy is presented, along with the deconvolved spectral components. As seen in Fig. 1, the 2823.1 eV energy corresponds to the first maximum in the absorption spectrum. Also presented in Table

1 are the energy positions, relative intensities and widths of the spectral components of (K-6.5eV) excited spectrum. Comparing the Cl Kβ (K-V) spectral components for (K - 6.5eV) excitation with the spectral components for (K + 3 eV) excitation, large differences in energy positions, relative intensities and line widths are observed. The relative energy-position shifts and the significant intensity changes can be understood in terms of perturbation effects due to the presence of an electron in the first unoccupied MO, when excited with (K - 6.5 eV) photon excitation [2].

When a 1s hole is produced using photon excitation above the ionization threshold, the electron is excited beyond the bound orbitals of the closed electron core to a continuum state. Therefore, the virtual core hole can be located anywhere in the core level width [9], such that the Lorentzian line width of the Cl Kβ (K-V) emission component is the sum of the natural line width of the core level (Lorentzian) and the valence MO involved in the x-ray transition. But, when a core electron is excited to an unoccupied orbital below the vacuum level, the "effective" hole production region in the core state [9] is limited by convolution of the the broadening of the unoccupied level and the band pass of the monochromator (neglecting the core hole reorganization effects). Since this "effective" core hole region is a fraction of the total 1s lifetime broadening, the line width of x-ray emission components from the exciton state will be smaller than the line widths of the above-threshold excited spectrum. This agrees with the observed narrow line widths in (K-6.5 eV) spectral components shown in Fig. 3 compared to (K+3 eV) spectral components in Fig. 2. These narrow line widths also indicate that the core hole relaxation process [9] is slower than the fluorescent decay process.

The 2823.8 eV (K-5.8 eV) excited Cl Kβ (K-V) spectrum of CF_3Cl is presented in Fig. 4, along with the deconvolved spectral components. Also presented in Table 1 are the energy positions, relative intensities and widths for the (K-5.8 eV) excited spectrum. As shown in Fig. 1, the 2823.8 eV excitation corresponds to half-height of the first discrete maximum in the Cl K absorption spectrum. Comparing energy positions in Table 1, the energy of spectral components in the (K-5.8) eV spectrum is about 0.8 eV higher than the corresponding component energy in the (K-6.5 eV) spectrum. This indicates that the "effective" core hole production region for (K-5.8 eV) is in a lower energy region of the core level, approximately the difference in excitation energy [10]. This phenomenon is possible since the core level (1s) line width is mainly due to the lifetime broadening. The line widths in the (K-5.8 eV) spectrum is much larger than corresponding line widths in the (K-6.5) spectrum, indicating the localized properties of relaxation and reorganization effects of the virtual core.

In summary, the Cl Kβ (K-V) spectra from a CF_3Cl molecule are obtained by selectively populating the unoccupied MOs below the vacuum level and comparing them to the Cl Kβ (K-V) spectrum from above-threshold excitation. The energy shifts and relative intensity changes observed are due to perturbation effects resulting from the electron in an unoccupied molecular orbital. The below-threshold

excitation limits the "effective" hole production region in the 1s level, resulting in narrow line widths in the x-ray emission spectrum.

References

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Table 1. *The energies of the spectral components, full width at half maximum (FWHM) of the Voight profile in eV, the relative intensities and lorentzian FWHM in eV for 2832.5 eV, 2823.1 eV and 2823.8 eV photon excitation*

