# Multivacancy Effects in Atomic and Molecular Spectra\*

### Richard D. Deslattes

National Bureau of Standards, Gaithersburg, MD 20899, U.S.A.

#### Abstract

Chemical applications of X-ray spectra are inhibited by the general occurrence of multivacancy processes. These manifest themselves in emission spectra as extra lines (or satellites) while opening of channels to these initial configurations leads to extra detail in absorption spectra. While there are a few simple cases where this situation has been more or less fully discussed, the more interesting areas are those which are both not simple and not understood. There is, however, a fairly general experimental procedure by which this complex situation could, in principle, be clarified. This involves carrying out high resolution emission spectroscopy as a function of exciting photon energy in regions containing both single and multiple vacancy thresholds. In earlier work summarised here, it was possible to demonstrate the procedure for a monatomic gas, argon. Subsequently, we have built and now operate a beamline designed specifically for such studies at the National Synchrotron Light Source (NSLS) in Brookhaven. Very recent results from this line and from a few experiments using conventional sources are summarised.

### 1. Introduction

The technical resources needed for systematic study of photon and electron emission spectra near single vacancy thresholds using photon excitation are only now becoming available. Clearly this statement applies more emphatically to the case of multiple vacancy thresholds. In both cases threshold behaviour as seen in photon-excited spectra are richer in detail than those observed with electron excitation. In the case of multiple vacancy thresholds, the advantage of photon experiments is even greater since there are many additional ways of energy sharing, the evidence of which would be effectively eliminated by an excitation mode allowing all configurations below the input energy.

We have now commissioned a beamline at the Brookhaven NSLS, designed particularly for studying threshold behaviour of photon and electron emission spectra (Cowan *et al.* 1986). Operation of this facility began rather recently and no appreciable body of results exists to date although some initial data have been obtained. While it might be possible to present several specific expectations which could be tested with this apparatus, I prefer to give some historical perspective on how we were led to undertake the exercise. From this point of view, perhaps one can see more clearly why an understanding of multiple vacancy threshold behaviour is important for future progress in the application of X-ray spectroscopy in non-trivial circumstances.

\* Paper presented at the Specialist Workshop on Excited and Ionised States of Atoms and Molecules, Strathgordon, Tasmania, 3-7 February 1986.

### 2. Historical Remarks

For somewhat more than 30 years I have from time to time entertained some fairly elementary questions about X-ray spectra as they are found in atoms, molecules and simple solids. Actually my progress in this area has been entirely backwards since I began with the belief common in the thirties and forties that X-ray spectroscopy was a tool 'at the ready' for the investigation of solid state band structures. Everyone knows this story very well since it still appears in texts. Specifically the emission bands are said to reflect the density of occupied states and the absorption fine structure of the corresponding empty levels except, of course, for symmetry restrictions.

Already by 1950 it was clear that things were going wrong whenever attempts were made to compare experiment and theory in reasonably well-understood circumstances, even slightly away from the 'good' metals which had supported the simple analysis in the first place. X-ray emission satellites were widely known, of course, and I was told as a student that with experience these could be readily identified. Faith in the efficacy of such experience got rather shaken by a controversy involving Lymann Parratt, John Slater and others about which of the two strongest lines in the K $\beta$  region of Cl in KCl was the parent single vacancy transition and which was the satellite. The point was that band calculations were already defensible in the mid-fifties to the extent that everyone agreed that the strong  $\beta$  line (ostensibly the parent) was too narrow for the conventional interpretation to be sustained while its weaker companion not only had an acceptable width but also an agreeable shape! This observation left only the problem of explaining the intense narrow line which was not only bigger than its presumptive parent but lay on the 'wrong' side. It was ultimately possible to resolve this part of the controversy by means of a crude form of threshold spectroscopy making use of a group of X-ray sources (La lines mostly) lying close to the K-edge of Cl (Deslattes 1964*a*, 1964*b*).

