

## Rotational branching ratios in (1 + 1) resonant-enhanced multiphoton ionization of NO via the $A^2\Sigma^+$ state

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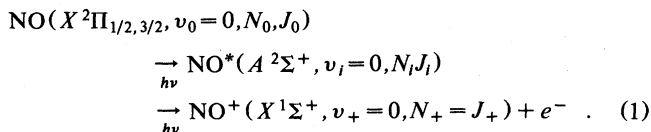
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The rotational branching ratios resulting from (1+1) resonant-enhanced multiphoton ionization of NO via the  $A^2\Sigma^+$  Rydberg state are analyzed. Theoretical results using *ab initio* molecular parameters agree reasonably well with recent experimental data. More importantly, the analysis underscores the importance of the molecular nature of the problem and its resulting complexities. It is shown that, for photoionization of a  $\Sigma$  state that leaves the ion in a  $\Sigma$  state, the allowed rotational states of the ion satisfy the selection rule  $\Delta N + l = \text{odd}$ , where  $\Delta N$  is the difference in (electronic + rotational) quantum numbers for the neutral and for the ion, and  $l$  is the partial wave of the electron. Based on this selection rule, it follows that the predominantly gerade  $3s\sigma$  Rydberg orbital of the  $A^2\Sigma^+$  state couples only to the ungerade channel in the continuum ( $l$  odd), thereby suppressing the  $\Delta N = \pm 1$  peaks, in agreement with experiment. The molecular nature of the ionic potential leads to strong  $l$  mixing in electronic continuum orbitals. In fact, the influence of a nearby shape resonance causes the  $f$  wave to be dominant in the  $\sigma$  channel.

Resonant-enhanced multiphoton ionization (REMPI), combined with photoelectron energy analysis, provides detailed information on the dynamics of the multiphoton ionization process and the photoionization of excited states. In an  $(n+m)$  REMPI process a molecule is excited to the resonant state by absorption of  $n$  photons and is ionized subsequently by absorption of additional  $m$  photons. The large number of REMPI studies<sup>1-17</sup> on diatomic molecules such as  $H_2$ , CO, NO, and  $N_2$  have revealed interesting features such as non-Franck-Condon behavior in vibrational branching ratios, sensitivity of photoelectron angular distributions to rotational and vibrational states, and Rydberg-valence mixing and autoionization. Despite such intense experimental activity, there have been few related theoretical studies. Recently, we have initiated a program of quantitative theoretical studies of these REMPI processes. The general framework for our analysis of the REMPI dynamics has been described elsewhere.<sup>18</sup> Application of this formalism along with an *ab initio* determination of molecular parameters to the study of the vibrational branching ratios in a (3+1) REMPI of  $H_2$  via the  $C^1\Pi_u$  state yielded satisfactory agreement between theory and experiment.<sup>19</sup>

There have been many experimental studies of REMPI processes in NO because of its low ionization potential. These  $(n+m)$  REMPI studies with different combinations of  $n$  and  $m$  (1+1, 2+2, 2+1, etc.) have revealed several interesting features that are not understood yet.<sup>7-17</sup> For example, the origin of the zero-energy electrons remains unexplained.<sup>8</sup> In one experiment, Wilson, Viswanathan, Sekreta, and Reilly<sup>12</sup> were able to resolve the rotational structure of the ion resulting from the (1+1) REMPI process:



In the above expression the  $v$ 's denote the vibrational quantum numbers, the  $N$ 's the quantum numbers for the electronic plus rotational angular momenta and the  $J$ 's denote total angular momentum quantum numbers. Most of the ions in the experiment of Wilson *et al.*<sup>12</sup> were produced in a state corresponding to  $\Delta N = 0$  (where  $\Delta N = N_+ - N_i$ ), and about 10–15% in states with  $\Delta N = \pm 2$ . More strikingly, no peaks were seen for  $\Delta N = \pm 1$ . While such a  $\Delta N = 0, \pm 2$  selection rule has been observed in rotationally resolved single-photon ionization of  $H_2$ ,<sup>20</sup> its apparent appearance in a heteronuclear molecule such as NO is surprising.