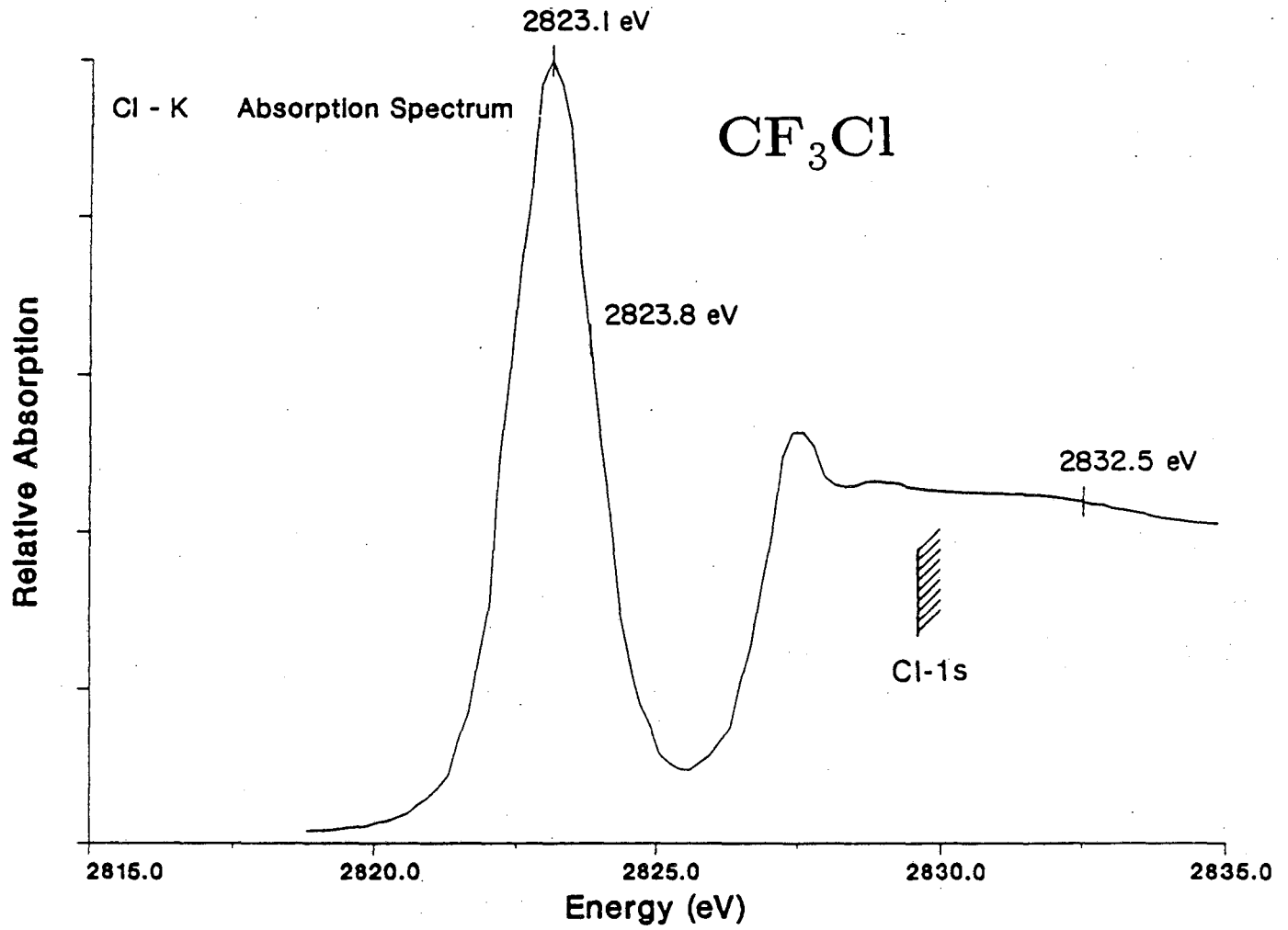| Peak	2832.5 eV Excitation				2823.1 eV Excitation				2823.8 eV Excitation			
	Energy (eV)	Total width (eV)	Rel. int.	Lorntz. width (eV)	Energy (eV)	Total width (eV)	Rel. int.	Lorntz. width (eV)	Energy (eV)	Total width (eV)	Rel. int.	Lorntz. width (eV)
A	2816.3	1.5	100	0.7	2814.9	1.2	100	0.3	2815.7	1.5	100	0.7
B	2814.2	1.5	28	0.7	2811.7	1.5	7	0.7	2812.2	1.6	8	0.9
C	2809.4	3.0	6	2.6	2806.8	2.6	3	2.2	2807.7	3.1	3	2.7