Two distinct realities remained after that work: firstly I wished never again to repeat such an arduous exercise and secondly the absorption spectrum lay completely untouched, rich in structure and incomprehensible since elementary associations expected on the basis of (rigid) band theory were not evident. At the same time two other independent efforts had identified avenues which clearly invited pursuit. Firstly the work of Snell and Pleasonton (1955) showed that production of single vacancy states was a possible but unlikely outcome of photoionisation. Secondly, Schnopper (1963) and later Wuilleumier (1965) saw unmistakable evidence of absorption structure that could only arise from the opening of a double vacancy channel or channels.

### 3. Molecular X-ray Spectra

In the absence of today's technology for synchrotron radiation, LaVilla and I began to study emission and absorption spectra of simple molecules and simple molecular families looking for regularities among homologous sequences and hoping that the multivacancy problems would not overwhelm the effort. We implicitly adopted the point of view ultimately developed by Manne (1970) regarding molecular emission spectra: inner vacancies on different atomic sites 'see' electrons from the valence molecular orbitals yielding emission intensities proportional to the symmetry-restricted MO amplitude at the atomic vacancy site. For absorption spectra we assumed that the approach of Hartree *et al.* (1934), already shown to be adequate for  $GeCl_4$  and GeBr<sub>4</sub>, could be rigorously extended to a large class of analogues including, for example, SF<sub>6</sub> (LaVilla and Deslattes 1966; LaVilla 1972).

Both unfortunately and fortunately, the experimental results were richer than expected. Their study, especially near threshold, formed part of the fabric that led Fano and collaborators, via various 'barrier' concepts, to the consideration of states of the 'inner well' and the 'outer well'. Although each of these developments was interesting and each experiment seemed to teach a little, nowhere was it easy to reach a comprehensive point of view from which X-ray spectra could emerge as a source of information rather than a sink thereof.

## 4. Experimental Approach toward Clarifying Experimental Data

Clearly in all X-ray spectra there are emission features due to multiple vacancy and/or multiply excited initial configurations. Similarly it is highly likely that at least some, and probably many, of the details seen in near-edge absorption spectra are due to the threshold behaviour of processes leading to these configurations. Similar expectations also hold for electron spectra excited by either electrons or photons near the energetic thresholds for double or multiple vacancy configurations.

A rather general approach to clarify the spectra would be to build a high flux, high resolution primary monochromator and equip its target region with high resolution photon and electron spectrometers. In a rudimentary manner, one could imagine reducing the primary photon energy to a value at which multiple vacancy production would be energetically forbidden. In this case emission satellites due to multiple vacancy initial configurations should be extinguished. Then as the exciting photon energy is increased through the various ionisation thresholds, satellites belonging to these configurations should appear, gradually increasing the complexity of the observed spectrum but in an informative way. At the same time, features in the absorption spectrum would tend to identify themselves as corresponding to such satellite processes. In fact, by noting the resemblance of yield spectra with absorption cross section, one could, in principle, omit those components of the absorption spectrum due to any identifiable emission process by assuming either a constant fluorescence yield or one whose energy dependence was otherwise determined.

Although this general line of argument appears almost tautologous, it needed demonstrating before we undertook an expensive and long-term effort to realise an appropriate dedicated beamline (now installed at the NSLS, Brookhaven). The prototype experiment was carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). Although long plagued by difficulties, this experiment ultimately succeeded in producing data which not only largely validated our conceptual framework but yielded as well a richer array of phenomena than we expected. This experiment and indeed all our detailed studies to date were carried out on atomic argon for reasons which will emerge in the following section.

### 5. Atomic Argon

In an over-worked phrase, the K series of atomic argon is the 'hydrogen atom' of X-rays. We were led to its re-examination by a wish to assure ourselves (and others) that our basic expectations could be realised in this simple case. In point of fact there were extreme constraints at SSRL on windows and beamline vacuum (none permitted) that rendered work at the chlorine and sulfur edges completely impossible,

while even at the argon edge we were in a region where available flux was steeply falling. Suffice it to say that the argon experiment was finally successful at SSRL only after extensive development of an efficient fluorescence spectrometer combining focusing crystal optics with a position-sensitive proportional counter and with the use of a multipole wiggler source during dedicated beamtime (Deslattes *et al.* 1983).



