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### Journal

Physical review A, 43(7)

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### Publication Date

1990-10-01



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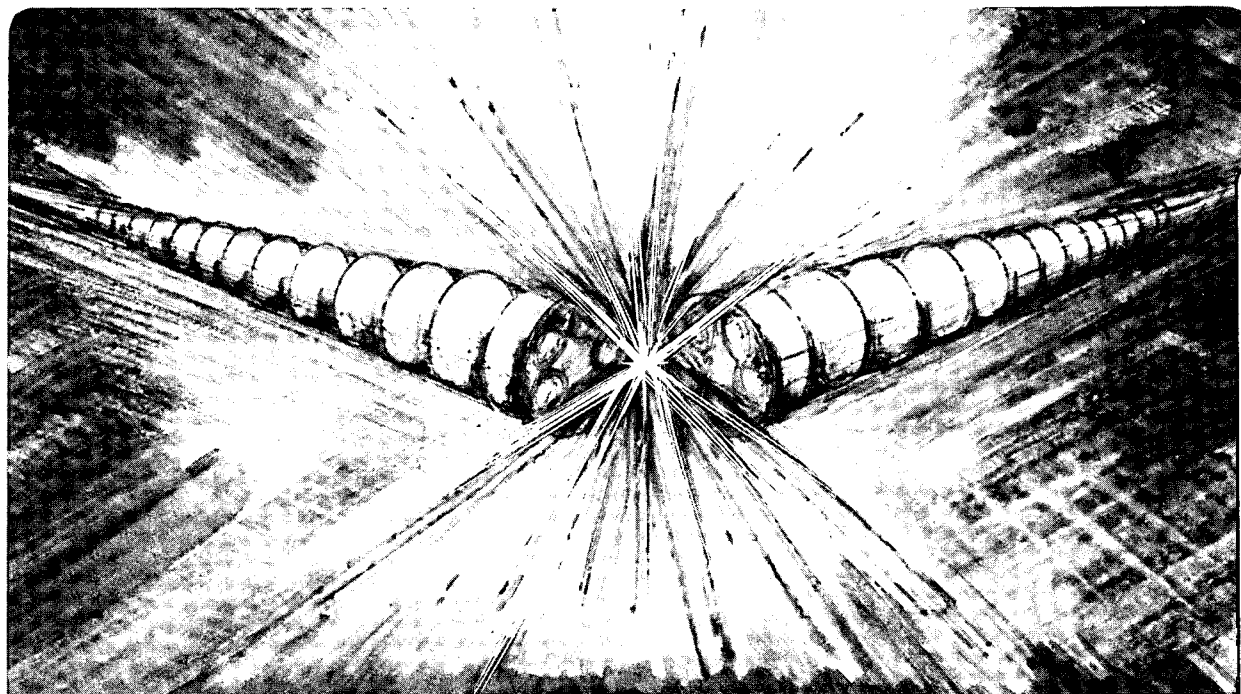
## Accelerator & Fusion Research Division

Submitted to Physical Review A

### Molecular-Orbital Studies Via Satellite-Free X-Ray Fluorescence: Cl K-Absorption and K-V Emission Spectra of Chlorofluoromethanes

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October 1990



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**MOLECULAR-ORBITAL STUDIES VIA SATELLITE-FREE X-RAY FLUORESCENCE:  
Cl K-ABSORPTION & K-V EMISSION SPECTRA OF  
CHLOROFLUOROMETHANES\***

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October 1990

### ABSTRACT

X-ray absorption and emission measurements in the vicinity of the chlorine K edge of the three chlorofluoromethanes have been made using monochromatic synchrotron radiation as the source of excitation. By selectively tuning the incident radiation to just above the Cl 1s single-electron ionization threshold for each molecule, less complex x-ray emission spectra are obtained. This reduction in complexity is attributed to the elimination of multielectron transitions in the Cl K shell, which commonly produce satellite features in x-ray emission. The resulting "satellite-free" x-ray emission spectra exhibit peaks due only to electrons in valence molecular orbitals filling a single Cl 1s vacancy. These simplified emission spectra and the associated x-ray absorption spectra are modeled using straightforward procedures and compared with semi-empirical ground-state molecular-orbital calculations. Good agreement is observed between the present experimental and theoretical results for valence-orbital energies and those obtained from ultraviolet photoemission, and between relative radiative yields determined both experimentally and theoretically in this work.

## I. INTRODUCTION

The general quantitative application of x-ray spectroscopy to structural and dynamical studies of atoms and molecules has proven problematical because of the obscuring effect of multivacancy processes, which are usually present in addition to single-vacancy transitions in conventional x-ray spectra.<sup>1</sup> These multivacancy processes, in which two or more electrons are excited or ionized, result in extra features, termed satellites, in x-ray absorption and emission spectra. With the availability of tunable monochromatic x-rays at synchrotron-radiation sources, it is now possible to selectively ionize core electrons near enough to the core-level threshold energy that multielectron transitions in the subshell of interest are energetically forbidden. Under these conditions, x-ray emission (fluorescence) is observed only from singly ionized atoms<sup>2</sup> or molecules, without contributions from multivacancy satellites: hence the term "satellite-free x-ray emission." Selective excitation, however, does not preclude the occurrence of multi-electron transitions in the x-ray emission process. But such transitions are expected to be very weak, because in x-ray emission, unlike in the initial photo-absorption process, there is no change in charge state to cause "shake-up" or "shake-off" phenomena.

In this work, we present a study of the valence electronic structure of the chlorofluoromethanes by chlorine K x-ray emission under satellite-free conditions. We demonstrate how this technique, based on the use of synchrotron radiation, can eliminate multivacancy effects that are inherent

in conventional x-ray spectroscopy.<sup>1</sup> For this report, Cl K absorption and Cl K-V (historically denoted as Cl K $\beta$ ) emission spectra of gas/vapor-phase CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, and CFC1<sub>3</sub> were measured using monochromatic synchrotron radiation from the National Institute of Standards and Technology (NIST) beamline X-24A at the National Synchrotron Light Source (NSLS) as the source of excitation. In order to estimate contributions from satellite features in the x-ray emission spectra,<sup>2,3</sup> Cl K-V fluorescence spectra were recorded for several incident x-ray energies in the vicinity of the single- and multiple-vacancy Cl K ionization thresholds. Appropriate photon energies for producing satellite-free spectra were selected, and single-vacancy Cl K emission spectra were recorded for all three samples. Comparison to previous core-level<sup>4,5</sup> and valence-shell<sup>6-8</sup> studies is made to assist in determining peak assignments. To further guide the interpretation of the satellite-free spectra, semi-empirical ground-state modified-neglect of diatomic-overlap (MNDO) calculations<sup>9</sup> were performed for the valence molecular orbitals (MOs). In these calculations, the molecular geometry was varied to minimize the orbital energies, while retaining the proper ground-state molecular symmetry.<sup>10</sup> Thus, the Cl K-V emission spectra have been analyzed by a method first described by Manne,<sup>11</sup> based upon atomic-orbital compositions of MO's.

We find that production of satellite-free x-ray emission spectra is feasible, and that simplified spectra are indeed obtained using selective photon excitation. Comparison of the K-V emission data with MO binding energies from ultraviolet photoelectron spectroscopy (UPS) and with calculated relative yields provides adequate explanations of the observed

spectra. With this demonstration, it is suggested that satellite-free x-ray-emission measurements can be helpful in the assignment of MO's in more complex molecules. This latter possibility exists in part because x-ray emission involves only a subset of valence MO's with appreciable electron density at the site of the initially produced core hole.