Fig. 1. Experimental Cl K absorption spectrum of CF₃Cl. The position of Cl 1s ionization threshold energy is indicated.
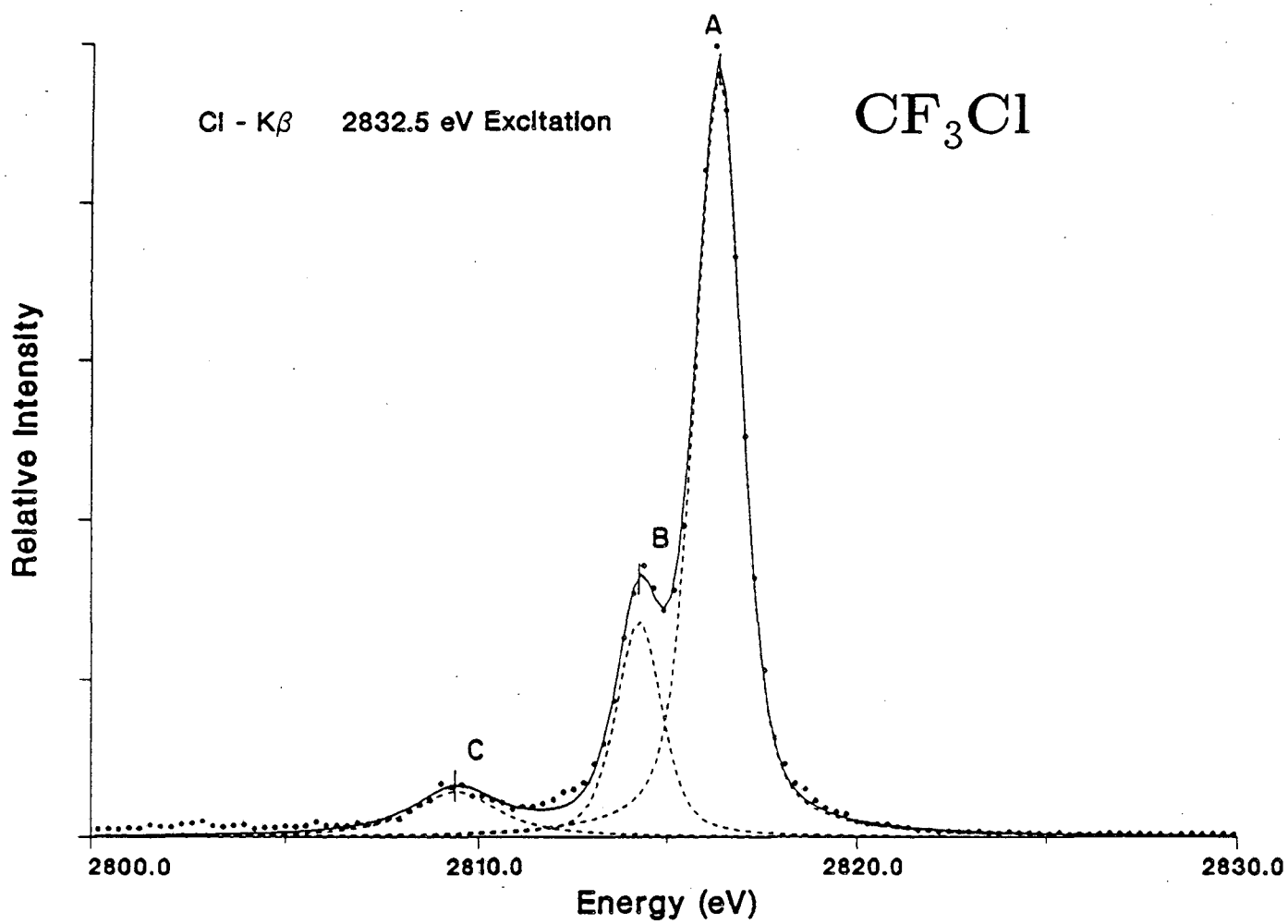
Cl - Kβ 2832.5 eV Excitation

CF$_3$Cl

Relative Intensity

Energy (eV)

