SINGLE AND MULTIPLE VACANCY EFFECTS IN MOLECULAR X-RAY SPECTRA

R. Lavilla, R. Deslattes

To cite this version:

R. Lavilla, R. Deslattes. SINGLE AND MULTIPLE VACANCY EFFECTS IN MOLECULAR X-RAY SPECTRA. Journal de Physique Colloques, 1971, 32 (C4), pp.C4-160-C4-164. <10.1051/jphyscol:1971429>. <jpa-00214630>

HAL Id: jpa-00214630
https://hal.archives-ouvertes.fr/jpa-00214630
Submitted on 1 Jan 1971

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
SINGLE AND MULTIPLE VACANCY EFFECTS IN MOLECULAR X-RAY SPECTRA

R. E. LAVILLA and R. D. DESLATTES

National Bureau of Standards, Washington, D. C. 20234

Résumé. — Nous discutons le spectre d'émission X Kβ des gaz moléculaires en utilisant l'exemple particulier de CH₃Cl. A l'aide d'une détermination expérimentale grossière de seuil, nous montrons que les processus à vacances multiples sont du côté des hautes énergies des raies spectrales saillantes de l'émission Kβ de Cl dans CH₃Cl. D'après un récent calcul d'orbitale moléculaire, les raies d'émission moléculaires Kβ de Cl s'identifient aux orbitales 3 e et 7 a₁ de CH₃Cl. Le spectre d'émission K de valence peut être interprété pour l'essentiel au terme de transitions à un électron et une vacance simple des couches internes vers les différentes orbitales moléculaires extérieures, la position de la raie spectrale et son intensité dépendant du niveau d'énergie moléculaire, de la symétrie et du recouvrement des orbitales. Pour étendre les études d'émission X moléculaires aux séries L des sulfures et chlorures, nous avons mesuré les spectres L₂₃ de l'argon afin d'étudier la réponse instrumentale dans cette région. Une extra-particularité remarquable de l'émission aux basses énergies a été trouvée dans le spectre L₂₃ de l'argon. Une particularité semblable est également observée dans l'émission L₂₃ de Cl et de K dans KCl. Ces extra-particularités sont interprétées comme preuves d'un processus à deux électrons.

Abstract. — The X-ray Kβ emission spectra from molecular gases is discussed with the use of a particular example, CH₃Cl. With the help of a crude threshold experiment, the multiple vacancy processes are shown to be on the high energy side of the prominent spectral lines in Cl Kβ emission from CH₃Cl. From a recent molecular orbital calculation, the Cl Kβ molecular emission lines are identified as the 3 e and 7 a₁ orbitals of CH₃Cl. The valence K emission spectra can be interpreted for the most part in terms of one electron single vacancy transitions from inner shells to the various outer molecular orbitals, where the spectral line position and intensity are dependent on the molecular term value, symmetry and orbital overlap. In the course of extending the X-ray molecular emission studies to the L series of sulphur and chlorine we measured the L₂₃ spectra from argon gas to study the instrumental response in this region. A prominent extra low energy emission feature was found in the Ar L₂₃ spectra. A similar feature is also observed in the L₂₃ emission of Cl and K from KCl. These extra features are interpreted as evidence of a double electron process.

In contrasting the study of X-ray spectra from free molecules and molecular ions in solids, the X-ray spectra of polyatomic molecular gases may be amenable to a possibly easier and more complete interpretation. This possibility arises from the fact that gaseous molecular X-ray spectra would not be complicated by solid state effects, and that there may be considerably more experimental control of decomposition of the specimen upon which the measurement is being made. Therefore, the resulting gaseous molecular X-ray spectra would have a better resolved spectral line distribution and be more reliably representative of the system presumed under investigation. The X-ray spectra of molecular gases thus provides an attractive subject for further attempts to elucidate the processes of X-ray emission and absorption.

Over the past few years, we have obtained X-ray spectra in both emission and absorption from several families of molecular gases, namely chlorinated ethylenes, chloro-fluoro-methanes [1, 2, 3] and a number of molecules [4, 5] containing various numbers of atoms of sulphur, oxygen, fluorine, carbon and hydrogen. We have investigated the valence-K region for most atoms in these molecules and certain valence-L regions. In this paper we shall report on some of these emission spectra.