## II. EXPERIMENTAL

Detailed descriptions of the soft x-ray beamline<sup>12</sup> and double crystal monochromator<sup>13</sup> are given elsewhere. Chlorine K absorption spectra are obtained by measuring incident and transmitted x-ray fluxes with ion chambers filled with a He/N<sub>2</sub> mixture at 1 atm. The Cl K-V fluorescence radiation is analyzed by a variable-radius curved-crystal<sup>14</sup> spectrometer consisting of a silicon (111) crystal of  $2d = 6.271 \text{ \AA}$  and a linear position-sensitive gas proportional counter<sup>15</sup> filled with a Xe (90% vol.)/CH<sub>4</sub> (10% vol.) mixture at a pressure of  $\approx 1$  atm. The sample gas, contained in a 7 mm long sample cell by 25 $\mu$ m thick beryllium windows, is located inside the Rowland circle of the secondary spectrometer. Further details of the spectrometer and its performance are given elsewhere.<sup>16</sup>

Energy calibration for the absorption spectra and the primary monochromator in this energy region was obtained using Cl K absorption spectra of the chlorofluoromethanes measured with a previously described<sup>17</sup> laboratory spectrometer. Energy calibration of the emission spectra was obtained using positions of x-ray emission features and elastically scattered x-rays. The elastic peaks were observed with excitation at energies below



all Cl-K absorption features to avoid self-absorption effects. The x-ray emission data presented in this work were measured for emission polarized perpendicular to the incident radiation polarization.<sup>18</sup> Observations to date indicate that fluorescence-polarization effects are generally small (<20%) for above-threshold excitation.<sup>19,20</sup>

All samples were obtained commercially with stated purities greater than 99% and used without further purification. Sample gas pressures are selected empirically to correspond to approximately one absorption length (i.e.,  $I=I_0/e$ ) at the peak of absorption. For spectra presented in this work, the sample pressures for  $CF_3Cl$ ,  $CF_2Cl_2$ , and  $CFCl_3$  were 150, 100, and 60 Torr, respectively.

### III. RESULTS AND DISCUSSION

One reason for studying the chlorofluoromethanes is the extensive body of results from previous studies employing a variety of techniques. For example, x-ray absorption measurements of  $CF_2Cl_2$  were made by Hanus and Gilberg.<sup>21</sup> X-ray excited Cl K-V emission spectra of  $CF_3Cl$ ,  $CF_2Cl_2$ , and  $CFCl_3$  were reported previously by LaVilla and Deslattes,<sup>4</sup> while Ehlert and Mattson<sup>5</sup> measured F K, C K, and Cl  $L_{II,III}$  emission spectra. Ultraviolet photoelectron spectra of the chlorofluoromethanes have been measured by Doucet et al.<sup>6</sup> and Jadrny et al.<sup>7</sup> using He I (21.2 eV) excitation. Cvitas et al.<sup>8</sup> confirmed and extended the UPS measurements with He I and He II (40.8 eV) radiation. All of the experimental photoelectron spectra are in good agreement.

For analyzing the present absorption spectra, a theoretical model suggested by Wainstein et al.<sup>22</sup> was used. The shape of an absorption spectrum is assumed to be determined mainly by the positive-charge core hole, with molecular effects reflected in the first one or two discrete (below-threshold) absorption features. An atomic-like Rydberg series is used to account for the absorption just below the K-shell threshold. Finally, the absorption continuum is described by an arctangent function such that the point of inflection coincides with the ionization threshold of the Cl 1s core level. Based upon these assumptions, the absorption spectra were decomposed into Voigt spectral components<sup>23</sup> to account for single-electron transitions to unoccupied valence MO's, a Rydberg series leading to the Cl K threshold, and an absorption continuum described by an arctangent function. The quantum defects<sup>24</sup> for the components of the Rydberg series were assumed to be the same, and the area encompassed by the entire Rydberg series depends upon the absorption coefficient in the continuum<sup>22</sup> (i.e., the maximum height of the arctangent function). For the modeling procedures in this work,<sup>24</sup> Rydberg series of  $n = 5$  to 25 were used. No attempt was made to model any of the above-threshold features in the chlorofluoromethane absorption spectra. Previously, Hanus and Gilberg<sup>21</sup> successfully used a similar procedure to describe Cl K core-level absorption measurements.

To facilitate interpretation of the experimental features in the present x-ray emission spectra, the spectra were modeled empirically using a SIMPLEX minimization technique.<sup>23</sup> For the modeling, the instrumental broadening was assumed to be Gaussian and the natural line width Lorentzian, resulting in Voigt spectral profiles. The Gaussian instrumental broadening was

estimated to be 1.0 eV by analyzing a series of x-ray emission spectra in this region. This value is consistent with direct measurements of the secondary-spectrometer resolution.

Modeling of the x-ray emission spectra permitted extraction of energies and relative intensities of the emission peaks. Assignments were then determined by comparison with known valence MO orderings from UPS measurements.<sup>6-8</sup> MNDO calculations<sup>9</sup> also were compared to the observed spectra and their assignments, in particular to identify those valence MO's with appreciable Cl 3p atomic-orbital character.<sup>11</sup> Only MO's with some Cl 3p character will contribute to the x-ray emission spectra. Finally, the MNDO calculations provided relative intensities in good agreement with observation, lending further confidence to the present assignments.<sup>25</sup>

#### A. Trifluorochloromethane (CF<sub>3</sub>Cl)

Trifluorochloromethane (C<sub>3v</sub> symmetry point group) has 32 valence electrons in the ground-state electronic configuration (6a<sub>1</sub>)<sup>2</sup>(3e)<sup>4</sup>(7a<sub>1</sub>)<sup>2</sup>(8a<sub>1</sub>)<sup>2</sup>(9a<sub>1</sub>)<sup>2</sup>(4e)<sup>4</sup>(5e)<sup>4</sup>(1a<sub>2</sub>)<sup>2</sup>(6e)<sup>4</sup>(10a<sub>1</sub>)<sup>2</sup>(7e)<sup>4</sup>. The first unoccupied valence MO's, based on MNDO calculations, are 11a<sub>1</sub>, 12a<sub>1</sub>, and 8e in order of increasing energy.

Using our Cl K-V x-ray emission data and UPS final-state binding energies (BE),<sup>7,8</sup> the Cl 1s ionization threshold of CF<sub>3</sub>Cl is estimated to be 2830.2(3) eV, compared to 2830.13 eV from the Rydberg peak positions in

this work. The Cl K-V emission spectra presented in Fig. 1 were obtained using photon excitation energies of 2833 and 2880 eV. The lower photon energy is about 3 eV above the Cl 1s ionization threshold, and below all double-vacancy thresholds, resulting in a satellite-free Cl K-V spectrum. A photon energy of 2880 eV is above most [KV] double-vacancy threshold energies, which correspond to production of initial states that make important contributions to emission satellites in this energy range. As seen in Fig. 1, the 2880-eV spectrum (dots) contains extra contributions which we attribute to multiple-vacancy transitions. The main satellite emission band thus obtained is located on the high-energy side of the single-vacancy spectrum. The primary concern for the present work is that the multivacancy emission features can be suppressed by selectively tuning the excitation energy, as was demonstrated originally for Ar K-edge x-ray emission spectra.<sup>2</sup>

The 2833 eV Cl K-V spectrum is presented again in Fig. 2, along with modeled Voigt spectral components and their sum. Listed in Table I are energies of the Voigt components and their relative areas, which are proportional to relative radiative yields. The Cl K absorption spectrum of CF<sub>3</sub>Cl also is shown in Fig. 2, along with the fit results. The energy positions and relative intensities for the discrete Cl K absorption features of CF<sub>3</sub>Cl also are given in Table I. As indicated earlier, no attempt was made to model the features above the ionization threshold; hence, no quantitative results will be reported for this feature at 2830 eV.

