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*Annual*  
TECHNICAL REPORT

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**Resonant Multiphoton Ionization Spectra  
of Molecules and Molecular Fragments**

**MASTER** *jav*

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## ● Overview

The objective of our research under this contract is to carry out studies of resonant enhanced multiphoton ionization (REMPI) processes in molecules. In the  $(n + 1)$  - REMPI process of interest an atom or molecule in a specific initial state absorbs  $n$  photons making a transition to an intermediate state from which it is subsequently ionized by absorption of an additional photon. A remarkable feature of resonant enhanced multiphoton ionization is that the narrow bandwidth radiation of lasers makes it possible (i) to select a specific rovibrational level in the initial state of a molecule or fragment, (ii) to resonantly pump this level up to a selected rotational-vibrational level of an excited electronic state, and (iii) to subsequently photoionize the state that has been resonantly excited. *The extreme state-selectivity and sensitivity make REMPI both a tool with several practical applications and an important technique for probing the photoionization dynamics of vibrationally and electronically excited states.* Some significant applications of this technique include its use (i) for state-specific detection of species and diagnostics in combustion and chemical etching media and plasmas, (ii) for state-specific generation of molecular ions for use in ion-molecule reaction studies, and (iii) as a probe of photofragmentation and gas-surface scattering including alignment and orientation effects in these processes.

Our studies are designed to provide a quantitatively robust analysis and prediction of key spectral features in several ongoing experimental studies and potentially practical applications of this technique. The specific problems of interest to us in our studies are (i) the vibrational distributions of ions that can be expected in REMPI of small molecules and molecular fragments with particular emphasis on their non-Franck-Condon behavior. Such non-Franck-Condon behavior introduces serious complications in the use of the technique for state-specific production of ions, e.g.,  $O_2^+(v)$  and  $OH^+(v)$ , and in the extraction of state populations from REMPI signals, (ii) rotational distributions of ions that can be produced in various REMPI schemes and how these distributions can be tuned by choice of the resonant state and influenced by the molecular character of the photoelectron, and (iii) the circular dichroism in photoelectron angular distributions, i.e., the difference in photoelectron angular distributions produced by right- and left-circularly polarized, and their use as a probe of molecular alignment.

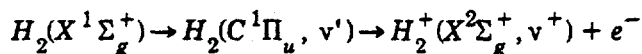
Below I will summarize the progress we have made to date in our studies of these features and applications of REMPI of molecules and molecular fragments. A significant feature of these studies, which will be explicitly assumed throughout our discussion below, is that they are carried out using quantitatively reliable molecular photoelectron orbitals. These photoelectron orbitals are solutions of a one-electron Hartree-Fock-like Schrödinger equation containing the potential of the molecular ion core. The nonspherical nature of these molecular ion potentials determines the angular momentum composition of the photoelectron orbital, i.e., they are now mixtures of the atomic-like s, p, d ... orbitals, which in turn exerts a strong influence on the dynamics of the photoionization process itself. The use of such photoelectron orbitals is essential in studying the dynamical aspects of the resonant enhanced multiphoton ionization processes of interest to us. A good illustration of this is in the determination of rotational distributions which essentially reflects the sharing of angular momentum between the photoelectron and molecular ion. In such studies crude approximations to these photoelectron orbitals can lead to very distorted descriptions of the dynamics of these processes. In recent years we have developed formulations and numerical procedures for obtaining such molecular photoelectron orbitals.

A summary of our specific accomplishments during this period is as follows:

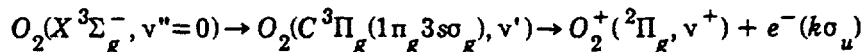
- *Vibrational distributions of ions produced by REMPI:* The vibrational distribution of ions produced via photoionization of a resonantly excited molecular state in an  $(n + 1)$ -REMPI scheme is generally expected to be Franck-Condon. More specifically, for a Rydberg state - the usual choice in many REMPI processes - ionization should occur primarily with preservation of vibrational quantum numbers. This assumption and expectation are central to many proposed applications of REMPI. In fact, deviations from such expected Franck-Condon distributions introduce severe complications into two very important uses of this technique, i.e., extraction of state populations from REMPI signals and its use for state-specific production of ions.

