

Multiple Atom Resonant Photoemission: A New Tool for Determining Near-Neighbor Atomic Identities and Bonding

A. W. Kay^{1,2}, E. Arenholz^{2,3}, B. S. Mun^{1,2}, J. Garcia de Abajo^{2,4}, C. S. Fadley^{1,2},
R. Denecke^{1,2,5}, Z. Hussain², and M. A. Van Hove²

¹Department of Physics, University of California, Davis, CA 95616

²Materials Sciences Division and Advanced Light Source,
Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA 94720

³The Miller Institute, University of California, Berkeley, CA 94720

⁴Permanent address: Departamento de CCIA y Departamento de Fisica de Materiales,
Universidad del Pais Vasco/EHU, 20080 San Sebastian, Spain

⁵Present address: Lehrstuhl fuer Physikalische Chemie II, Universitaet Erlangen-Nuernberg, Erlangen, Germany

INTRODUCTION

Recent experiments have provided evidence of a previously unconsidered resonant process between interatomic electronic levels [1]. The process is conceptually similar to the well-known resonant phenomena between electronic levels within a single atom. However, the multiple atom nature of the new phenomenon is expected to make the process useful as a tool for studying near-neighbor bonding information.

The mechanism involved in multiple atom resonant photoemission (MARPE) is best introduced by comparison with the familiar single atom case (SARPE). In the SARPE case, it is known that as the photon energy is tuned across a given level in an atom, the photoemission from another less deeply bound level may be significantly enhanced [2, 3, 5, 6]. As an example, consider the case of atomic Mn shown in Fig. 1. In this case, the Mn3d photoemission is enhanced as the photon energy crosses the deeper Mn3p level. The Mn3p level is excited into Mn3d but decays, producing an electron of the same energy as if the Mn3d had been directly excited by the photon. This process is then providing a second coherent channel for the Mn3d to photoelectron process. The figure presents experimental [3] and theoretical [5] results for this particular process.

In the case of MARPE, we find that the two levels involved in the resonance do not need to be associated with the same atom. In Fig. 2A, the process is diagrammed for the case of O1s resonating with Mn2p_{3/2,1/2}. As depicted in the figure, the photon energy must be sufficient to excite the Mn2p_{3/2} and 2p_{1/2} electrons into a Mn3d level. The process couples to the O1s when the Mn3d decays back to Mn2p, simultaneously producing an electron from the O1s level with the same energy as if the photon had directly excited an O1s electron.

As the absorption edge of Mn2p_{3/2} is crossed, we experimentally find the O1s intensity to be enhanced by a factor of about 11% when integrated over the entire range of the Mn2p_{3/2} contribution. For comparison, the SARPE case shown in Fig. 1B indicates an overall enhancement of the Mn3d intensity of about 63% when similarly integrated across the extent of the effect.

EXPERIMENT

All experimental data was recorded at the Advanced Photoelectron Spectrometer/Diffractometer on beamline 9.3.2 of the Advanced Light Source in Berkeley [8,9]. The beamline allows photon energy to be selected between 30 to 900 eV. For these experiments, linearly polarized light was chosen. This instrument allows significant degrees of freedom in the experimental geometry. A sample manipulator permits an arbitrary sample angle relative to the spectrometer acceptance (or photon incidence). Furthermore, a rotatable Scienta ES200 analyzer allowed the analyzer acceptance and photon incidence to be adjusted independent of the manipulator degrees of freedom.

Samples used in this study were single crystal MnO(001), single crystal Fe₂O₃(001), and La_{0.7}Sr_{0.3}MnO₃(001). Photoelectron diffraction measurements confirmed each sample to have a highly ordered surface and allowed precise orientation of the sample geometry during subsequent measurements [8].

For clarity, we will discuss the experimental method in the specific case of an MnO sample where the O1s level (binding energy ~530eV) is in resonance with the Mn2p_{3/2} and 2p_{1/2} levels (binding energies ~639 and 650eV). The details may be trivially modified to apply to subsequent examples. We are interested in the variation of the O1s peak intensity as the photon energy is scanned through the Mn2p edge. We recorded an O1s spectrum for incremental photon energies across the Mn 2p range: 634 to 657eV. For each peak, the