To understand the dynamical origins of these effects, we have undertaken a theoretical investigation of the rotational branching ratios for the REMPI process of Eq. (1). Such (1+1) REMPI is free of accidental resonances and is, therefore, more readily amenable to accurate, *ab initio* theoretical calculations. Our results for the rotational branching ratios agree well with experiments of Wilson *et al.*<sup>12</sup> We also find  $\Delta N = 0$  as the dominant channel and  $\Delta N = \pm 2$  as the next strongest channels. However, we obtain nonzero branching ratios ( $\sim 5$ –10% of the  $\Delta N = 0$  transition) for  $\Delta N = \pm 1$  transitions. The detailed analysis of our results exemplifies the molecular nature of the process and its resulting complexities. We show, quite generally, that photoionization out of a  $\Sigma$  state of the neutral molecule leaving the ion in a  $\Sigma$  state must obey the selection rule

$$\Delta N + l = \text{odd} \quad (2)$$

where  $l$  is the partial wave of the photoelectron. This selection rule does not depend upon the method of creating the initial  $\Sigma$  state or upon the anisotropy of this state. Therefore, it is applicable to single-photon ionization out of a  $\Sigma$  state as well as to  $(n+1)$  REMPI via a  $\Sigma$  state. For photoionization of homonuclear molecules,  $l$  is either even ( $g$  symmetry for photoelectron) or odd ( $u$  symmetry) implying,

respectively, that  $\Delta N$  is either odd ( $g$  symmetry photoelectron) or even ( $u$  symmetry photoelectron). This result is consistent with the observations by Pratt, Poliakoff, Dehmer, and Dehmer<sup>1</sup> in  $(3+1)$  REMPI of  $H_2$  via the  $B^1\Sigma_u^+$  states and those by Pollard *et al.*<sup>20</sup> in single-photon ionization of the  $X^1\Sigma_g^+$  state. Note that  $\Delta N = \Delta J$  for singlet states. For heteronuclear molecules, both even and odd  $l$ 's are allowed and one should have  $\Delta N = 0, \pm 1, \pm 2, \dots$ . As we show in this paper, the suppression of  $\Delta N = \pm 1$  peak in NO occurs due to the near-homonuclear nature of the  $6\sigma$  orbital of the  $A^2\Sigma^+$  state.

We now present a brief theoretical analysis of the process of Eq. (1). We will use the lowest-order perturbation-theory results to calculate the rotational branching ratios. For the laser powers used in the experiments of Wilson *et al.*,<sup>12</sup> this should be a good approximation. For linearly polarized light, ionization originating from each of the  $(2J_0+1)$  magnetic sublevels of the initial state forms an independent channel. Denoting by  $|0\rangle$ ,  $|i\rangle$ , and  $|f\rangle$  the  $|J_0M_{J_0}\rangle$  initial state,  $|J_iM_{J_i}\rangle$  intermediate state, and the continuum state of the (ion + electron) system, the two-photon ionization differential cross section is given by

$$\frac{d\sigma}{d\Omega} \propto \sum_{M_{J_0}} \left| \frac{\langle f|D_{\mu_0}|i\rangle \langle i|D_{\mu_0}|0\rangle}{E_i - E_0 - \hbar\omega + i\Gamma_i} \right|^2 \quad (3)$$

In this equation,  $\Gamma_i$  denotes the width of the intermediate state  $|i\rangle$ ,  $D_{\mu_0}$  the electronic dipole moment operator, and  $\mu_0$  the light polarization index in the laboratory frame. Furthermore, for the relative branching ratios of interest here, the constant implied in Eq. (3) is unimportant and will be suppressed hereafter.

The bound-bound and bound-continuum dipole matrix elements needed in Eq. (3) are calculated by extending the formalism of Ref. 18 to include the spin. The details will be published elsewhere.<sup>21</sup> The bound-bound matrix element