We have examined three different mechanisms which can be expected to lead to non-Franck-Condon distributions of molecular ions in REMPI. These mechanisms, along with the examples chosen to illustrate them are

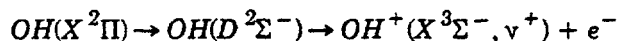
- electronic autoionization of doubly excited states in  $H_2$ :



- the presence of a shape or "one-electron" resonance in the ionization continuum:



- the presence of a Cooper minimum in the photoelectron spectrum:

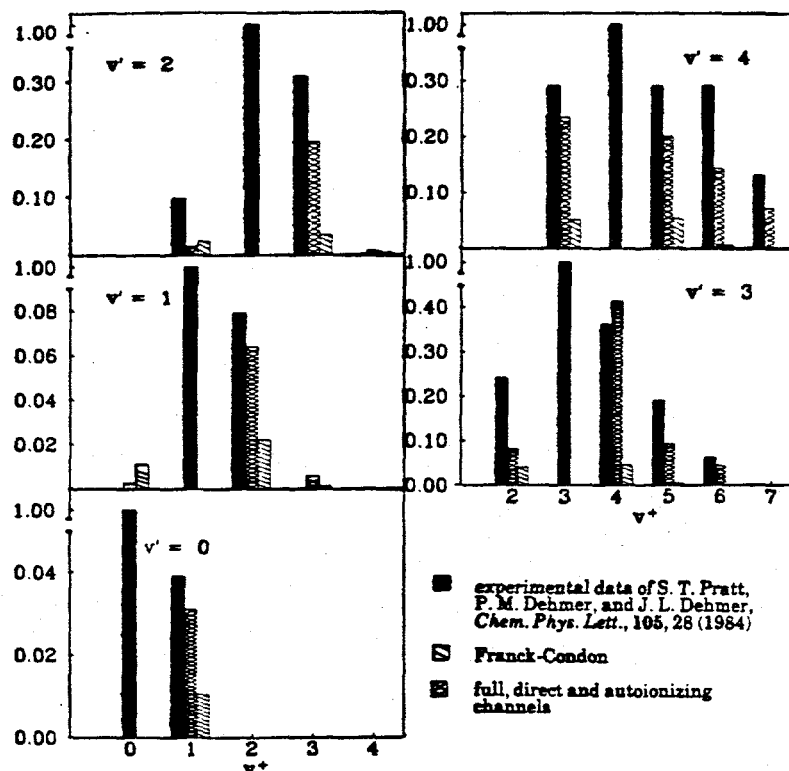


The objective of these studies is to assess the importance of these processes, in parallel with experimental efforts where possible, and to identify REMPI schemes where such non-Franck-Condon vibrational distributions could be avoided. We will see that although the role of the first two mechanisms, i.e., autoionizing and shape resonances, in leading to non-Franck-Condon behavior has also been recently studied experimentally, our demonstration that strong non-Franck-Condon effects can arise in the photoionization of molecular Rydberg states which display Cooper minima in their photoelectron spectra has not yet been confirmed experimentally. This mechanism should be most pronounced in REMPI of hydrides such as OH and CH, fragments of considerable interest.

Some highlights of these studies of non-Franck-Condon vibrational ion distributions in REMPI are

(i) Experimental studies of the (3+1)-REMPI of  $H_2$  via specific vibrational levels  $v'$  of the  $C^1\Pi_u$  state show very non-Franck-Condon ion vibrational distributions.<sup>1</sup> The near-identity of the resonant ( $C^1\Pi_u$ ) and ionic potential surfaces was expected to lead to Franck-Condon distributions with  $\Delta v = v^+ - v' = 0$ . To account for this observed non-Franck-Condon behavior we first included the internuclear and energy dependence of the photoelectron matrix element for direct ionization only, i.e., neglecting any contribution from doubly-excited autoionizing states, in the calculation of the vibrational branching ratios.<sup>2</sup> Although these results accounted for the non-Franck-Condon ion vibrational distributions for ionization via the  $v'=0$  and 1 levels of the  $C^1\Pi_u$  state, the calculated branching ratios deviated significantly for the  $v'=2, 3$ , and 4. Following the suggestion of Chupka<sup>3</sup> that perturbations of the direct ionization process by doubly-excited

autoionizing states could be responsible for these ion vibrational distributions we have completed studies of the branching ratios for (3 + 1)-REMPI of  $H_2$  via the  $v=0-4$  levels of the  $C^1\Pi_u$  state incorporating both the direct and autoionizing channels, i.e.,  $^1\Pi_g(1\sigma_u 1\pi_u)$ .