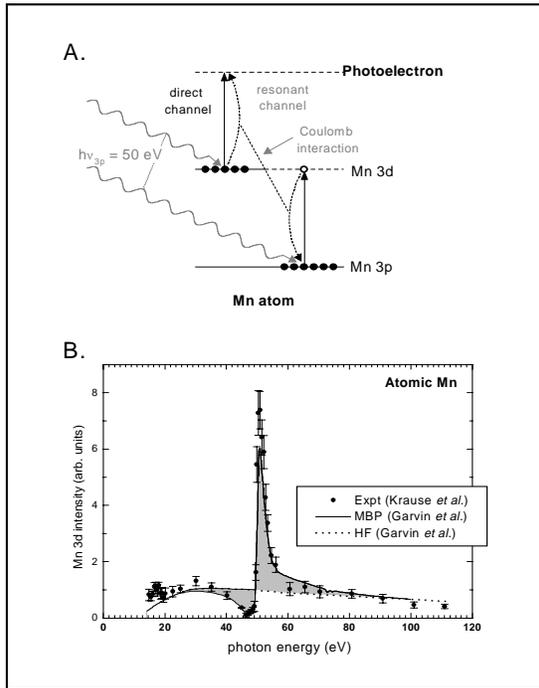


Figure 1:

- A. Single Atom resonant photoemission (SARPE) for the case of Mn3d emission from atomic Mn with the resonance occurring via the mn3p level. The direct excitation is indicated by the solid arrow from the Mn3d to the continuum while the resonant process is shown by the solid arrow between the Mn3p and 3d levels and the dashed arrows representing the autoionization decay.
- B. The measured variation of the Mn3d emission with photon energy (solid points) shown with Hartree-Fock (HF) and many-body perturbation theory (MBPT) theoretical models. By defining the nonresonant contribution by a smoothly varying background through photon energy range of about 30 to 87eV, we find the integrated resonant contribution to be 63% above the nonresonant contribution.

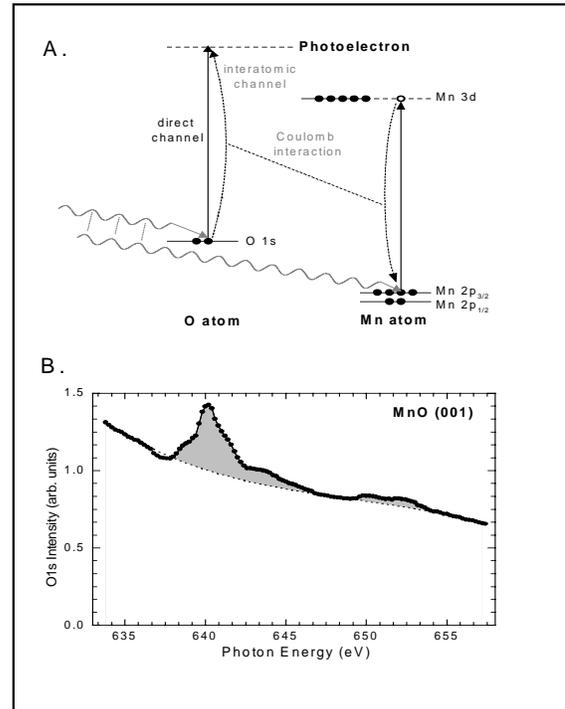


Figure 2:

- A. Multi-atom resonant photoemission for the case of O1s emission from MnO, with the resonance occurring via the Mn2p_{3/2} level (or at a slightly higher photon energy, also the Mn2p_{1/2} level). The solid arrow from the O1s level to the continuum indicates the direct excitation. The resonant process is indicated by the other arrows, showing a Mn2p to Mn3d excitation along with the decay and coupling back to O1s to continuum excitation.
- B. Our measured variation of the O1s intensity over the Mn2p_{3/2} and Mn2p_{1/2} edges. The nonresonant intensity is given by the smoothly varying background (dashed line) through this region. In this case, the resonant contribution is 11% above the nonresonant background.

inelastic background was then subtracted and the curve fit in order to obtain the peak intensity (area). Fig. 3A shows examples of such fit curves for the particular cases of on- resonance and off-resonance. This intensity as a function of excitation energy is plotted in Fig. 2B, showing the MARPE enhancement as a deviation from a smooth non-resonant background. From this curve, we remove the contribution of the non-resonant background by subtraction of a smooth polynomial and setting of the new baseline to unity as shown in Fig. 3C. Note in Fig. 3A that the O1s peak lies on an inelastic background whose magnitude varies across the Mn2p edge. The variation of this background is a measure of the X-ray absorption of the Mn2p levels as illustrated by Fig. 3B where the background level as a function of photon energy is compared to previous measurement of the X-ray absorption by Butorin, et al [7].