Fig. 2. The Cl Kβ (K-V) spectrum of CF$_3$Cl excited with 2832.5 eV
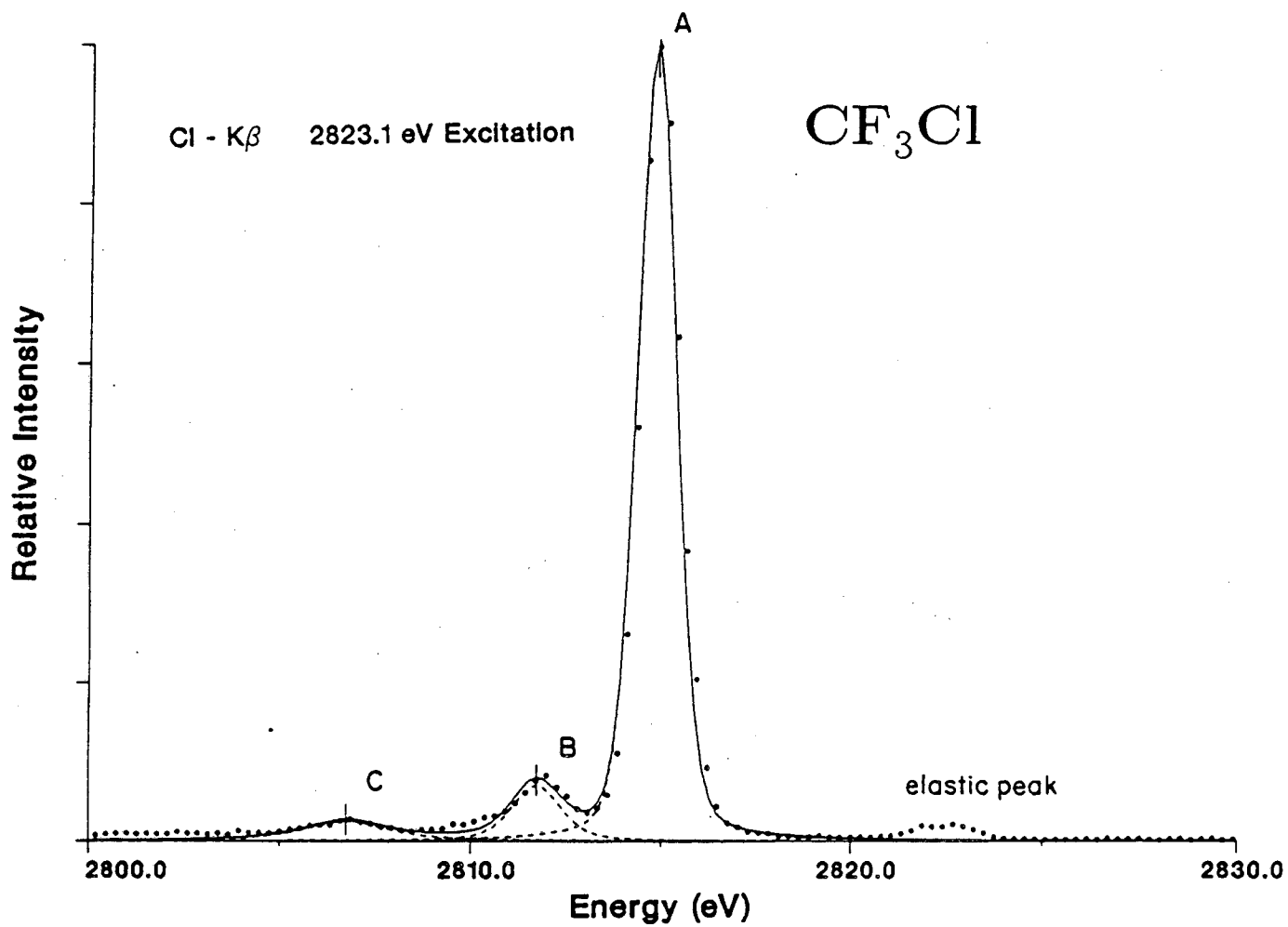photon energy along with the deconvolved Voigt spectral
components.