The resulting branching ratios are shown in the insert along with the measured values of ref. 1. The agreement between these calculated and measured branching ratios is seen to be quite good. The inclusion of both the direct and resonant channels is required in these studies since interference between them is substantial for some levels.

These results represent the first *ab initio* studies of the role of autoionization in ion vibrational distributions in REMPI of molecules. Such autoionizing states can be expected to occur at similar photoelectron energies in other molecules and, hence, to perturb the ion distributions, particularly for the higher vibrational levels which are of considerable interest in studies of ion-molecule reactions. In fact, both ongoing theoretical and experimental studies have already identified their importance in  $O_2$ .<sup>4,5</sup> On the other hand, these results demonstrate that REMPI has the potential to be a unique and precise probe of doubly-excited states at lower energies and larger internuclear distances.

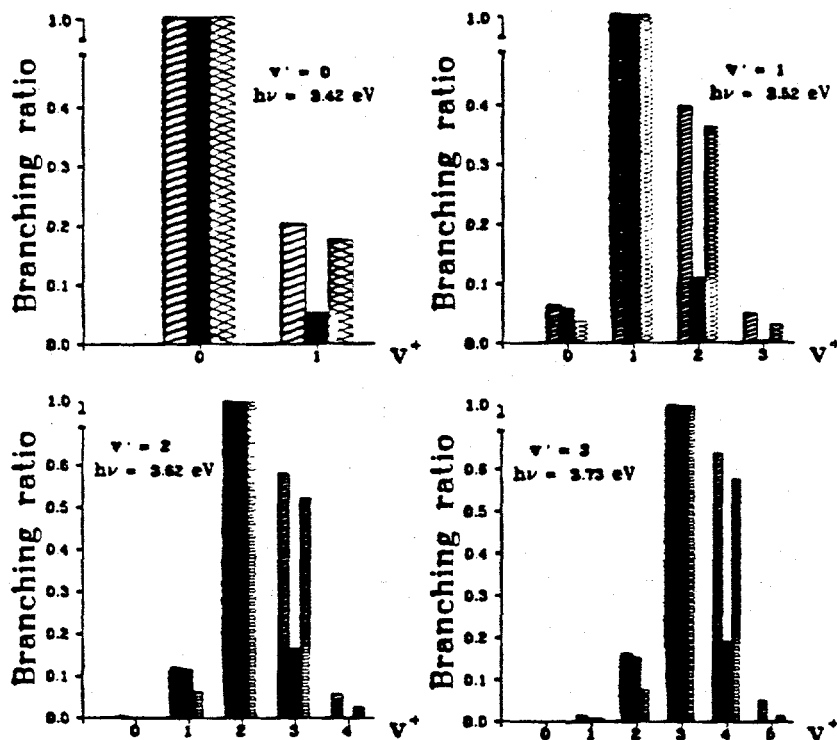
(ii) Recent measurements of vibrationally-resolved (2 + 1) REMPI spectra of  $O_2$  via the  $C^3\Pi_g(1n_g 3s_g)$  Rydberg state of  $O_2$  show pronounced non-Franck-Condon ionic state distributions, evident in the observation of intense off-diagonal peaks

$(\Delta v = v' \neq 0)$ .<sup>5</sup> This scheme was originally selected for its promise for producing  $O_2^+$  in specific vibrational levels. We have established that a significant part of the observed non-Franck-Condon distributions arise from a  $\sigma_u$  shape resonance occurring near threshold. This shape or "one-electron" resonance is essentially a continuation of the  $3\sigma_u$  orbital responsible for the strong  $1\pi_g \rightarrow 3\sigma_u$  intravalence transition which lies below the ionization threshold for larger internuclear distances. Inclusion of this effect in our calculated photoelectron spectra accounts for many significant features seen experimentally.<sup>4,5</sup> Some major discrepancies between theory and experiment remain in portions of the spectra. There is strong evidence that these discrepancies are due to perturbations by doubly-excited autoionizing states. A very likely candidate for this autoionizing state is the  $B^3\Sigma_u^-(1\pi_u^3 1\pi_g^3)$  state of  $O_2$ , well-known in the absorption spectrum of  $O_2$ . Calculations including the effects of both this autoionizing state and the shape resonance on the ion vibrational distributions in the REMPI of  $O_2$  are underway.