RESULTS

The three samples used in this investigation allowed us to observe interatomic resonance between a variety of levels. In the MnO sample, we measured the previously discussed O1s resonance with the Mn2p_{3/2} and 2p_{1/2} levels. As indicated in Fig. 3B and discussed above, our extracted X-ray absorption coefficient exhibits excellent agreement with previous work. Referring to Fig. 3C, the resonance contributes up to 43% to the O1s photoelectron intensity with an overall enhancement of 11% across the entire Mn2p_{3/2} level.

In the Fe₂O₃ sample, we observe the O1s resonance with the Fe2p_{3/2} and 2p_{1/2}. Again, our X-ray absorption coefficient matches previous work, in this case by Kuiper et al [10]. The resonance enhancement of the O1s intensity is here as large as 62% and integrates to 24% across the Fe2p_{3/2} portion of the effect.

Figure 3

- A. O1s photoelectron spectra taken on (hollow points) and off (solid points) resonance, $h\nu = 640.2$ eV and 637.6 eV respectively. Note the increased inelastic background on resonance (dashed curves).
- B. X-ray absorption coefficient for MnO, as measured in this study from the energy dependence of the inelastic background under the O1s spectra (solid curve) and from ref.7 (dashed curve).
- C. O1s intensities above inelastic background for normal emission as a function of $h\nu$, with the smoothly varying nonresonant intensity at each energy (see Fig2B) subtracted and set to unity. Note the similar results for two different incident photon angles (solid and dashed curves).
- D. X-ray absorption coefficient for Fe_2O_3 over the $\text{Fe}2p_{3/2}$ and $2p_{1/2}$ levels as measured in this work (solid curve) and from ref. 10 (dashed curve).
- E. O1s intensity in resonance with $\text{Fe}2p_{3/2}$ and $2p_{1/2}$ for Fe_2O_3 after normalization of the nonresonant contribution. Note the difference between the solid and dashed curves, obtained at varied electron entrance angle and fixed photon-electron angle.

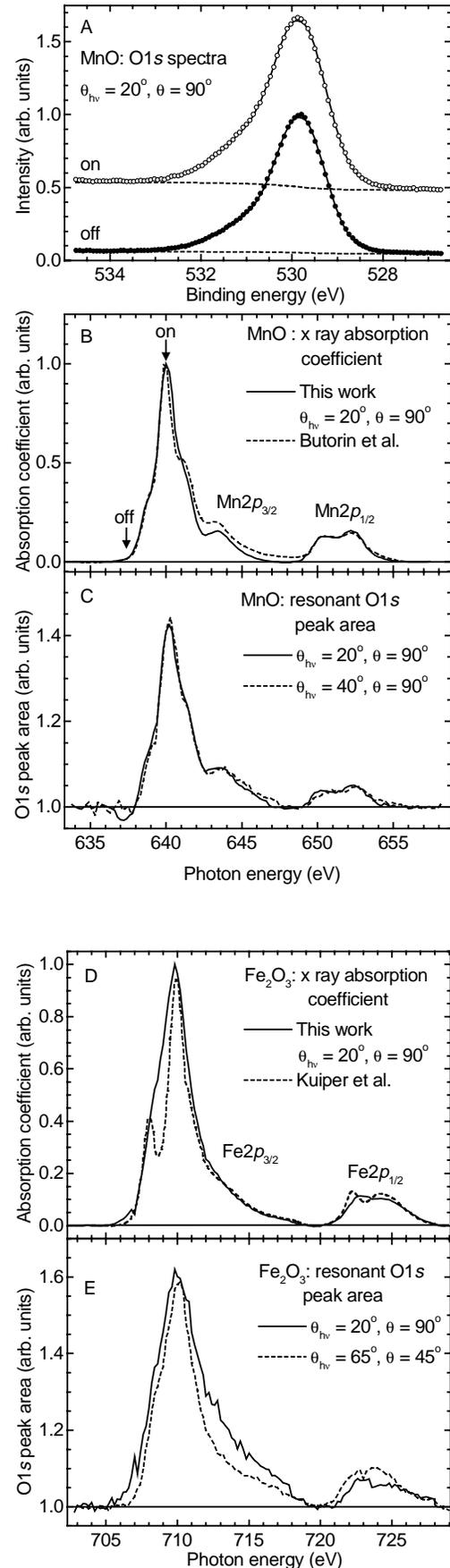
The $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ sample provided another example of O1s resonating with the Mn2p levels. In this case, the effect was as large as 33% and integrated to 17% over the Mn2p_{3/2}. Resonance between the O1s and the La3d_{5/2,3/2} levels exhibited O1s enhancements of up to ~100% and an integrated effect of 29% over the La3d_{5/2} edge. Finally, resonance between the Mn2p and the La3d_{5/2,3/2} levels show a maximum and integrated enhancement of 60% and 20%, respectively. In each case, we were able to demonstrate agreement of our own extracted X-ray absorption coefficient with previous results [11, 12, 13].