The lowest-energy absorption feature in the Cl K region of  $\text{CF}_3\text{Cl}$ , labeled D in Fig. 2, is assigned to a transition of a Cl 1s electron to the unoccupied  $11a_1$  valence MO. The small-amplitude feature E at 2826.5 eV that may be derived from transitions to the  $12a_1$  or  $8e$  valence MO's. As seen for the derived components in Fig. 2, feature F results from transitions to the 4p Rydberg state, whereas feature G is attributed to overlapping transitions to 5p and higher Rydberg states leading to the Cl 1s ionization threshold. These assignments are summarized in Table I. The broad structure above the 1s threshold, is tentatively attributed to a shape resonance structure. Similar suprathreshold structures were observed and identified<sup>3</sup> in Cl-K emission and absorption spectra of  $\text{CH}_3\text{Cl}$ .

Because of selective excitation of  $\text{CF}_3\text{Cl}$  at 2833 eV, all emission features in the Cl K-V spectrum in Fig. 2 have a common initial state; namely, a single Cl 1s vacancy. Thus, the most probable transitions in the K-V emission spectrum involve electrons from valence MO's with Cl 3p character.<sup>11</sup> A reasonable estimate of the chlorine 3p character in a valence MO can be obtained from a simple ground-state calculation, such as MNDO, as shown in Ref. 10. Therefore, we have calculated energies and compositions for the valence MO's of  $\text{CF}_3\text{Cl}$  by the MNDO method, and the results are listed in Table II. Atomic-orbital compositions can be obtained from the squared coefficients for each contributing atomic orbital to the  $\text{CF}_3\text{Cl}$  molecular orbitals.

Comparison of the observed CF<sub>3</sub>Cl K-V emission features with calculated energies and intensities is shown in Table III. The stronger emission components, peaks C and B, are assigned to dipole-allowed transitions of electrons in the 7e and 10a<sub>1</sub> valence MO's, respectively, filling the initial Cl 1s vacancy. The weaker emission peaks B' and A are assigned to allowed dipole transitions from the 5e and the 9a<sub>1</sub> + 4e valence MO's, respectively. As seen from Table III, experimental values agree reasonably well with the calculated radiative yields based upon ground-state calculations. The experimental binding energies are only in fair agreement since the ordering of valence MO's suggested by the MNDO method interchanges the 1a<sub>2</sub> and 6e, and the 9a<sub>1</sub> and 4e valence MO's. This shortcoming to the MNDO calculation is expected because the method treats the MO's as combinations of atomic orbitals, with little detailed optimization of the MO energies. Therefore, we stress that our assignments are based primarily on energetic grounds using UPS binding-energy measurements. The MNDO results are used only to determine which MO's have appreciable Cl 3p atomic-orbital character, and for a rough comparison with the observed emission intensities.

#### B. Dichlorodifluoromethane (CF<sub>2</sub>Cl<sub>2</sub>)

Dichlorodifluoromethane (C<sub>2v</sub> point group) also has 32 valence electrons which are distributed among 16 different valence molecular orbitals. The ground-state valence electronic configuration is (7a<sub>1</sub>)<sup>2</sup>(2b<sub>1</sub>)<sup>2</sup>(8a<sub>1</sub>)<sup>2</sup>(6b<sub>2</sub>)<sup>2</sup>(9a<sub>1</sub>)<sup>2</sup>(7b<sub>2</sub>)<sup>2</sup>(10a<sub>1</sub>)<sup>2</sup>(3b<sub>1</sub>)<sup>2</sup>(11a<sub>1</sub>)<sup>2</sup>(2a<sub>2</sub>)<sup>2</sup>(4b<sub>1</sub>)<sup>2</sup>(8b<sub>2</sub>)<sup>2</sup>(12a<sub>1</sub>)<sup>2</sup>(3a<sub>2</sub>)<sup>2</sup>(5b<sub>1</sub>)<sup>2</sup>(9b<sub>2</sub>)<sup>2</sup>. The lowest unoccupied valence MO's of CF<sub>2</sub>Cl<sub>2</sub>, based on MNDO calculations, are 13a<sub>1</sub>, 10b<sub>2</sub>, 14a<sub>1</sub>, and 6b<sub>1</sub> in order of increasing energy.

The Cl K-V emission spectra from  $\text{CF}_2\text{Cl}_2$  using 2833 eV and 2880 eV photon-energy excitation are presented in Fig. 3 for comparison. As in  $\text{CF}_3\text{Cl}$ , increased intensity contributions for 2880-eV excitation visible in Fig. 3 are attributed to multiple-vacancy transitions. The satellite-free Cl K-V x-ray emission spectrum of  $\text{CF}_2\text{Cl}_2$  also is presented in Fig. 4, along with the derived Voigt spectral components. The energies and relative intensities of the prominent spectral features are listed in Table I.

The Cl K absorption spectrum of  $\text{CF}_2\text{Cl}_2$  is shown in Fig. 4 along with the model components. The component energies, relative intensities, and their assignments are listed in Table I. The first discrete absorption maximum (feature D) and feature E are assigned to dipole-allowed transitions of the ground state chlorine 1s electron to the unoccupied  $13a_1$  and  $10b_2$ , and the  $14a_1$  and  $6b_1$  valence MO's, respectively. As seen from the derived components in Fig. 4, features F and G result from overlapping of transitions to 4p, 5p, and higher Rydberg states leading to the chlorine 1s ionization threshold. The broad structure above the 1s threshold, is tentatively attributed to a shape resonance structure. These results for Cl K absorption of  $\text{CF}_2\text{Cl}_2$  are consistent with previous lower-resolution measurements.<sup>21</sup>

For the Cl K-V emission spectrum of  $\text{CF}_2\text{Cl}_2$ , the calculated orbital compositions and relative radiative yields are presented in Table IV. The results in Table IV suggest that the strongest feature, C, in Fig. 4 results from overlapping, dipole-allowed, transitions from the  $9b_2$ ,  $5b_1$ , and  $3a_2$  valence MO's, whereas feature C' is assigned to transitions from the

12a<sub>1</sub> and 8b<sub>2</sub> valence MO's. The broad feature B, (correspond to two derived components) is assigned to transitions from the 2a<sub>2</sub> and 11a<sub>1</sub> orbitals, whereas the feature A is assigned to transitions from the 3b<sub>1</sub>, 10a<sub>1</sub>, and 7b<sub>2</sub> valence MO's. Very weak features resulting from transitions that originate from inner-valence 8a<sub>1</sub> and 9a<sub>1</sub> MO's are perhaps present near 2806 eV. These assignments are summarized in Table I.

The calculated and experimental valence MO energies and Cl K-V relative radiative yields for CF<sub>2</sub>Cl<sub>2</sub> are compared in Table V. The ordering of valence MO's suggested by the MNDO method does not agree with the assignment of the UPS spectra. However, the relative intensities are in good agreement, after putting the MNDO results in the correct order.