The main process in the valence-K emission spectra is the radiative filling of a single inner shell vacancy by an electron from one of the outer molecular orbitals. The distribution of the emission lines and their relative intensity are, naturally, dependent on the molecular symmetry and the orbital overlap.

Figure 1 is an illustrative example of some chlorine Kβ emission molecular spectra obtained in fluorescence. These measurements [4] were made with primary radiation from a silver anode operating at
SINGLE AND MULTIPLE VACANCY EFFECTS IN MOLECULAR C4-161

**FIG. 1.** - An illustrative sampling of a few Cl $K\beta$ molecular emission spectra from some chlorinated hydrocarbon gases. Included is a spectrum (b) from a film of polyvinyl chloride. The energy zero is set to coincide with Cl $K\alpha$ peak from KCl (not shown).

2-3 kW on a double crystal spectrometer [7] using calcite crystals. The spectrum in b is from a film of solid polyvinyl chloride, the others are from gas phase systems. All have only one chlorine atom per molecule or molecular unit. The comparison gives a graphic example of the range of structure in the $K\alpha$ emission from chlorinated molecular gases with the sole emitting atom, chlorine, located in a variety of different environments.

In addition to the five molecular systems in figure 1, we obtained in fluorescence the chlorine $K\beta$ molecular emission spectra from a number of other chlorinated ethylene and chloro-fluoro-methane gases [4], and the sulphur $K\beta$ molecular emission from a number of sulphur compounds [5], all on a double crystal spectrometer. We also obtained the oxygen $K\alpha$ and fluorine $K\alpha$ molecular emission spectra from some oxygen and fluorine containing molecular gases. The oxygen and fluorine $K\alpha$ emission spectra were excited by direct electron bombardment at 10 kV and 100 mA. This was done by crossing the electron beam with a continuous flow of gas from a conventional slit nozzle. The radiation was dispersed by a vacuum single crystal planar Bragg spectrometer using a KAP crystal, and detected by a flowing gas proportional counter followed by conventional electronic data logging with automated step-scanning.

To study the contributions of multiple vacancy processes to X-ray molecular emission spectra, a rather crude threshold experiment was conducted on a few of the chlorinated molecular gases. An example of these experiments is the chlorine $K\beta$ emission of CH$_3$Cl shown in figure 2. The measurements [2, 3]

**FIG. 2.** - The threshold study of the Cl $K\beta$ molecular emission from CH$_3$Cl. The solid line is the emission measured with the primary radiation from a Ag anode, the circles from a Pd anode. The two spectra are normalized to equal heights of the highest peak.

were made with the primary radiation sources of Ag (solid line) and Pd (circles) anodes operating at 2-3 kW, on a double crystal spectrometer [6]. In these experiments, we take advantage of the fact that the Pd $L\alpha$ group lies close to the chlorine $K\delta M$ thresholds, while the Ag $L\alpha$ group is at a much higher energy. The profiles as shown in figure 2 are normalized to equal heights at the highest peak. It is quite apparent that the intensity distribution of the difference between the two profiles lies on the high energy side of the main lines in the region of the well-known satellite, $K\alpha$.. This satellite, $K\beta\alpha$, prominent in the Cl $K\beta$ emission of alkali chlorides, is a complex multiplet, due to multiple vacancy transitions [7]. Thus, although there are high energy satellite ($k\delta M \rightarrow MM$) contributions to the Cl $K\delta$ emission from molecular CH$_3$Cl, these experiments demonstrate that the origin of the low energy peak is not a multiple vacancy process.

