

CONF-881002-32
For publication in the Proceedings of the Fourth International Laser Science Conference (ILS-IV)
(Advances in Laser Sciences - IV) Mariott Marquis Hotel, Atlanta, Georgia, October 2-6, 1988, to be
published by the American Institute of Physics

**MULTIPHOTON IONIZATION PHOTOELECTRON
SPECTROSCOPY OF XENON:
EXPERIMENT AND THEORY***

DEC 1 1988

S. J. Bajic and R. N. Compton
*Chemical Physics Section, Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37831-6125
and Department of Chemistry, The University of Tennessee
Knoxville, Tennessee 37996*

X. Tang, A. L'Huiller, and P. Lambropoulos
*Department of Physics, University of Southern California
Los Angeles, California 90089*

CONF-881002--32

November 1988

DE89 004182

*Research sponsored by the Office of Health and Environmental Research,
U.S. Department of Energy under contract DE-AC84OR21400
with Martin Marietta Energy Systems, Inc.

"The submitted manuscript has been
authored by a contractor of the U.S.
Government under contract DE-
AC05-84OR21400. Accordingly, the U.S.
Government retains a nonexclusive,
royalty-free license to publish or reproduce
the published form of this contribution, or
allow others to do so, for U.S. Government
purposes."

DISCLAIMER

MASTER

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.

cr/s
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MULTIPHOTON IONIZATION PHOTOELECTRON SPECTROSCOPY OF XENON: EXPERIMENT AND THEORY

S. J. Bajic and R. N. Compton
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6125
and Department of Chemistry, The University of Tennessee
Knoxville, Tennessee 37996

X. Tang, A. L'Huiller, and P. Lambropoulos
Department of Physics, University of Southern California,
Los Angeles, California 90089

ABSTRACT

Photoelectron energy and angular distributions for resonantly enhanced multiphoton ionization (REMPI) of xenon via the three-photon-allowed $7s[\frac{3}{2}]_1^0$ and $5d[\frac{3}{2}]_1^0$ states have been studied both experimentally and theoretically. The electron kinetic energy spectra give the probability of leaving Xe^+ in either the ${}^2P_{1/2}$ or ${}^2P_{3/2}$ core. The measured branching ratio for leaving each ionic core is used to test the theoretical description of the REMPI process. Measurements of *both* the angular distributions and the [3+1] REMPI via the 5d state are adequately reproduced by multichannel quantum defect theory. However, measurements of angular distributions for the electrons resulting from [3+1] via the $7s[\frac{3}{2}]_1^0$ state into $\text{Xe}^+ {}^2P_{3/2}$ (core preserving) or $\text{Xe}^+ {}^2P_{1/2}$ (core changing) are in striking disagreement with theory.

INTRODUCTION

Coupling experimental and theoretical studies of REMPI and photoelectron spectroscopy (PES) can provide unique information about the photoionization dynamics of excited states. REMPI-PES studies of the rare gases have mostly been confined to xenon primarily because the lowest Rydberg states are easily accessible using available lasers. Recently, Blazewicz et al.¹ have shown that multichannel quantum defect theory (MQDT) can provide an excellent description of the [3+2] and [3+1] REMPI processes via the $\text{Xe } 6s[\frac{3}{2}]_1^0$ and $6s'[\frac{1}{2}]_1^0$ states, respectively. We have extended this work to the $7s[\frac{3}{2}]_1^0$ and $5d[\frac{3}{2}]_1^0$ states of xenon. The apparatus for this experiment has been described elsewhere¹ and will not be discussed here.

RESULTS

Figure 1 shows the energy distribution of the photoejected electrons for the [3+1] REMPI process via the $5d[\frac{3}{2}]_1^0$ level of Xe at 357.6 nm. Electrons with an energy of 1.7 eV dominate the spectrum. This corresponds to a non-core-changing ionization process. In addition, a small signal at 0.4 eV is seen which corresponds to photoelectrons leaving the $\text{Xe}^+ {}^2P_{1/2}$ ionic core. The approximate ratio of the two observed signals is comparable with that predicted from MQDT calculations. Figure 1 also shows the polar plot of the measured angular distribution for the electrons resulting from REMPI via the $5d[\frac{3}{2}]_1^0$ level. The electron signal corresponding to leaving the ${}^2P_{1/2}$ core was

too weak to obtain a reliable angular distribution measurement. Fitting the angular distribution data to a Legendre polynomial expansion required terms up to $P_8(\cos \theta)$:

$$\text{Xe}^+ \ ^2P_{3/2} : I(\theta) = 1 + 1.23P_2 + 0.75P_4 + 0.20P_6 - 0.70P_8$$

The calculated angular distribution from MQDT for the $^2P_{3/2}$ electrons quantitatively reproduces the angular distribution observed in the experiment.

