

Studies of resonance enhanced multiphoton ionization of molecules

Vincent McKoy

Citation: [AIP Conference Proceedings](#) **225**, 132 (1991); doi: 10.1063/1.40552

View online: <http://dx.doi.org/10.1063/1.40552>

View Table of Contents:

<http://scitation.aip.org/content/aip/proceeding/aipcp/225?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Resonance enhanced multiphoton ionization spectroscopy of carbon disulphide](#)

J. Chem. Phys. **104**, 6117 (1996); 10.1063/1.471277

[Experimental visualization of photoelectron angular distributions](#)

AIP Conf. Proc. **295**, 779 (1993); 10.1063/1.45246

[Photodissociation dynamics probed by laser induced fluorescence or resonance enhance multiphoton ionization](#)

AIP Conf. Proc. **225**, 139 (1991); 10.1063/1.40553

[Multiphoton ionization photoelectron spectroscopy of xenon: Experiment and theory](#)

AIP Conf. Proc. **191**, 466 (1989); 10.1063/1.38663

[Theory of multiphoton ionization of atoms](#)

AIP Conf. Proc. **147**, 169 (1986); 10.1063/1.35983

STUDIES OF RESONANCE ENHANCED MULTIPHOTON IONIZATION OF MOLECULES

Vincent McKoy
California Institute of Technology, Pasadena, CA 91125

In Resonance Enhanced Multiphoton Ionization (REMPI) laser radiation is used to prepare a molecule in an excited state via multiphoton absorption and to subsequently ionize that state before it can decay. A remarkable and significant feature of REMPI is that the very narrow bandwidth of laser radiation makes this process highly selective with respect to both the initial and resonant intermediate state. Coupled with high-resolution and angle-resolving photoelectron spectroscopy, REMPI is clearly an important probe of the photoionization dynamics of molecular excited states at a quantum-state-specific level. Other important applications of REMPI include its use for ultrasensitive and state-specific detection of species and for state-specific production of ions.

In my talk I will discuss some results of our studies of REMPI processes in molecules which we have carried out with many collaborators during the last few years. The objective of these studies is to provide insight into the underlying molecular photoelectron dynamics of these processes and, where possible, a quantitative description and prediction of key spectral features of interest in several experimental studies of REMPI of molecules. I will begin by giving a brief and physically motivated overview of the theoretical methods we have developed for carrying out these studies. This will include a discussion of our procedures for obtaining the molecular photoelectron orbitals which play a key role in studies of this type. I will then use several examples which illustrate the kind of objectives we have and the progress we have made. An outline and some highlights of these examples are as follows:

(i) *anomalous or non-Franck-Condon ion vibrational distributions*: non-Franck-Condon behavior in the vibrational distributions of ions produced by REMPI introduces serious complications into such important applications of this technique as its use for state-specific production of ions and for the determination of state populations from ion signals. For example, the resonant level in many REMPI schemes is often chosen to be a molecular Rydberg state. Photoionization of such states is generally expected to occur with the preservation of vibrational quantum number due to the similarity of the neutral and ionic potential energy surfaces.¹ Important exceptions to this behavior can arise from the presence of autoionizing and shape resonances in the photoionization continuum. I will present results of studies of such anomalous vibrational ion distributions seen in (3+1) REMPI of H₂ via the $C^1\Pi_u$ state² and which are due to electronic autoionization of the dissociative $^1\Pi_g(1\sigma_g 1\pi_u)$ state³⁻⁵ and in (2+1) REMPI of O₂ via the $C^3\Pi_g$ state⁶ where they arise from the combined presence of a σ_u shape resonance and autoionization by repulsive valence states.^{7,8} These effects arise solely from consideration of final-state photoioniza-

tion dynamics. I will also report on studies of significant non-Franck-Condon ion vibrational distributions in REMPI of OH and NH which arise from a combination of rapid changes in Rydberg orbital character at intermediate to larger internuclear distances and the presence of Cooper minima.⁹ These effects are predicted to be a common occurrence in first-row diatomic hydrides.^{10,11}