### C. Trichlorofluoromethane (CFCl<sub>3</sub>)

Trichlorofluoromethane (C<sub>3v</sub> symmetry) has a ground-state valence configuration of (7a<sub>1</sub>)<sup>2</sup>(8a<sub>1</sub>)<sup>2</sup>(6e)<sup>4</sup>(9a<sub>1</sub>)<sup>2</sup>(10a<sub>1</sub>)<sup>2</sup>(7e)<sup>4</sup>(8e)<sup>4</sup>(11a<sub>1</sub>)<sup>2</sup>(9e)<sup>4</sup>(10e)<sup>4</sup>(2a<sub>2</sub>)<sup>2</sup>. From the MNDO calculations, the lowest unoccupied valence MO's are 12a<sub>1</sub>, 11e, and 13a<sub>1</sub> in order of increasing energy. Chlorine K-V x-ray emission spectra of CFCl<sub>3</sub> in the vapor phase were measured using 2835 eV and 2880 eV excitation, and are presented in Fig. 5 for comparison. Note the increase in intensity resulting from multiple-vacancy transitions. However, their contributions appear less prominent than in CF<sub>3</sub>Cl or CF<sub>2</sub>Cl<sub>2</sub>.

A satellite-free Cl K-V x-ray emission spectrum of CFCl<sub>3</sub> is presented in Fig. 6 along with the modeled Voigt spectral components. The component



energies and relative intensities of the spectral features are listed in Table I. The orbital compositions and Cl K-V relative radiative yields suggested by the ground-state MNDO MO calculations are presented in Table VI.

The Cl K absorption spectrum of  $\text{CFCl}_3$  also is shown in Fig. 6 along with its modeled components. The energies, relative intensities, and their assignments are presented in Table I. Feature D, the first discrete maximum in the absorption spectrum, is assigned to the dipole-allowed transition of a chlorine 1s electron to the unoccupied valence  $12a_1$  MO, whereas feature E is attributed to transitions to the  $11e$  and  $13a_1$  unoccupied valence MOs. Again, feature F results from 4p and higher Rydberg states, and it is suggested that the broad feature H might be a shape resonance.

For the Cl K-V emission spectrum, the main features, C and C', are assigned to dipole-allowed overlapping transitions from the  $2a_2$  and  $10e$ , and the  $9e$  and  $11a_1$  valence MO's, respectively, whereas the weak feature B is assigned to a transition from the  $8e$  valence MO. The prominent peak, A, is assigned to a transition from the  $7e$  valence MO.<sup>20</sup> These assignments are listed in Table I. As seen from Table VII the calculated and experimental valence MO energies and Cl K-V relative radiative yields for  $\text{CFCl}_3$  are in fair agreement. Also the ordering of valence MO's suggested by the MNDO method is the same as the assignment of the UPS spectra.

## CONCLUSION

We have demonstrated the feasibility of producing gas-phase molecular x-ray emission spectra free of the complicating influences of multielectron (multivacancy-satellite) effects. These so-called "satellite-free" spectra can be interpreted adequately using relatively simple theoretical models, giving insight into the assignments and relative yields for the observed valence-molecular-orbital x-ray transitions. Such simplified x-ray emission spectra may be particularly useful for more complex molecules, where the advantages of the propensity to follow atomic dipole selection rules (e.g., Cl 3p→1s) will be most profound.

## Acknowledgements

We thank Barry Karlin for assisting in the measurements, Dana Berkeland and Mark Thomas for their invaluable assistance in analyzing data, and Pat Weir for her assistance in preparation of the manuscript. One of the authors (R.C.C.P.) acknowledges the support by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under the Contract No. DE-AC03-76SF00098. This work was performed at NSLS, which is supported by the U. S. Department of Energy under contract No. DE-AC020-76CH00016.

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24. The energy of the nth Rydberg peak from the ionization threshold energy  $\Delta E \propto 1/(n-q)^2$ , where q is the quantum defect. For the modeling procedure in this work, Rydberg series of n=5,25 were used. The resulting quantum defects from this procedure for CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub> and CFCl<sub>3</sub> are 0.70, 0.72 and 0.66 respectively.
25. [Additional information also can be obtained using polarized x-ray emission spectroscopy (PXES).<sup>18,19</sup> A case in point<sup>20</sup> is emission peak A for CFCl<sub>3</sub>, where PXES results strongly indicate assignment to only the 2e MO, although the 4a<sub>1</sub> MO is energetically possible as well. This result will be discussed in more detail in Ref. 20].

FIGURE CAPTIONS:

Fig. 1. Comparison of 2880 eV photon-energy excited Cl K-V spectrum of  $\text{CF}_3\text{Cl}$  (circles) with a 2833 eV excited spectrum indicated by the solid curve. The increased intensity contributions in the 2880 eV excited spectrum are attributed to multiple-vacancy transitions.

Fig. 2. Experimental 2833 eV photon-energy excited chlorine K-V emission and K-absorption spectra of  $\text{CF}_3\text{Cl}$  (dots) along with fitted spectral components (dashed curves) and the sum of the derived components (solid curves). The component energies and assignments are given in Table I.

Fig. 3. Cl K-V emission spectra from  $\text{CF}_2\text{Cl}_2$  using 2880 eV (circles) and 2833 eV (solid curve) photon-energy excitation.

Fig. 4. The 2833 eV excited Cl K-V emission and K-absorption spectra of  $\text{CF}_2\text{Cl}_2$ , as in Fig. 2.

Fig. 5. Cl K-V emission spectra of  $\text{CFCl}_3$  using 2835 eV (solid curve) and 2880 eV (circles) photon-energy excitation.

Fig. 6. The 2835 eV excited Cl K-V emission and K-absorption spectra of  $\text{CFCl}_3$ , as in Fig. 2.

Table I. Energies, relative radiation yields, and assignments for the major components in the Cl K-absorption and Cl K-V emission spectra of CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, and CFC1<sub>3</sub>.

PEAK	CF <sub>3</sub> Cl			CF <sub>2</sub> Cl <sub>2</sub>			CFC1 <sub>3</sub>		
	ENERGY (eV)	RELATIVE INTENSITY	ASSIGNMENT	ENERGY (eV)	RELATIVE INTENSITY	ASSIGNMENT	ENERGY (eV)	RELATIVE INTENSITY	ASSIGNMENT
<u>EMISSION</u>									
A	2810.1(3)	5	9a <sub>1</sub> +4e	2810.4(3)	13	3b <sub>1</sub> +10a <sub>1</sub> +7b <sub>2</sub>	2811.5(4)	19	7e
B'	2813.6(3)	2	5e						
B	2815.1(3)	27	10a <sub>1</sub>	2813.1(5)	17	2a <sub>2</sub> +11a <sub>1</sub>	2814.4(5)	22	8e
C'				2815.8(3)	48	12a <sub>1</sub> +8b <sub>2</sub>	2816.3(3)	88	9e+11a <sub>1</sub>
C	2817.1(3)	100	7e	2817.0(3)	100	9b <sub>2</sub> +5b <sub>1</sub> +3a <sub>2</sub>	2817.4(3)	100	2a <sub>2</sub> +10e
-----									
<u>ABSORPTION</u>									
D	2823.5 <sup>a</sup>		Cl 1s → 11a <sub>1</sub>	2823.0 <sup>a</sup>		Cl 1s → 13a <sub>1</sub> +10b <sub>2</sub>	2822.8 <sup>a</sup>		Cl 1s → 12a <sub>1</sub>
E	2827.4(3)		Cl 1s → 12a <sub>1</sub> +8e	2826.4(3)		Cl 1s → 14a <sub>1</sub> +6b <sub>1</sub>	2825.7(5)		Cl 1s → 11e+13a <sub>1</sub>
F	2827.8(3)		Cl 1s → 4p	2827.2(3)		Cl 1s → 4p	2827.1(3)		Cl 1s → 4p....
IP	2830.2 <sup>b</sup> (3) 2830.13 <sup>c</sup>		Cl 1s → ∞	2829.6 <sup>b</sup> (6) 2829.60 <sup>c</sup>		Cl 1s → ∞	2829.3 <sup>b</sup> (5) 2829.30 <sup>c</sup>		Cl 1s → ∞

(a) Peaks used in calibration of absorption spectra

(b) From UPS and Cl K-V

(c) From Rydberg peaks (this work).