DISCUSSION

For each case considered above, the resonance enhancement or MAPRE signal is seen to be a significant contribution to the non-resonant intensity. Through monitoring of the inelastic background intensity upon which the photoelectron peak lies, the X-ray absorption coefficient of the level may be reliably extracted. Note also the similarity between the x-ray absorption profile and the MARPE profile. The MARPE signal closely if not exactly follows the x-ray absorption in each case studied.

In Fig. 3C, note that the resonance profile has been measured for two cases differing only in the incident photon angle. Within the statistics of the experiment, the curves are indistinguishable. This is important evidence that the effect is in fact due to MARPE and not to any X-ray attenuation length changes as the edge of the deeper level is crossed.

In Fig. 3E, we demonstrate evidence for angular dependence in the resonance effect. For two different photoelectron emission angles, the resonance curves have similar, but obvious differences. Furthermore, the energy integrated magnitude of the effect differs: over the $\text{Fe}2p_{3/2}$ portion of the curve, the normal emission case ($\theta = 90^\circ$) shows an enhancement of 24% compared to 17% for the 45° off-normal emission case.



CONCLUSIONS

Future study of this effect promises to be quite rewarding. The very existence of the MARPE effect, especially at the magnitudes so far observed, is inherently interesting. Further investigations of the effect are therefore justifiable simply to further understand the basic process.

Even more interesting is the potential of this effect to be used as a quantitative tool in determining near-neighbor bond information. Initial theoretical calculations have indicated that the resonance will be primarily between near-neighbor atoms and the magnitude of that effect will be very sensitive to the atomic separations.

In both cases, it will also be interesting to observe the effect in new systems and with different methods. Besides the photoelectron spectroscopy used to record the presented data, one could observe the secondary Auger electrons emitted in process. Similarly, the secondary fluorescent photons could also be monitored, with the experiment then becoming much more bulk sensitive.

ACKNOWLEDGMENTS

We are indebted to M. P. Klein and J. Kortright for helpful discussions, and the S.A. Chambers and K. Krishnan for providing samples used in these experiments.

REFERENCES

- [1] A. Kay, et al., *Science*, 281 (1998), 679.
- [2] U. Fano and J. W. Cooper, *Rev. Mod. Phys.* 40, 493 (1968).
- [3] M. O. Krause, et al., *Phys. Rev. A* 30, 1316 (1984), and references therein.
- [4] L. J. Garvin, et al., *J. Phys. B* 16, L269 (1983).
- [5] A. Tanaka and T. Jo, *J. Phys. Soc. Jpn.* 63, 2788 (1994), and references therein.
- [6] M. Weinelt, et al., *Phys. Rev. Lett.* 78, 967 (1997), and references therein.
- [7] S. M. Butorin, et al., *Phys. Rev. B* 54, 4405 (1996).
- [8] C. S. Fadley, et al., *Prog. Surf. Sci.* 54, 341 (1997), and references therein.
- [9] Z. Hussain, et al., *J. Electron Spectrosc. Relat. Phenom.* 80, 401 (1996).
- [10] P. Kuiper, et al., *Phys. Rev. Lett.* 70, 1549 (1993).
- [11] A. Kay, et al., data not shown.
- [12] M. A. Brewer et al., *Advanced Light Source Compendium of User Abstracts and Technical Reports*, Report LBNL-39981, UC-411 (Lawrence Berkeley National Laboratory, Berkeley, CA, 1997), p. 411; K. Krishnan, personal communication.
- [13] B. T. Thole, et al., *Phys. Rev. B* 32, 5107 (1985).

This work has been supported by the Office of Energy Research, Material Sciences Division, of the U.S. Department of Energy, under contract DE-AC03-76F00098. Additional support from the Miller Institute (E. A.), the D.F.G.-Germany (R. D.), and the Basque Government (F. J. G. deA.) is gratefully acknowledged.

Principal investigator: C. S. Fadley, Department of Physics, University of California, Davis. Email: csfadley@ucdavis.edu or csfadley@lbl.gov. Telephone: 510-486-5446.