If we assume that the two peaks in figure 2 result from a transition between a single inner shell vacancy and an outer molecular orbital ($s \rightarrow p$ like transitions), then the main peak in figure 2 is the transition from the most easily ionized orbital of CH$_3$Cl, and can be identified as the 3 $e$ orbital made up of the chlorine lone-pair 3 $p$ electrons. The next most easily ionized orbital in the CH$_3$Cl scheme is the 7 $a_1$, made up
primarily of the C-Cl σ bonding orbital. An approximate Hartree-Fock calculation for CH₃Cl by Krause [8] determined the energy separation of the 3_e and 7_a₂ orbitals to be 2.7 eV. The separation as determined from the photoelectrons spectra of CH₃Cl is 3.16 eV [9]. From figure 2, the measured separation of the two peaks is 3.0 eV, in reasonable agreement. Accepting the identification of Cl Kβ emission peaks, we can then obtain the binding energy of the chlorine K shell electron by adding the observed ionization potential of the 3_e orbital (11.3 eV) [9] to the photon energy at which it occurs in the X-ray emission experiments. A comparison of K shell binding energies calculated in this way for a family of molecules, when the data is available, is a far better measure of any chemical effects to the K shell level by chemical combination than emission line shifts.

On the assumption that multiple vacancy production in general is about the same as in the few molecules we studied, we have correlated the peak positions and relative intensities in the valence-K emission spectra with the orbital energies and population analysis from various available molecular orbital calculations and the peak positions with the orbital binding energies ascertained from photoelectron spectra of the individual molecules. We conclude that the prominent features of the valence-K emission spectra can be interpreted [10] as a result of one electron single vacancy transition, whose relative position and intensity is dependent on the binding energy and contribution of electrons from the constituent atom to the particular molecular orbitals of the system. This immediately suggests the possibility of constructing a fairly complete term system within the limits of the selection rules.

With this possibility in mind we proceeded to make some minor necessary changes in the instrument used for our oxygen and fluorine studies to extend our X-ray molecular emission measurements to the sulfur and chlorine L₂,₃ region (50-80 Å).

In order to get a measure of the instrumental performance in this long wavelength region, we measured the L₂₃ - M₁ emission from argon gas, whose K series spectrum is reasonably well understood. The surprising spectra we obtained suggested the further measurement of the chlorine and potassium, L₂₃ spectra from KCl, with the same setup. The analyzing crystal used in these measurements was a lead myristate (2d = 80.5 Å), Langmuir-Blodgett type multilayer analyzer.

In figure 3 are shown the L₂₃ emission spectra from argon gas, and chlorine and potassium from KCl. The error bars indicate the range of scatter of repeated measurements. The dashed line in the K(KCl) is the estimated shape of the low energy tail of carbon Kα from pump oil on the KCl crystal. Beneath the Ar and K(KCl) spectra are indicated the Ly (L₂₋1M₁) and Li (L₃₋1M₁) splitting and the positions of the known 2s levels in Ar II and K III relative to 3s 3p⁶ 2S. Above the main peak in the Ar spectrum is indicated the region where double vacancies would appear.

and the carbon Kα from graphite. The rising background under the K L₂₃ spectrum is the tail of the broad carbon Kα emission from pump oil deposited on the KCl specimen.

The separation of the low energy feature from the main peak is about 6, 11, 14 eV in Cl, Ar and K, respectively. The peak separations for Cl and K in KCl are in good agreement with some early measurements in the 1930's by Siegbahn and Magnusson [11]. The
low energy peak in the Ar L\textsubscript{23} spectra has not been previously observed to our knowledge. From energy systematics the main peak in Ar can be identified as containing the unresolved L\textsubscript{\eta} and L\textsubscript{I} doublet due to a single vacancy. By analogy, a similar identification is made for the Cl and K main peak.

To help elucidate the origin of the low energy peak it would be desirable to do a threshold experiment on the L\textsubscript{23} spectrum from Ar. However, in this region of the spectrum such experiments are far more difficult than in the 3-5 Å region. For the case of solids in this spectral region, some threshold experiments have been reported in the literature. Henke and Smith [12], using a carbon coated anode for primary radiation recorded a fluorescent Cl L\textsubscript{23} spectrum from NaCl that is very similar to our Cl L\textsubscript{23} spectrum from KCl. Crisp [13] noted no change in the relative peak intensity of a similar low energy peak in the L\textsubscript{23} spectrum from potassium metal when the excitation voltage was reduced below the K shell binding energy of potassium. We can therefore conclude that a K shell vacancy in the ion, that may lead to multiple vacancies, is not responsible for the prominent features of the L\textsubscript{23} spectra.