(iii) An important assumption in the REMPI of molecular Rydberg states which are well-described by a single-excited electron with a specific ionic core is that photoionization should occur with preservation of vibrational quantum number. The examples above demonstrate that important exceptions to this result arise from the presence of autoionizing and shape resonances. These effects derive from considerations of final-state dynamics. We have identified and assessed another mechanism for producing significant non-Franck-Condon vibrational distributions which are solely due to properties of the initial Rydberg orbital. These properties are: (i) the Rydberg level must have at least one radial node in its wavefunction so that a Cooper minimum may occur in some portion of the photoelectron spectrum, and (ii) the Rydberg orbital should evolve rather rapidly into its united or separated atom limits over a range of internuclear distance associated with low vibrational levels, e.g.,  $v' \sim 1-3$ . Molecular Rydberg orbitals with these characteristics typically occur in diatomic hydrides, an important class of species in multiphoton ionization and photofragmentation problems.

We have illustrated this mechanism with specific predictions of ionic vibrational distributions for a proposed (3 + 1) one-color or (2 + 1) two-color REMPI of OH via the  $D^2\Sigma^-(1\pi^2 5\sigma)$  state. The resulting vibrational distributions (see insert) show surprisingly large deviations from Franck-Condon values. Enhancements by factors ranging from 3 to 100 can be seen in the population of some vibrational levels

over the Franck-Condon predictions. Similar studies are under way for CH and NH, fragments of considerable interest.



● Vibrational branching ratios for REMPI of OH via the  $D^2\Sigma^-$  state. Note that there is no experimental data for this system. The solid bars represent the Franck-Condon predictions while the cross-hatched columns give the values calculated with the velocity and length forms of the photoelectron matrix element.

### Publications

1. Shape-resonance-induced non-Franck-Condon effects in (2 + 1) resonant enhanced multiphoton ionization of the  $C^3\Pi_g$  state of  $O_2$   
J. A. Stephens, M. Braunstein, and V. McKoy  
*J. Chem. Phys.*, **89**, 3923 (1988).
2. Shape resonance and non-Franck-Condon effects in (2 + 1) REMPI of  $O_2$  via the  $C^3\Pi_g$  state  
M. Braunstein, J. A. Stephens, and V. McKoy  
*J. Chem. Phys.*, (in press) - preprint attached
3. Electronic autoionization effects on the vibrational state distributions in resonant enhanced multiphoton ionization of  $H_2$   
S. N. Dixit, D. L. Lynch, V. McKoy, and A. U. Hazi  
*Phys. Rev. A*, (in preparation) - abstract attached

4. Non-Franck-Condon effects induced by Cooper minima in excited-state photoionization of OH

J. A. Stephens and V. McKoy

*Phys. Rev. A.*, (submitted) - preprint attached

● *Rotationally-resolved laser photoelectron spectroscopy*: Coupled with high-resolution photoelectron spectroscopy, REMPI offers wide possibilities for producing rotationally-selected ions while providing highly-detailed dynamical information on the molecular photoionization process. Rotationally selected ions are of considerable interest in studies of state-specific reactions. Whereas ion rotational levels have been readily resolved in the photoelectron spectra of  $H_2$  with its large rotational spacing, rotational resolution has been difficult for heavier ions. However, the groups of Reilly<sup>6</sup> and Zare<sup>7</sup> have recently obtained rotationally-resolved ion spectra in REMPI of NO via high J levels of the resonant state. Furthermore, Schlag and co-workers<sup>8</sup> have also developed a novel method for obtaining rotationally-resolved photoelectron spectra at zero-kinetic-energy (ZEKE) with a resolution of  $1\text{-}2\text{ cm}^{-1}$ . This resolution makes the technique applicable to low rotational states of ions.