**Table 2. Results from ground-state semi-empirical MNDO calculations for CF<sub>3</sub>Cl**

Assignment	Orbital Composition					
	Carbon		Fluorine		Chlorine	
	2s	2p	2s	2p	3s	3p
7e	---	---	---	.047	---	1.953
10a <sub>1</sub>	.006	.066	---	.587	.006	.335
6e	---	.018	.008	1.974	---	---
1a <sub>2</sub>	---	---	---	1.000	---	---
5e	---	.002	.001	1.984	---	.013
4e	---	.419	.194	1.366	---	.022
9a <sub>1</sub>	.001	.259	.022	.549	.040	.129
8a <sub>1</sub>	.203	.001	.199	.294	.254	.050
7a <sub>1</sub>	.092	.049	.066	.051	.695	.046
3e	---	.255	1.698	.045	---	.002
6a <sub>1</sub>	.269	.020	.650	.054	.001	.007

Table 3. Comparison of experimental and calculated orbital energies and Cl K-V relative intensities for CF<sub>3</sub>Cl.

Peak	Orbital	Energy (eV)		Relative Intensity	
		UPS <sup>a</sup>	Calculated	Experimental	
	Calculated				
C	7e	13.08	14.1	100	100
B	10a <sub>1</sub>	15.20	15.2	27	17
	1a <sub>2</sub>	15.80	17.0		0
	6e	16.72	16.8		0
B'	5e	17.71	17.3	2	1
A	9a <sub>1</sub>	20.20	20.9	5	7
	4e	21.2	20.8		1
	8a <sub>1</sub>	23.8	24.6	3	
	7a <sub>1</sub>		27.4	2	
	3e		45.4	0	
	6a <sub>1</sub>		52.3	0	

<sup>a</sup>Refs. 6-8



**Table 4. Results from ground-state semi-empirical MNDO calculations for CF<sub>2</sub>Cl<sub>2</sub>**

Assignment	Orbital Composition					
	Carbon		Fluorine		Chlorine	
	2s	2p	2s	2p	3s	3p
9b <sub>2</sub>	---	.016	---	.010	.001	.973
3a <sub>2</sub>	---	---	---	.010	---	.990
5b <sub>1</sub>	---	---	---	.039	---	.961
12a <sub>1</sub>	.002	.005	---	.043	---	.950
8b <sub>2</sub>	---	.084	---	.410	.005	.500
11a <sub>1</sub>	.004	.038	.002	.782	.004	.171
4b <sub>1</sub>	---	.005	.002	.992	---	.001
2a <sub>2</sub>	---	---	---	.990	---	.010
7b <sub>2</sub>	---	.262	---	.517	.040	.180
3b <sub>1</sub>	---	.209	.095	.669	---	.026
10a <sub>1</sub>	.002	.243	.040	.540	.030	.144
9a <sub>1</sub>	.152	---	.109	.156	.507	.076
6b <sub>2</sub>	---	.035	---	.006	.948	.010
8a <sub>1</sub>	.215	.054	.113	.056	.451	.112
2b <sub>1</sub>	---	.127	.851	.021	---	.002
7a <sub>1</sub>	.223	.042	.675	.045	.001	.014

Table 5. Comparison of experimental and calculated orbital energies and Cl K-V relative intensities for CF<sub>2</sub>Cl<sub>2</sub>.

Peak	Orbital	Energy (eV)		Relative Intensity	
		UPS <sup>a</sup>	Calculated	Experimental	Calculated
C	9b <sub>2</sub>	12.25	13.4		33
	5b <sub>1</sub>	12.53	14.2	100	33
	3a <sub>2</sub>	13.11	13.9		34
C'	12a <sub>1</sub>	13.45	14.3	48	33
	8b <sub>2</sub>	14.36	14.8		17
	4b <sub>1</sub>	15.9	16.9		0
B	2a <sub>2</sub>	16.3	17.2	8	<1
	11a <sub>1</sub>	16.9	16.5	9	6
	3b <sub>1</sub>	19.5	20.4		1
A	10a <sub>1</sub>	19.5	20.5	13	1
	7b <sub>2</sub>	20.4	20.4		6
	9a <sub>1</sub>	22.5	24.7		3
	6b <sub>2</sub>		26.6		<1
	8a <sub>1</sub>		28.4		4
	2b <sub>1</sub>		45.4		0
	7a <sub>1</sub>		50.7		<1

<sup>a</sup>Refs. 6-8

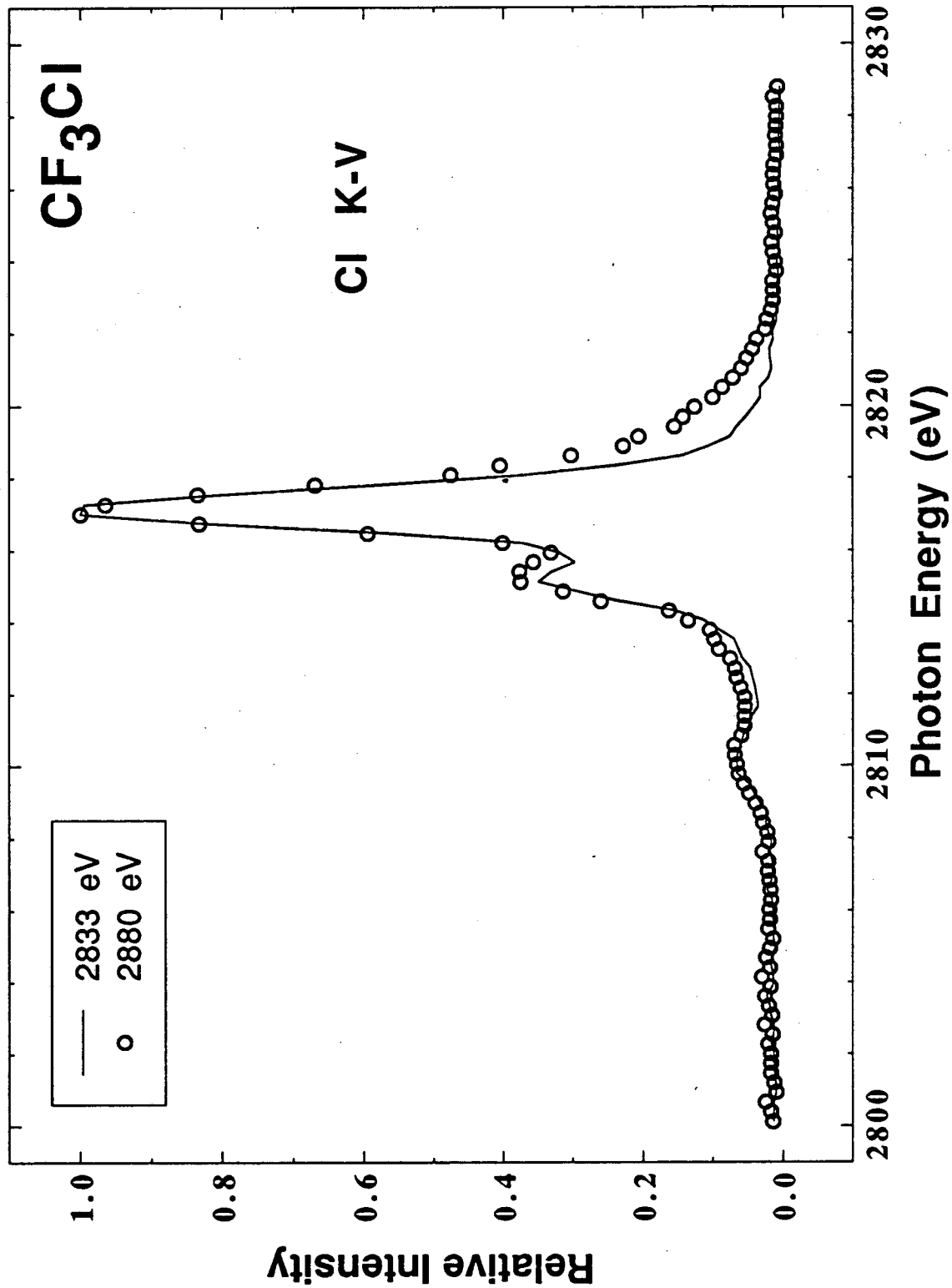
**Table 6. Results from ground state semi-empirical MNDO Calculations for CFCl<sub>3</sub>**

