

X-Ray L<sub>82,15</sub> Emission Spectrum of Ru in Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>R.C.C. Perera\*, J. Barth<sup>#</sup>, R.E. LaVilla<sup>o</sup>, and C. Nordling<sup>+</sup>\* Center for X-Ray Optics, Lawrence Berkeley Laboratory,  
University of California, Berkeley, CA 94720 USA# IBM Thomas J. Watson Research Center, Yorktown Heights,  
NY 10598 USAo Quantum Metrology Group, National Bureau of Standards,  
Washington, DC 20234 USA+ Institute of Physics, University of Uppsala, Box 530,  
S-751 21, Uppsala, Sweden

One of the broader applications of synchrotron radiation has been to EXAFS studies for material structure determination, i.e., for an analysis of x-ray absorption over an extended energy region beyond a core ionization limit. Studies of the near edge structure (XANES) give a different type of information, characteristic of the local symmetry and electronic configuration of the absorbing atom. This type of information is reflected also in the x-ray emission spectra, in particular for transitions involving the valence levels. Examination of the near edge absorption or the emission spectrum does not require an instrument capable of scanning a wide energy range with high counting statistics, as does EXAFS; the needs are rather for good resolution and a reliable calibration of the energy scale.

Some of the problems of near edge spectra were particularly evident in our investigation of Ru-L<sub>82,15</sub> emission from Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>. The Ru-L<sub>82,15</sub> emission was measured with a laboratory Rowland circle x-ray spectrometer with a curved quartz (1010) crystal (radius = 22 inches) in a fixed position appropriate to the energy range, and a position sensitive detector which can be positioned along the Rowland circle [1]. The Ru spectrum was excited mainly by Sn-L<sub>α</sub> primary radiation from a Sn anode in a demountable x-ray tube operating at 13 kV and 120 mA. The resolution of the instrument in this region is 1.5 eV. An accurate calibration of the energy scale was conveniently obtained by measuring a reference x-ray emission line in the same instrumental configuration. In the present case the Pd-L<sub>α</sub> emission line [2] at 2838 eV was used to establish the energy scale. The energy dispersion of the instrument was determined from the Cl-K<sub>β</sub> emission spectrum of CH<sub>3</sub>Cl between 2810 eV and 2830 eV [1] and Pd-L<sub>α1,2</sub> and extrapolated to the energy region of the recorded emission spectrum.

Figure 1 shows a composite of our experimental Ru-L<sub>82,15</sub> emission spectrum and the corresponding Ru-L<sub>III</sub> absorption recorded by Sham in a recent investigation using the focussed EXAFS spectrometer at SSRL [3,4]. In the Ru-L<sub>III</sub> absorption spectrum the peak labelled A was assigned to a transition to the partially occupied t<sub>2</sub>(4d<sup>5</sup>) orbital [3,4]. The emission spectrum corresponds to transitions involving the same orbital and also, the e(4d) and a<sub>1</sub>(5s) orbitals with relatively higher binding energies. One would usually expect the peak A to have an energy position at or above the high energy edge of the emission spectrum, in contrast to Fig. 1.