We have studied some features of the rotationally-resolved REMPI spectra of NO via the  $D^2\Sigma^+(3p\sigma)$  and  $A^2\Sigma^+(3s\sigma)$  states for which recent experimental data reveal some dynamically significant aspects:

(i) measured rotational branching ratios for (2 + 1) REMPI of NO via the  $D^2\Sigma^+(3p\sigma)$  state show a very strong  $\Delta N = 0$ , the change in angular momentum, exclusive of spin, between the resonant and ionic states. A selection rule governing possible values of the angular momentum  $\ell$ , i.e.,  $\Delta N + \ell = \text{odd}$ ,<sup>9</sup> establishes that this  $\Delta N = 0$  peak arises from a  $3p \rightarrow kp$  ionizing transition, a forbidden process in an atomic-like model. Our calculated rotational branching ratios show a significant  $\Delta N = 0$  peak which can be explicitly attributed to a substantial p ( $\ell = 1$ )-wave component in the photoelectron orbital.<sup>10</sup> The p-wave character arises, in turn, from angular momentum coupling in the photoelectron wave function caused by the molecular ion potential. This is purely a molecular effect. Such angular momentum coupling in molecular photoelectron orbitals determines the rotational distributions of ions that will be produced in REMPI via a given resonant state.

(ii) the rotational resolution in the experiments referred to above was achieved by going through high  $J$  levels of the resonant state.<sup>6</sup> The technique of ZEKE-photoelectron spectroscopy<sup>8</sup> with a resolution of about  $1 \text{ cm}^{-1}$  has been used to study the rotational branching ratios for (1+1) two-color REMPI of NO via the  $A^2\Sigma^+$  ( $3s\sigma$ ) state for low rotational levels, i.e.,  $N_A = 0, 1, 2,$  and  $3$ . The spectra show that, as expected,<sup>9</sup> the  $\Delta N = \text{even}$  peaks are dominant but that angular momentum coupling in the photoelectron orbital leads to odd  $\Delta N$  peaks.<sup>8</sup> These features are also in general agreement with earlier theoretical predictions.<sup>9</sup> However, an additional striking feature of these spectra was the strong dependence of the angular momentum transfer,  $\Delta N$ , on the initial value of  $N_A$ . Explicit calculations at very low, but finite, photoelectron energies reproduce the strong decrease in the ratio of  $\Delta N = 0$  and  $\Delta N = 2$  peaks seen experimentally as  $J_A$  increases from  $1/2$  to  $3/2$  but do not show the rapid die-off of the  $\Delta N \neq 0$  peaks for higher  $J_A$  levels seen experimentally.<sup>8</sup> The trend in the  $\Delta N = 0$  to  $\Delta N = 2$  peak ratios for  $N_A = 1/2$  and  $3/2$  could be explained on the basis of simple angular momentum transfer arguments. These arguments also predict that this trend in the  $\Delta N = 0$  to  $+2$  peak intensities with increasing angular momentum observed for the specific branch ( $P_{11}$ ) of the experiments<sup>8</sup> should not be expected in other branches.

		$\Delta N = N_e - N_i$				
		-2	-1	0	1	2
$R_{21}(20.5)$	calculated					
	experimental					
$Q_{11}(21.5) + P_{21}(21.5)$	calculated					
	experimental					

- Photoelectron angular distributions for specific rotational levels of  $\text{NO}^+$  produced by (1+1') REMPI via the  $R_{21}(20.5)$  and  $Q_{11}(21.5) + P_{21}(21.5)$  branches of the  $A^2\Sigma^+$  state. The experimental data is from ref. 11.

(iii) recently Zare and Allendorf<sup>7</sup> have successfully measured the photoelectron angular distributions for specific rotational levels of  $\text{NO}^+$  produced by REMPI via the  $J_A = 21.5$  level of the  $A^2\Sigma^+$  state. Such rotationally-resolved photoelectron angular distributions reflect the way angular momentum is shared between the molecular ion and the photoelectron. A dynamically important question that immediately arises is: how different are these angular distributions for different  $\Delta N = N_+ - N_i$  values? The insert above shows our calculated photoelectron angular distributions for several values of  $\Delta N$  in  $(1+1')$  REMPI of the  $A^2\Sigma^+$  state of  $\text{NO}$  via different rotational branches along with the measured values of Allendorf and Zare.<sup>11</sup> The results show a surprising and interesting dependence on the ion rotational level. Further studies of such rotationally-resolved photoelectron angular distributions for REMPI via other states of  $\text{NO}$  are under way.