Assignment	Orbital Composition					
	Carbon		Fluorine		Chlorine	
	2s	2p	2s	2p	3s	3p
2a <sub>2</sub>	---	---	---	---	---	1.000
10e	---	.049	---	.012	.002	1.938
9e	---	.032	---	.079	.002	1.888
11a <sub>1</sub>	.002	.002	---	.052	---	.943
8e	---	.149	---	.926	.011	.915
7e	---	.507	---	.920	.072	.501
10a <sub>1</sub>	.002	.243	.067	.512	.019	.157
9a <sub>1</sub>	.109	---	.044	.062	.694	.090
6e	---	.070	---	.007	1.902	.021
8a <sub>1</sub>	.350	.045	.110	.028	.278	.189
7a <sub>1</sub>	.155	.071	.721	.034	.002	.018

Table 7. Comparison of experimental and calculated orbital energies and Cl K-V relative intensities for  $\text{CFCl}_3$ .

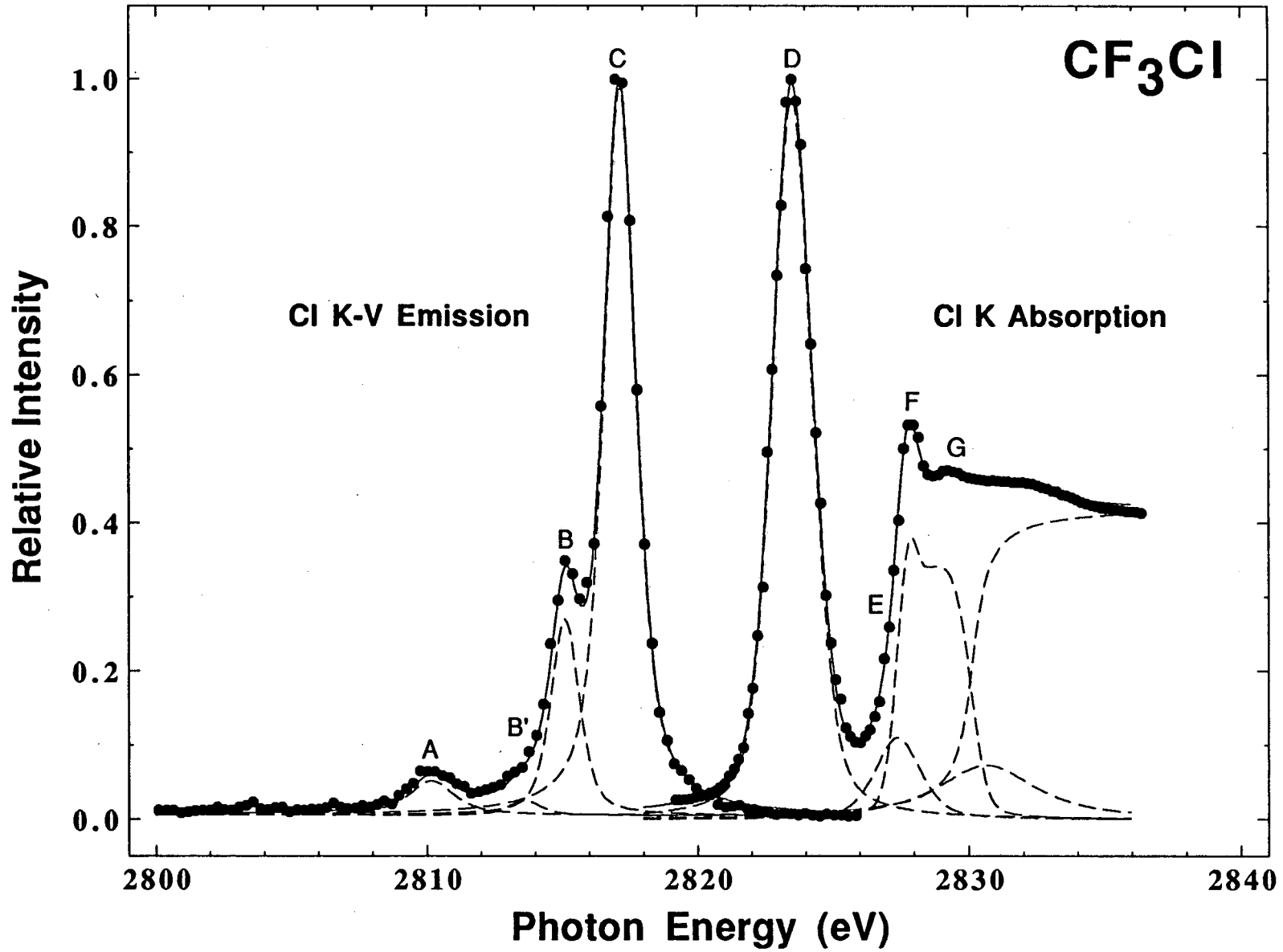
Peak	Orbital	Energy (eV)		Relative Intensity	
		UPS <sup>a</sup>	Calculated	Experimental	Calculated
C	2a <sub>2</sub>	11.73	13.3	100	34
	10e	12.13	13.4		66
C'	9e	12.97	14.1	88	64
	11a <sub>1</sub>	13.45	14.3		32
B	8e	15.05	15.8	22	31
A	7e	18.2	19.7	19	17
	10a <sub>1</sub>	18.2	19.9		5
	9a <sub>1</sub>	21.5	24.7		3
	6e		26.5		1
	8a <sub>1</sub>		30.2		7
	7a <sub>1</sub>		48.7		1