(ii) *rotational distributions of molecular ions*: Coupled with high-resolution and angle-resolving photoelectron spectroscopy, rotationally resolved REMPI provides a very significant window on quantum-state-specific photoionization dynamics. These rotational ion distributions directly reflect the angular momentum coupling in photoelectron orbitals which arises from the torques exerted by nonspherical potentials associated with molecular ions. Such angular momentum mixing can be expected to exert a strong influence on the photoionization dynamics and to lead to rotational distributions which cannot be accounted for on the basis of an atomic-like model of the photoionization of resonant Rydberg orbitals. I will illustrate such non-atomic-like behavior with results of studies of the rotational distributions of ions produced in REMPI of NO via high J levels of the $A^2\Sigma^+(3s\sigma)$ and $D^2\Sigma^+(3p\sigma)$ states.¹²⁻¹⁵ For the $A^2\Sigma^+$ state I will also show photoelectron angular distributions for individual rotational levels of the ions which will be seen to be ready fingerprints of the different partial wave composition of the photoelectron associated with each ion rotational level.^{16,17} Furthermore, these photoelectron angular distributions depend strongly on the alignment created in the resonant state. These results illustrate the striking loss of information when the rotational state of the ion is not resolved in such experiments.

I will also discuss several examples which show the striking influence that rapid orbital evolution of a resonant Rydberg orbital with internuclear distance and the presence of Cooper minima exert on rotational ion distributions. I will illustrate the role of orbital evolution with results of studies of the ion rotational distributions produced by REMPI of CH via its $E'^2\Sigma^+$ state where the Rydberg orbital changes primarily from $3p$ character at small internuclear distances to predominantly $3s$ character at larger internuclear distances.¹⁸ This orbital evolution results in a dramatic dependence of the partial-wave composition of the transition moment with internuclear distance, i.e., from even waves (s, d, \dots) at small distances to odd waves (p, f, \dots) at larger distances. Due to the selection rules¹⁹ governing changes in the rotational quantum number between the intermediate and final ion state, ΔN , and the partial wave component of the photoelectron orbital, ℓ , this orbital evolution leads to a very strong dependence of the ion rotational distributions on the vibrational state accessed in the resonant state.¹⁸

In our next examples we will see how the presence of Cooper minima in the photoelectron matrix element can exert significant influence on the ion rotational distributions.²⁰ At these Cooper minima specific partial wave components of the photoionization matrix element go through zero. On the basis of selection rules governing angular momentum changes between the resonant and final ion state

and the photoelectron angular momentum ℓ we can again expect to see a very strong dependence of ion rotational distributions in regions of Cooper minima. In fact, we will see that this behavior could be exploited to achieve a high degree of ion rotational selectivity in some cases.²⁰

(iii) *circular dichroism in photoelectron angular distributions from aligned molecular states*: We have recently shown that photoelectron angular distributions resulting from ionization of aligned linear molecules should be dichroic, i.e., angular distributions from optically aligned resonant states are different for photoionization by left- and right-circularly polarized light.^{21,22} This circular dichroism in angular distributions (CDAD) –defined as the difference between angular distributions for photoionization with right- and left-circularly polarized light– arises in the electric dipole approximation and should be a direct signature of the alignment of the molecule.^{21,22} Furthermore, CDAD is due only to interference between degenerate photoelectron continua differing by ∓ 1 in their m values for linear molecules. Initial estimates showed that these CDAD spectra from optically aligned rotational levels of the $A^2\Sigma^+$ state of NO should be about 15-25% of the “right” or “left” photoelectron spectra, suggesting that measurements were possible.²¹ I will report on the results of joint theoretical and experimental studies of these CDAD spectra in optically aligned NO ($A^2\Sigma^+$)²³ and in ground state NO ($X^2\Pi$) where the alignment is induced by photodissociation of CH₃ONO (ref. 24). These results establish the utility of the CDAD method for probing chemical processes in which spatial alignment plays a role.