Fig. 1. Overview of the argon K absorption spectrum together with illustrations of K $\beta$  emission spectra as obtained when the incident beam is set at the places indicated. The KM region referred to below is the aggregate structure seen in the vicinity of 20 eV above the initial absorption resonance.

In general, our expectations were fully realised as indicated in Fig. 1. Satellites of  $K\beta_{1,3}$  are clearly extinguished below the double vacancy threshold and generally turn on about where one would expect on the basis of satellite-parent separation. Even at this crude level, one is left with a few qualitative puzzles. One asks why there is the rapid decrease in cross section between K and KM (see caption). This question has been addressed by Manson and Inokuti (1980) and Amusia *et al.* (1981) but more recently in a rather satisfying analysis by Tulkki and Åberg (1985). Also one asks how  $\beta''$  appears both 'simple' and to require a triple vacancy initial state. The answer appears to be that the three-hole state needed belongs to the neutral atom and is thus an isolated level rather than a manifold.

When one begins to look at the KM region in more detail, its complexity becomes both obvious and daunting. As seen in Fig. 2, this region, as obtained earlier at SSRL (Dyall and LaVilla 1986) and more recently at the NSLS, is structurally rich with hints of Fano profiles and some features resembling pre-edge Rydbergs and edges.



Fig. 2. An expanded view of the KM region showing obvious complexity. Configurations suggested are due to calculations by Dyall and LaVilla (1986).

### 6. Data from Molecules

Although a considerable body of emission and absorption spectra for molecular gases can be found in the literature, the fraction of these in which excitation diagnosis was performed is extremely small. At present I have no results from what is possibly the only beamline apparatus specifically designed to produce such results. Nonetheless, especially before it was possible to contemplate a dedicated beamline for such studies, results could be obtained using characteristic X-ray lines with (when needed) appropriate absorption filters. Several years ago I carried out such an experiment on crystalline KCl (Deslattes 1964*a*, 1964*b*), while LaVilla and I used the same technique in identifying the satellite features of the Cl K $\beta$  region in CH<sub>3</sub>Cl and CH<sub>2</sub>CHCl (Deslattes and LaVilla 1967; LaVilla 1982).

Still more recently, Perera *et al.* (1985) used a Pd target filtered by Ru and a curved crystal, spectral imaging instrument to obtain data on  $CH_3Cl$  with good statistics as illustrated in Fig. 3. This excitation energy, although not very precisely defined, is rather close to the single vacancy threshold and yields spectra relatively free of satellites.

Without this kind of selective excitation, one typically obtains spectra such as those illustrated in Fig. 4. In the case of these simple systems, the main satellite of the non-bonding emission line is fairly obvious. What is less obvious is that the other MO emission lines have relatively strong satellites underlying and distorting their higher energy neighbours. In less simple systems the general situation is far less clear but the resolution and intensity precision evidently available clearly offer hope for orbital analysis, if the confusing effects of multivacancy emission processes can be suppressed.



Fig. 3. The K $\beta$  region and K absorption of Cl in CH<sub>3</sub>Cl obtained with an imaging spectrometer and position sensitive detector. Excitation was primarily by Pd L $\alpha_1$  with use of a Ru filter to further lower the excitation energy so that multivacancy production is suppressed (Perera *et al.* 1985).



Fig. 4. Examples from early work in which spectra were produced with high excess energies leading to satellite production, part of which is evident due to its separation from the single vacancy MO group. Other satellites are likely to be present also distorting both relative intensities and positions of the predominantly single vacancy emission bands. The Cl K $\beta$  absorption of HCl is from Gilberg (1970) and the Cl K absorption of HCl is from Stephenson *et al.* (1951). The S K $\beta$  and K absorption of H<sub>2</sub>S are from LaVilla (1975).