<sup>a</sup>Ref. 6-8



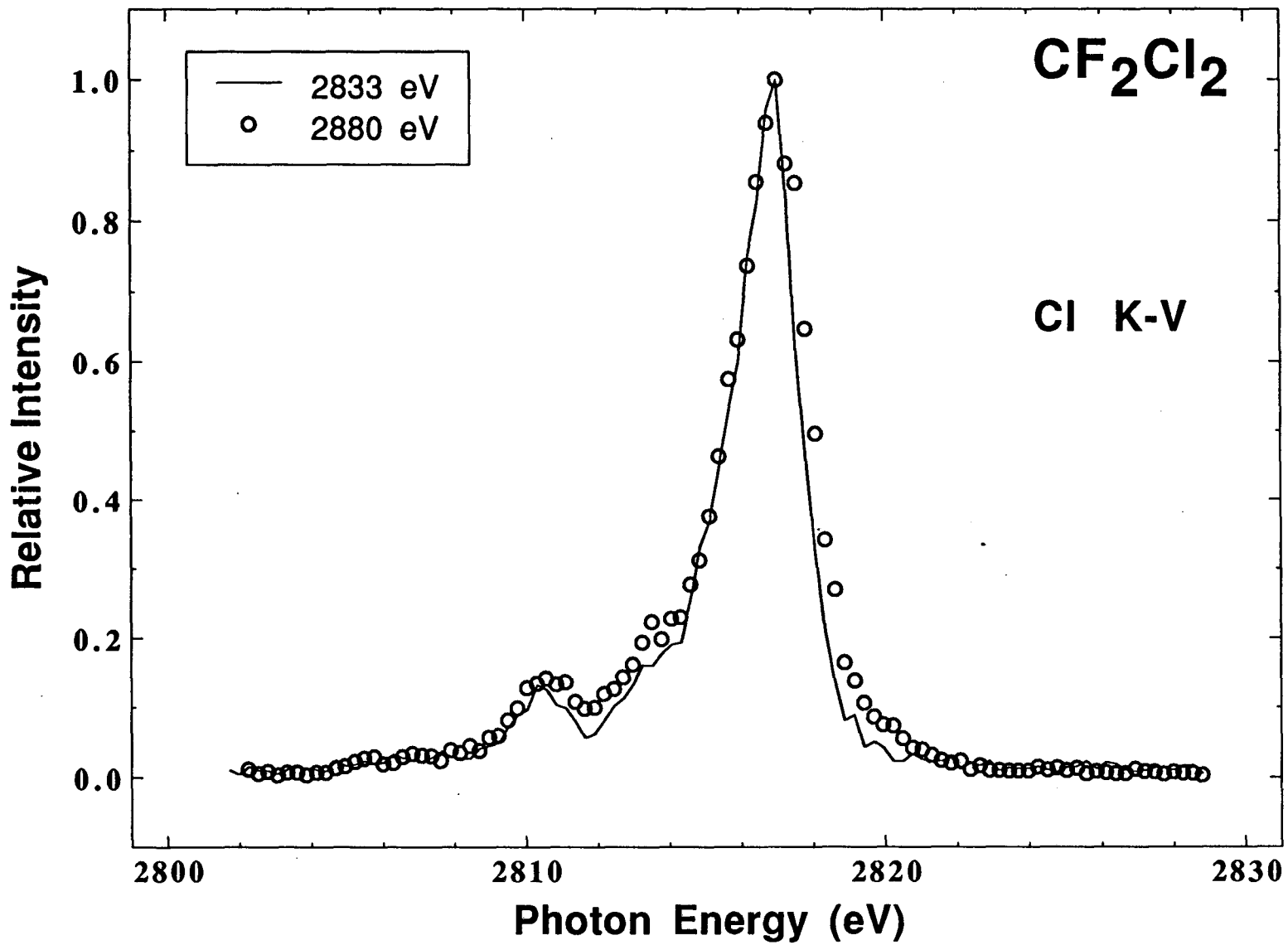
XBL 896-2299

Figure 1



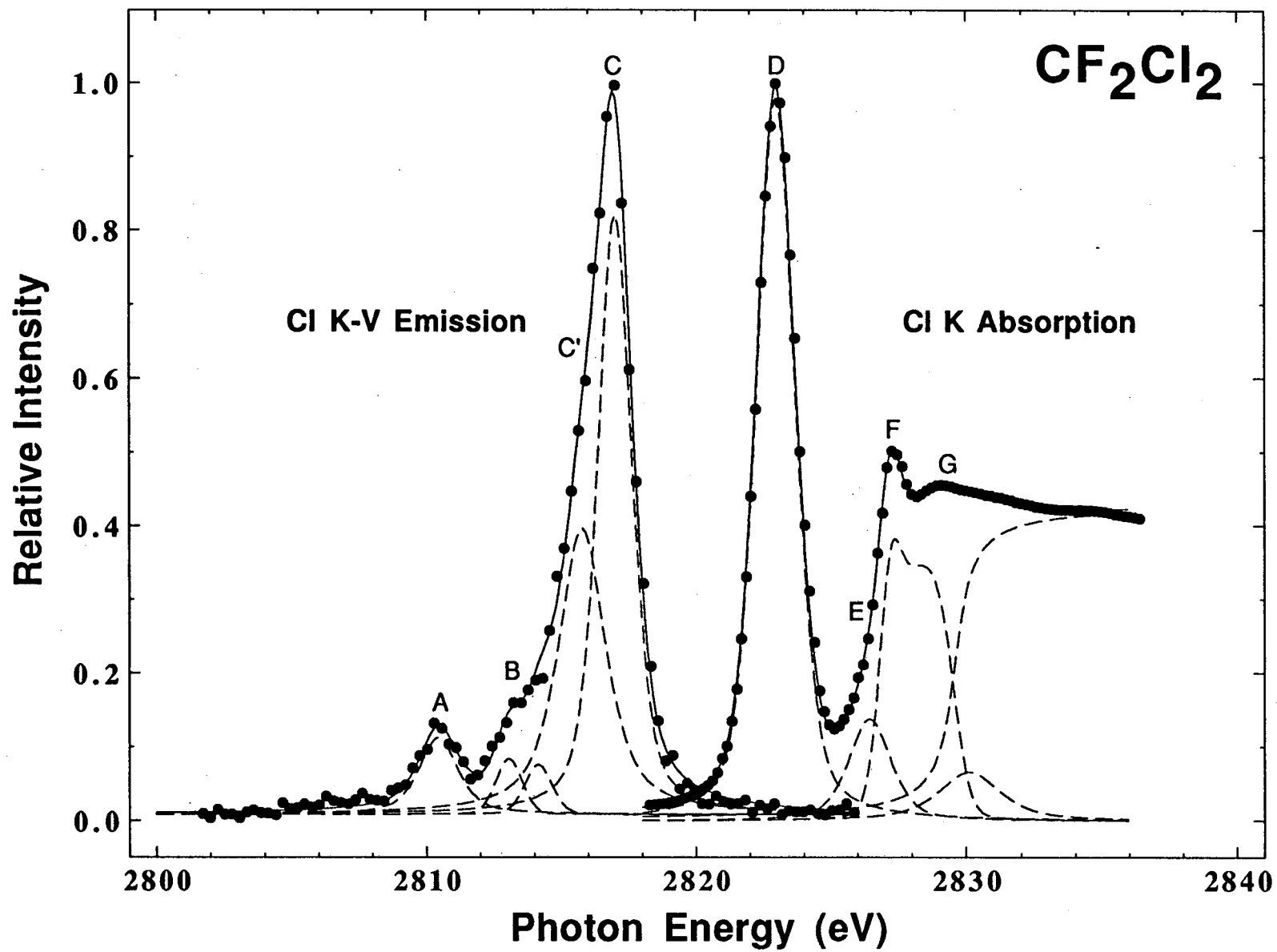
XBL 896-2302

Figure 2



XBL 896-2300

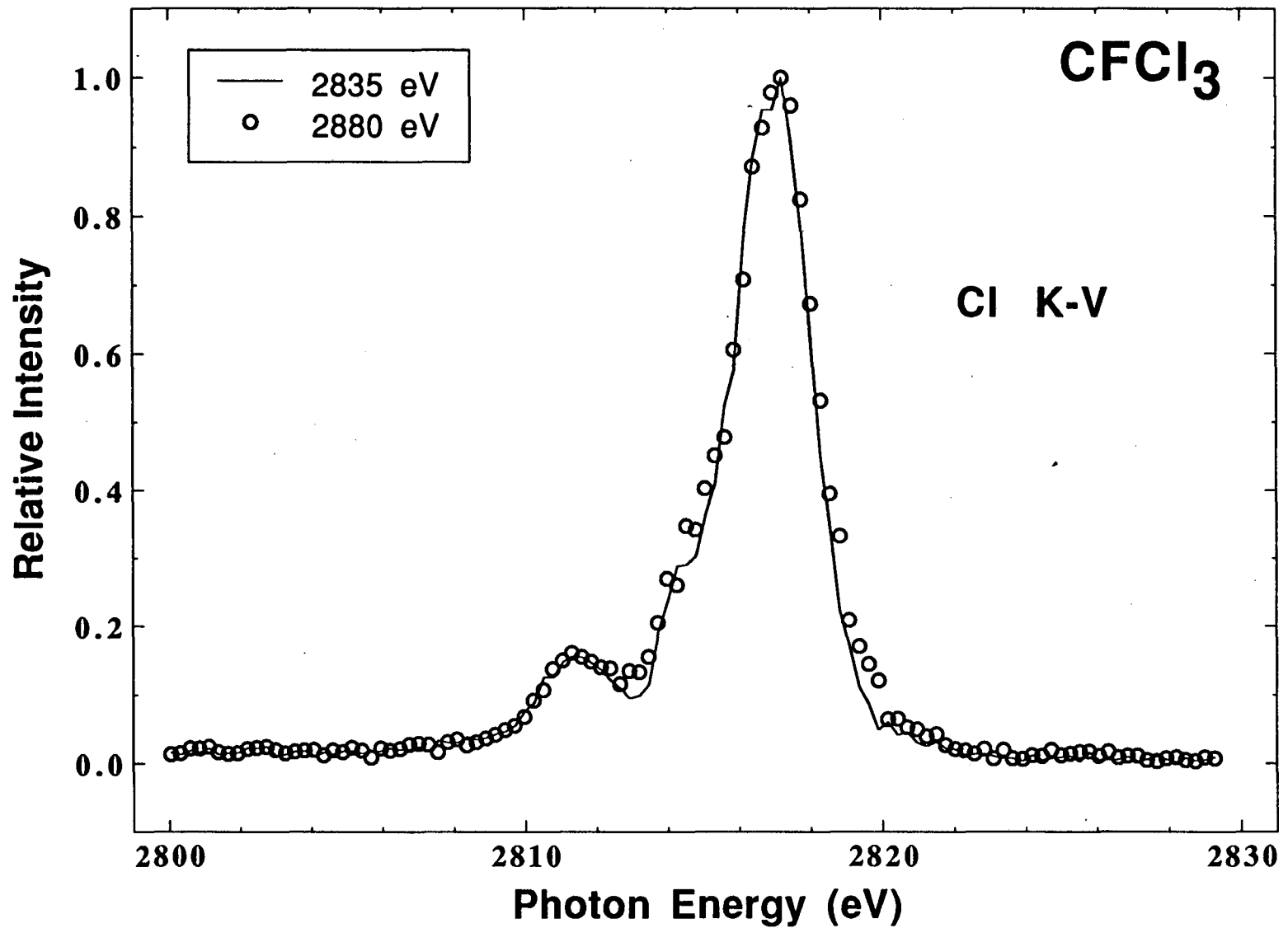