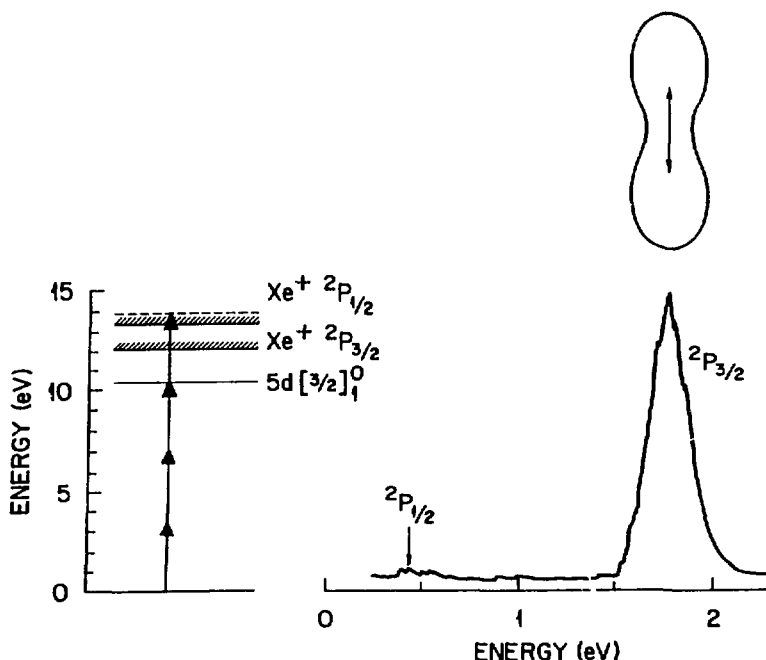


Figure 1. PES and angular distribution for REMPI via the 5d state.

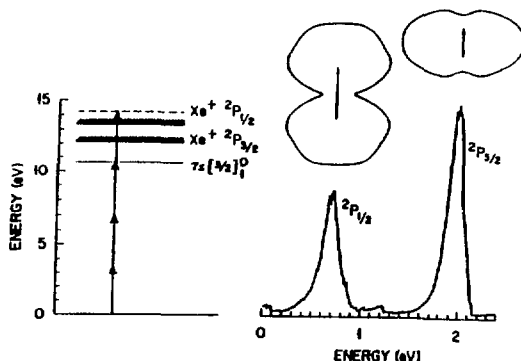


Figure 2. PES and angular distributions for REMPI via the 7s state.

Figure 2 shows the energy distribution of the photoelectrons for the [3+1] REMPI process through the $7s[\frac{3}{2}]_1^0$ state of Xe at 351.1 nm. Two groups of electrons are observed at 0.7 eV and 2.0 eV which correspond to leaving the $\text{Xe}^+ \ ^2P_{1/2}$ and $^2P_{3/2}$ ionic cores respectively. The ratio of the two signals (approx. 2:1) compares favorably with that predicted from MQDT.

The polar plots of the experimental angular distributions for the two groups of electrons are shown above their respective energy distributions. As can be seen, the two groups yield quite different angular distributions. The experimental angular distributions were also fitted to a Legendre polynomial

expansion. It was found that terms up to $P_8(\cos \theta)$ were needed to fit both the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ data.

$$\text{Xe}^+ {}^2P_{3/2} : \quad I(\theta) = 1 - 0.33P_2 + 0.02P_4 - 0.03P_6 - 0.04P_8$$

$$\text{Xe}^+ {}^2P_{1/2} : \quad I(\theta) = 1 + 0.78P_2 - 0.42P_4 + 0.30P_6 - 0.16P_8$$

MQDT calculations semiquantitatively agree with the general shape of the experimental angular distribution for the ${}^2P_{1/2}$ electrons except for a predicted small maxima at $\pi/2$ where a sharp minima is observed in the experiment. MQDT calculations predict that the angular distribution for the ${}^2P_{3/2}$ core-preserving electrons should have a deep and somewhat broad minima at $\pi/2$ and a maxima at 0 and π . However the experiment shows that the angular distribution is somewhat isotropic with an unexpected maxima at $\pi/2$ and minima at 0 and π . This discrepancy is not understood at this time.

Research sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCE

1. P. R. Blazewicz, X. Tang, R. N. Compton, and J.A.D. Stockdale, J. Opt. Soc. Am. B., 4(5), 770 (1987).