With the active collaboration of Dr. John W. Cooper, of NBS, the low energy feature is interpreted as direct evidence of a «semi-Auger» two electron process. Bloch [14], Cady and Tomboulian [15], had postulated such a process, whereby an inner shell hole is filled by an outer shell electron and simultaneously another outer shell electron is excited, with the emission of a single photon. A related process a «radiative Auger effect» has recently been reported by Åberg and Utairainen [16], in the K shell emission from Al, Si and S. However, in contrast to the L\textsubscript{23} emission, the intensities of the «radiative Auger effect» features in K emission are < 1 % of the parent line, whereas, the low energy feature in the L\textsubscript{23} emission (Fig. 3) is more than 10 % of the parent line.

The low energy structure in Figure 3 is attributed [17] to the strong mixing of the final state configuration 3 s 3 p\textsuperscript{6} 2S with the even levels 3 s\textsuperscript{2} 3 p\textsuperscript{4} ns\textsuperscript{2} 2S and 3 s\textsuperscript{2} 3 p\textsuperscript{4} nd\textsuperscript{2} 2S. Plotted below the Ar and K L\textsubscript{23} spectra are the positions of all the known 2S levels in Ar II and K III relative to 3 s 3 p\textsuperscript{6} 2S. These levels were taken from C. Moore's Atomic Energy Levels [18]. The corresponding levels for CI \textsubscript{I} are not known.

The possible interpretation in terms of double vacancies has been considered also. Above the Ar spectra in figure 3, is indicated the range of energies where double vacancy transitions (L\textsubscript{23} M\textsubscript{23} → M\textsubscript{1} M\textsubscript{3}) would appear. These possible positions were obtained from the L\textsubscript{1} and L\textsubscript{23} Auger spectra on Ar, by Melhorn [9]. The early X-ray emission measurements of Cl L\textsubscript{23} spectra by Siegbahn and Magnusson, with higher resolution, suggest the presence of these double vacancy transitions more clearly. Needless to say such double vacancies can be produced by Coster-Kronig transitions or shake-off processes.

Hence, the L\textsubscript{23} single vacancy can radiatively be filled by a single electron process L\textsubscript{23} → M\textsubscript{1}, or a double electron process where one M\textsubscript{23} electron fills the L\textsubscript{23} vacancy with the simultaneous excitation of another electron to conserve parity. Ehlerl and Mattson [20], have reported the Cl L\textsubscript{23} molecular emission spectra from a number of chlorinated methane molecules. These spectra exhibit a feature about 6-7 eV below the main peak that could be interpreted as due to a double electron rather than a single electron process. The identification of this double electron process in solid KCl, and an appearance of similar features in the Cl L\textsubscript{23} spectra of other simple chlorides [21], and in K metal [13], suggests its importance in X-ray emission spectra of other solids. Its presence in the spectra of other elements of the periodic table and various other chemical combinations of them remains to be investigated.

In conclusion, the results of the interpretive work on the L\textsubscript{23} emission spectra in figure 3 do not contradict the conclusions of the possibilities of the valence-K molecular emission spectra. However, the hope of extending our study in a straightforward manner to the L\textsubscript{23} region has been complicated by the presence and magnitude (~~ 10 % of the parent line) of a second process in the decay of single inner shell vacancies. It is possible that the close coupling of the 3 s and 3 p electrons for Cl and K will be considerably lessened when the atoms are in different chemical combinations than those already cited above. This is suggested by the changes in relative intensity of the low energy peak in the Cl L\textsubscript{23} spectra of a number of different chlorides reported by Fischer and Baun [21] and the structureless intensity on the low energy side of the main peak in the Cl L\textsubscript{23} spectrum of the polymer Saran by Henke and Smith [12].

Acknowledgement. — We would like to thank Dr. M. Krause for many valuable discussions during the course of this work.

References

recently given a molecular orbital interpretation to the molecular X-ray emission spectra from some hydrocarbons and carbon oxide molecules.