Figure 3



XBL 896-2303

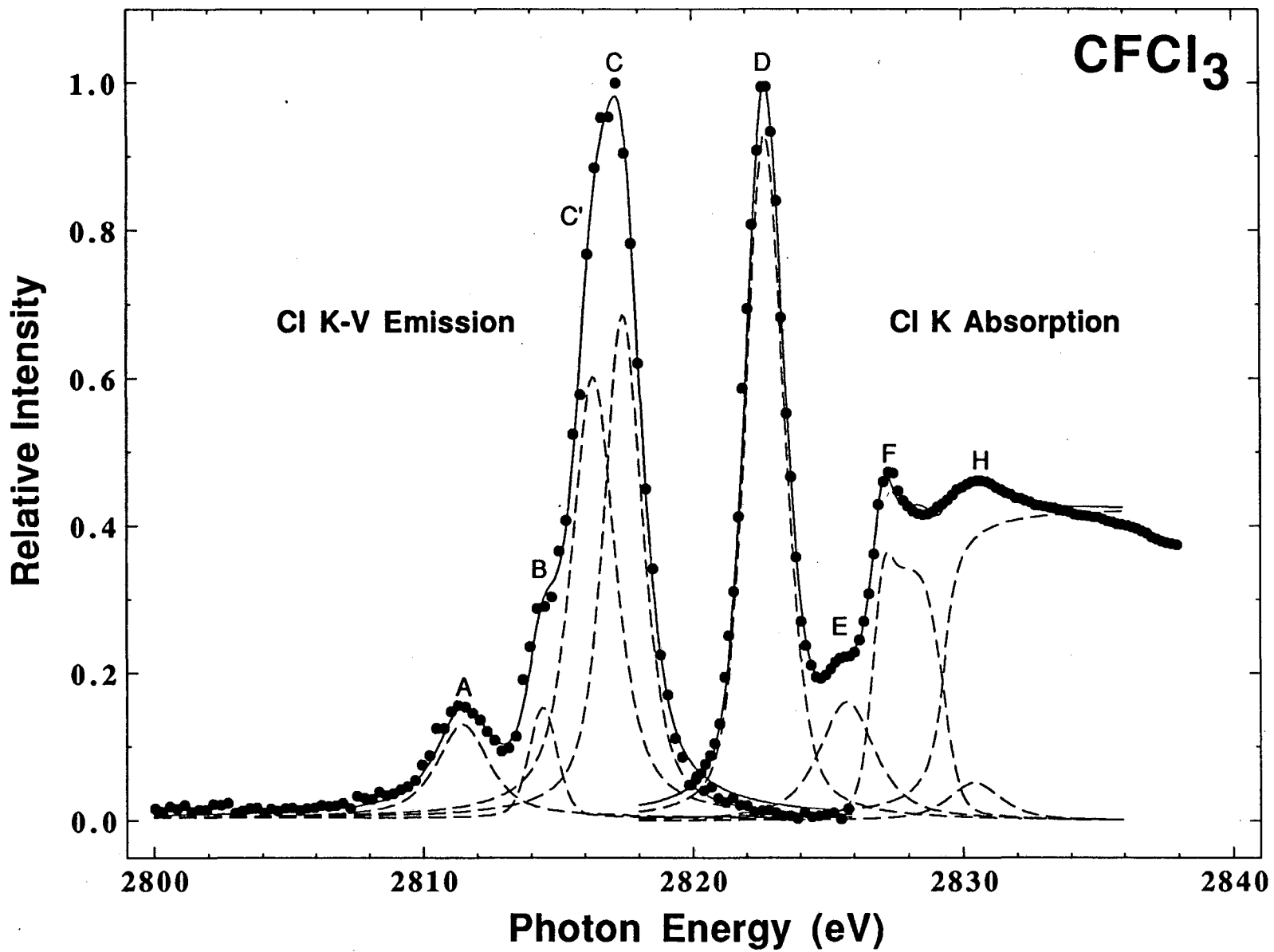
Figure 4





XBL 896-2301

Figure 5



XBL 896-2304

Figure 6

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