The approach to satellite suppression or diagnosis described above is clearly limited to instances in which there is a fortuitous relationship between characteristic lines of tractable anode materials and absorption thresholds for elements of interest. Besides that, there is no evident way to reach the origins of absorption features. Both limitations are overcome in the case of the continuous tuneability and good energy resolution available at synchrotron light sources.

### 7. First Results and Outlook

In test runs with our new apparatus at NSLS we returned to atomic argon both as a bench-mark and because we had not extended the earlier work in detail to the K $\alpha$  spectrum and to the sub-threshold Raman process. In most respects the results to date confirm the earlier work while showing improved detail in response to design changes. There is already one very striking aspect of the data which we had not anticipated but seems qualitatively reasonable. The unexpected result was seen in the K $\alpha_{1,2}$  spectrum as the primary excitation energy was tuned through the pre-edge Rydberg features. Subtle changes would not have been unexpected, but those found were very dramatic indeed concerning both sharper than normal doublet spectra and spectra in which there was little hint of an underlying doublet at all. Also, it is surprising that these large changes in emission spectra were brought about by changing primary excitation energies in steps of 0.1-0.2 eV.

The overall conclusion I offer is that the originally designed program for solving multivacancy effects in molecular spectra and spectra from (at first) simple solids remains a valid exercise with results near at hand. At the same time it appears that we need to be alert for surprises along the way, perhaps as unexpected as the effects noted for the argon  $K\alpha_{1,2}$  spectrum.

#### Acknowledgments

I am grateful for timely assistance in preparing this report from my colleagues R. LaVilla, P. Cowan and S. Brennan.

### References

Amusia, M. Ya, Ivanov, V. K., and Kupchenko, V. A. (1981). J. Phys. B 14, L667.

Cowan, P. L., Brennan, S., Deslattes, R. D., Henins, A., Jach, T., and Kessler, E. G. (1986). Nucl. Instrum. Methods A 246, 154.

Deslattes, R. D. (1964 a). Phys. Rev. 133, A390.

Deslattes, R. D. (1964 b). Phys. Rev. 133, A399.

Deslattes, R. D., and LaVilla, R. E. (1967). Appl. Opt. 6, 39.

Deslattes, R. D., LaVilla, R. E., Cowan, P. L., and Henins, A. (1983). Phys. Rev. A 27, 923.

Dyall, K. G., and LaVilla, R. E. (1986). The argon K suprathreshold structure. *Phys. Rev.* A 34 (in press).

Gilberg, E. (1970). Z. Phys. 236, 21.

Hartree, D. R., Krönig, R. DeL., and Peterson, H. (1934). Physica 1, 895.

LaVilla, R. E. (1972). J. Chem. Phys. 57, 899.

LaVilla, R. E. (1975). J. Chem. Phys. 62, 2209.

LaVilla, R. E. (1982). 'Advances in X-ray Spectroscopy', p. 240 (Pergamon: New York).

LaVilla, R. E., and Deslattes, R. D. (1966). J. Chem. Phys. 44, 4399.

Manne, R. (1970). J. Chem. Phys. 52, 5733.

Manson, S., and Inokuti, M. (1980). J. Phys. B 13, L323.

Perera, R. C. C., Barth, J., LaVilla, R. E., Deslattes, R. D., and Henins, A. (1985). Phys. Rev. A 32, 1489.

Schnopper, H. W. (1963). Phys. Rev. 131, 2558.

Snell, A. H., and Pleasonton, F. (1955). Phys. Rev. 100, 1396.

Stephenson, S. T., Krogstad, R., and Nelson, W. (1951). Phys. Rev. 84, 806.

Tulkki, J., and Åberg, T. (1985). J. Phys. B 18, L489.

Wuilleumier, F. (1965). J. Phys. (Paris) 26, 776.

Manuscript received 4 February, accepted 14 April 1986