#### *Publications*

5. Ionic rotational branching ratios in REMPI of  $\text{NO}$  via the  $A^2\Sigma^+$  ( $3s\sigma$ ) and  $D^2\Sigma^+$  ( $3p\sigma$ ) states  
H. Rudolph, S. N. Dixit, V. McKoy, and W. M. Huo  
*J. Chem. Phys.*, **88**, 637 (1988)
6.  $(1+1)$  REMPI via the  $A^2\Sigma^+$  state of  $\text{NO}$ : Ionic rotational branching ratios and their intensity dependence  
H. Rudolph, S. N. Dixit, V. McKoy, and W. M. Huo  
*J. Chem. Phys.*, **88**, 1516 (1988)
7. Rotational branching ratios at low photoelectron energies in REMPI of  $\text{NO}$   
H. Rudolph, V. McKoy, and S. N. Dixit  
*J. Chem. Phys.*, (accepted for publication) - preprint attached

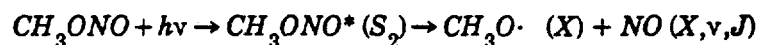
● *Molecular alignment from photoelectron angular distributions*: Studies of molecular alignment - molecules with preferred directions in space - are of increasing interest due to the detailed dynamical insight these studies can provide on processes such as photofragmentation, chemical reactions, and gas-surface scattering.<sup>12</sup> Conventionally fluorescence techniques have been used to probe state alignment. On the other hand, angle-resolved  $(n+1)$  REMPI, i.e., absorption of  $n$

photons to the resonant state which is subsequently ionized by another photon, is not commonly used to probe alignment. This is primarily due to the fact that in such photoelectron angular distributions state alignment is intimately entangled with the photoionization dynamics.

We have shown that photoelectron angular distributions resulting from ionization of aligned *linear* molecules should exhibit dichroic behavior, i.e., angular distributions from aligned states are different from photoionization with right- and left-circularly polarized light.<sup>13</sup> Historically, circular dichroism has been associated with chiral molecules which lack a plane of symmetry and an inversion center. Our prediction asserted that these circular dichroic angular distributions (CDAD) - defined as the difference between the angular distributions for right- and left-circularly polarized light - should exist for linear molecules, arises in the electric dipole approximation, and would be a direct signature of the state alignment of the molecule. Questions that immediately arise are: will these CDAD spectra be large enough to make their measurement experimentally feasible and how readily can alignment parameters associated with photofragments be extracted from such spectra?<sup>7</sup> Answers to these questions will obviously determine whether CDAD spectra could become a practical probe of alignment. To answer these questions we showed, by direct calculation, that the CDAD spectra of optically aligned rotational levels, i.e., alignment created by photon absorption, of the  $A^2\Sigma^+$  state of NO should be about 15-25% of the right or left photoelectron spectra, suggesting that measurements of these spectra were indeed possible. Subsequently, in a joint experimental-theoretical study with M. G. White of Brookhaven National Laboratory, the CDAD spectra were measured for these optically aligned levels of NO and shown to be of the predicted magnitude and behavior.<sup>14</sup> These studies also showed that CDAD spectra provide information about excited state alignment in both their phase and magnitude.

We have also demonstrated that ground state alignment induced by processes such as photofragmentation and gas-surface scattering can be extracted from CDAD spectra in a straightforward manner, independently of the photoionization dynamics, by simply carrying out the measurements via two different spectral branches. This proposed scheme clearly removed one of the potentially serious obstacles to possible use of the CDAD technique experimentally. In a further collaboration with M. G. White of Brookhaven National Laboratory the CDAD

technique has been used to probe the spatial alignment of NO photofragments produced by UV photodissociation of methyl nitrite, i.e.,



These measurements clearly establish the utility of the CDAD method for probing chemical processes in which spatial alignment plays an important role.

### *Publications*

8. Atomic and molecular alignment from photoelectron angular distributions in  $(n+1)$  resonantly enhanced multiphoton ionization  
R. L. Dubs, V. McKoy, and S. N. Dixit  
*J. Chem. Phys.*, **88**, 968 (1988)
9. Circular dichroism in photoelectron angular distributions from two-color  $(1+1)$  REMPI of NO  
J. R. Appling, M. G. White, R. L. Dubs, S. N. Dixit, and V. McKoy  
*J. Chem. Phys.*, **87**, 6927 (1987)
10. A REMPI study of the photodissociation dynamics of the  $\text{S}_2$  state of  $\text{CH}_3\text{ONO}$   
J. W. Winniczek, R. L. Dubs, J. R. Appling, V. McKoy, and M. G. White  
*J. Chem. Phys.*, (accepted for publication) - preprint attached

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14. J. R. Appling, M. G. White, R. L. Dubs, S. N. Dixit, and V. McKoy, *J. Chem. Phys.*, **87**, 6927 (1987).