MASTER

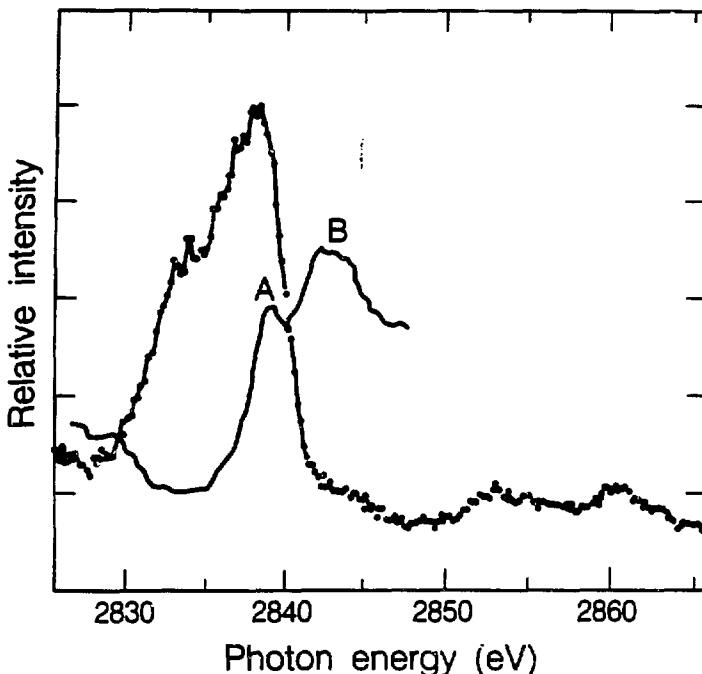


Figure 1. A composite of the measured Ru-LB<sub>2,15</sub> emission spectrum (left) and Ru-L<sub>III</sub> absorption spectrum (A & B structures) from Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> displayed on the calibrated emission spectrum energy scale. Binding energy measurement (see text) suggest a 2 to 3 eV shift of the Ru-L<sub>III</sub> absorption to a higher energy.

This observation suggested an investigation of the binding energies in Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> to precisely place x-ray absorption and emission spectra on a common energy scale. Due to the energetic coincidence between the Pd-L<sub>o</sub> emission line and the Ru-L<sub>III</sub> binding energy in the metal [5] we were able to use this energy as a fixed reference point to which other binding energies from Ru compounds are connected by relative measurements.

We determined the Ru-L<sub>III</sub> binding energy for Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> by means of an X-Ray Photoelectron Spectroscopy (XPS) measurement using Ti-K<sub>α</sub> radiation on "Kratos XSAM-800" instrument. The samples were physically mixed with finely divided silver to provide an experimental silver L<sub>III</sub> binding energy to correct for charging of the sample. We determined that the Ru-L<sub>III</sub> binding energy for Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> to be 2840.4 ± 0.8 eV, which is a chemical shift of +2.4 eV relative to Ru metal. The Ru-L<sub>III</sub> binding energy agrees well with the fluorescence emission spectrum (Fig. 1) in that the inflection point of the high energy edge is at the same energy position. Thus, we suggest a shift to the Ru-L<sub>III</sub> absorption spectrum from Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> by 2 to 3 eV towards higher energy [6].

Beyond the implications of this result for the particular compound studied, we conclude with some general remarks. A conventional laboratory spectrometer would be useful as a complementary tool for the investigation of near edge absorption spectra since it provides information about the occupied states and reliable energy calibration with the help of reference emission lines. This is of interest for synchrotron radiation experiments in general where the energy calibration of monochromators is a continuing problem due to the heating of the dispersive crystals by the absorbed x-ray power.

#### Acknowledgments

We would like to thank R.D. Deslattes for his encouragement and continuing interest in this study and S. McCartney for the binding energy measurements. One of the authors (R.C.C.P.), acknowledges support by the U.S. Department of Energy (Contract No. DE-AC03-76SF00098).

#### References

1. R.C.C. Perera, J. Barth, R.E. LaVilla, R.D. Deslattes, and A. Henins: (to be published).
2. J.A. Bearden: Rev. Mod. Phys. 39, 78 (1967)
3. T.K. Sham: J. Am. Chem. Soc. 105, 2269 (1983)
4. T.K. Sham and B.S. Brunschwig in "EXAFS and Near Edge Structure," eds., A. Bianconi, L. Incoccia, and S. Stipcich (Springer Verlag, Berlin 1983)
5. J. Barth, R.C.C. Perera, R.E. LaVilla, and C. Nordling: (to be published).
6. Our suggested shift appears to be within the limits of accuracy of the energy calibration of the absorption measurement which was extrapolated from the Pd-L<sub>III</sub> edge at 3173 eV (T.K. Sham: private communication).

#### **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.