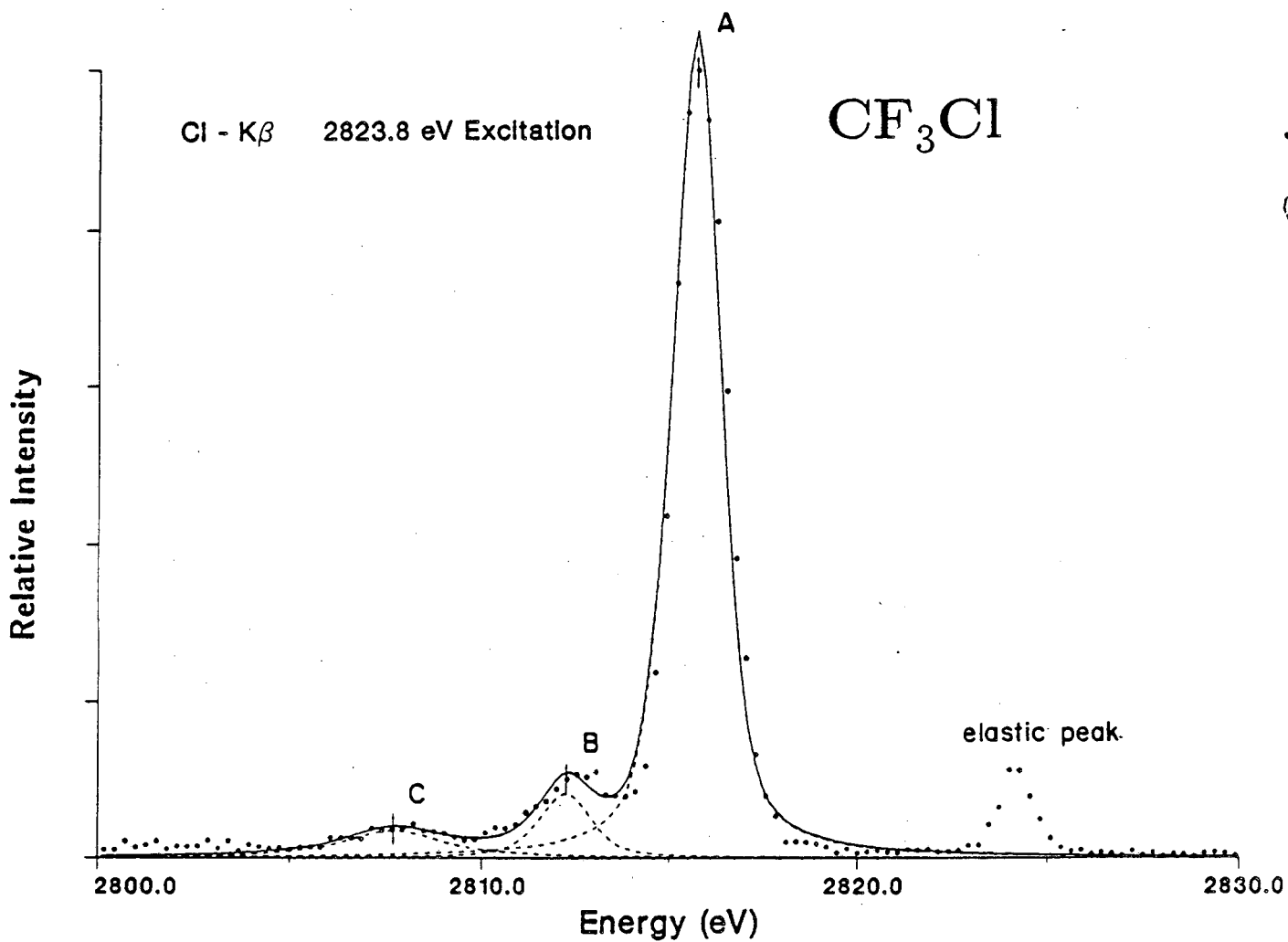Fig. 3. The Cl Kβ (K-V) spectrum of CF$_3$Cl excited with 2823.1 eV photon energy.

Fig. 4. The Cl Kβ (K-V) spectrum of CF₃Cl excited with 2823.8 eV photon energy.