As a final example I will show that CDAD, resulting from REMPI of an aligned molecular state, can be a highly sensitive probe of the presence of Cooper minima.²⁵ I will illustrate this potentially useful application of CDAD with results of studies of (1 + 1') REMPI of the $D^2\Sigma^+(3p\sigma)$ state of NO where a Cooper minimum is found in the $\ell = 2$ wave of the $K\Pi$ continuum at a photoelectron energy of 3.2 eV.

Finally, I would like to thank my students, research fellows, and collaborators (Matt Braunstein, Sham Dixit, Richard Dubs, Mu-Tao Lee, Diane Lynch, Henrik Rudolph, Jeff Stephens, and Kwangshi Wang) who have carried out the work I will speak about. Over the years this research has been supported by the U.S. National Science Foundation, Air Force Office of Scientific Research, and the Department of Energy (OHER).

REFERENCES

1. See, for example, P. M. Dehmer, J. L. Dehmer, and S. T. Pratt, Comments At. Mol. Phys. 19, 205 (1987), Sec. 3.
2. S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, Chem. Phys. Lett. 105, 28 (1984).
3. W. A. Chupka, J. Chem. Phys. 87, 1488 (1987).
4. A. P. Hickman, Phys. Rev. Lett. 59, 1553 (1987).
5. S. N. Dixit, D. L. Lynch, B. V. McKoy, and A. U. Hazi, Phys. Rev. A. 40,

- 1700 (1989).
6. P. J. Miller, L. Li, W. A. Chupka, and S. D. Colson, *J. Chem. Phys.* **89**, 3921 (1988).
 7. J. A. Stephens, M. Braunstein, and V. McKoy, *J. Chem. Phys.* **89**, 3923 (1988).
 8. J. A. Stephens, M. Braunstein, D. L. Lynch, and V. McKoy, *J. Chem. Phys.* (to be published).
 9. J. A. Stephens and V. McKoy, *Phys. Rev. Lett.* **62**, 889 (1989).
 10. J. A. Stephens and V. McKoy, *J. Chem. Phys.* **93**, 7863 (1990).
 11. K. Wang, J. A. Stephens, and V. McKoy, *J. Chem. Phys.* **93**, 7874 (1990).
 12. K. S. Wiswanathan, E. Sekreta, E. R. Davidson, and J. P. Reilly, *J. Phys. Chem.* **90**, 5078 (1986).
 13. S. N. Dixit, D. L. Lynch, V. McKoy, and W. M. Huo, *Phys. Rev. A* **32**, 1267 (1985).
 14. H. Rudolph, S. N. Dixit, V. McKoy, and W. M. Huo, *Chem. Phys. Lett.* **137**, 521 (1987).
 15. H. Rudolph, S. N. Dixit, and V. McKoy, *J. Chem. Phys.* **91**, 2216 (1989).
 17. H. Rudolph and V. McKoy, *J. Chem. Phys.* **91**, 2235 (1989).
 18. H. Rudolph, J. A. Stephens, V. McKoy, and M.-T. Lee, *J. Chem. Phys.* **91**, 1374 (1989).
 19. S. N. Dixit and V. McKoy, *Chem. Phys. Lett.* **128**, 49 (1986).
 20. H. Rudolph and V. McKoy, *J. Chem. Phys.* **91**, 7995 (1989).
 21. R. L. Dubs, S. N. Dixit, and V. McKoy, *J. Chem. Phys.* **85**, 656 (1986).
 22. R. L. Dubs, S. N. Dixit, and V. McKoy, *J. Chem. Phys.* **88**, 968 (1988).
 23. J. R. Appling, M. G. White, R. L. Dubs, S. N. Dixit, and V. McKoy, *J. Chem. Phys.* **87**, 6927 (1987).
 24. J. W. Winniczek, R. L. Dubs, J. R. Appling, V. McKoy, and M. G. White, *J. Chem. Phys.* **90**, 949 (1989).
 25. H. Rudolph, R. L. Dubs, and V. McKoy, *J. Chem. Phys.* **93**, 7513 (1990).