$$\begin{aligned} \langle f|D_{\mu_0}|i\rangle &= \langle \gamma_+ \Lambda_+ N_+ S_+ J_+ M_{J_+}; m_\sigma | D_{\mu_0} | \gamma_i \Lambda_i N_i S_i J_i M_{J_i} \rangle \\ &= \left( \frac{4\pi}{3} \right)^{1/2} [(2N_i+1)(2N_++1)(2J_i+1)(2J_++1)(2S_i+1)]^{1/2} \\ &\quad \times \sum_{\substack{l, m, M_+ M_{S_+} \\ N_i, m_i, M_i, M_{S_i}}} Y_{lm}(\hat{k}) (2N_++1) (-1)^P \begin{pmatrix} N_i & S_i & J_i \\ M_i & M_{S_i} & -M_{J_i} \end{pmatrix} \begin{pmatrix} N_+ & S_+ & J_+ \\ M_+ & M_{S_+} & -M_{J_+} \end{pmatrix} \begin{pmatrix} S_+ & \frac{1}{2} & S_i \\ M_{S_+} & m_\sigma & -M_{S_i} \end{pmatrix} \\ &\quad \times \begin{pmatrix} N_+ & N_i & N_i \\ -M_+ & M_i & m_i \end{pmatrix} \begin{pmatrix} N_i & 1 & l \\ -m_i & \mu_0 & -m \end{pmatrix} (-i)^l e^{i\eta_l} \left[ \sum_{\substack{\lambda, \mu \\ \lambda_i}} \bar{r}_{fi}^{(\mu)} (-1)^\mu \begin{pmatrix} N_+ & N_i & N_i \\ -\Lambda_+ & \Lambda_i & \lambda_i \end{pmatrix} \begin{pmatrix} N_i & 1 & l \\ -\lambda_i & \mu & -\lambda \end{pmatrix} \right], \quad (6) \end{aligned}$$

where

$$P = M_+ - \Lambda_+ + \mu_0 - N_i + S_i - M_{J_i} - N_+ - M_{J_+} + \frac{1}{2} - M_{S_i}.$$

In the single-particle picture,  $\bar{r}_{fi}^{(\mu)}$  is the dipole matrix element between the initial orbital and photoelectron wave function in the molecular frame; viz.,

$$\bar{r}_{fi}^{(\mu)} = \int \chi_{v_+}(R) \chi_{v_i}(R) r_{fi}^{(\lambda\mu)}(R) dR, \quad (7)$$

can be written as

$$\begin{aligned} \langle i|D_{\mu_0}|0\rangle &\equiv \langle \gamma_i J_i M_{J_i} | D_{\mu_0} | \gamma_0 J_0 M_{J_0} \rangle \\ &= (-1)^{J_i - M_{J_i}} \begin{pmatrix} J_i & 1 & J_0 \\ -M_{J_i} & \mu_0 & M_{J_0} \end{pmatrix} \langle \gamma_i J_i || D || \gamma_0 J_0 \rangle, \quad (4) \end{aligned}$$

where  $\gamma_0$  and  $\gamma_i$  include all other quantum numbers necessary for unambiguous designation of states  $|0\rangle$  and  $|i\rangle$ . The reduced matrix element  $\langle \gamma_i J_i || D || \gamma_0 J_0 \rangle$  contains the  $X \rightarrow A$  dipole transition moment and depends on the coupling schemes used for representing the states  $|0\rangle$  and  $|i\rangle$ . The  $A^2\Sigma^+$  state belongs to Hund's case (b) for all  $J_i$ , and thus can be represented<sup>22</sup> as  $|\gamma_i \Lambda_i N_i S_i J_i M_{J_i}\rangle$  with  $N_i$ ,  $\Lambda_i$ , and  $S_i$  denoting, respectively, quantum numbers for electronic plus rotational angular momentum, its projection along the internuclear axis, and the total spin ( $\frac{1}{2}$  in this case). On the other hand, the coupling scheme for the  $X^2\Pi$  state changes from case (a) to case (b) with increasing  $J_0$ . The transition from case-(a) to case-(b) coupling occurs around  $2J_0 \sim A/B (\equiv \lambda)$ , where  $A$  and  $B$  are, respectively, the spin-orbit coupling and the rotational constants. For the  $X^2\Pi$  state,<sup>23</sup>  $A = 123.139 \text{ cm}^{-1}$ ,  $B = 1.696 \text{ cm}^{-1}$ , and  $\lambda = 72.6$ . Thus spin uncoupling occurs around  $J_0 \sim 35.5$ . Since  $J_0 \sim 21.5$  in the experiment of Wilson *et al.*,<sup>12</sup> the intermediate coupling scheme is the appropriate scheme to describe the initial-state wave function. While this question is important in calculating absolute REMPI cross sections, the choice of the coupling scheme does not influence the relative branching ratios of interest here. This comes about as the reduced matrix element  $\langle \gamma_i J_i || D || \gamma_0 J_0 \rangle$  factors out of Eq. (3). However, the 3- $j$  symbol in Eq. (4) must be retained, as it describes the anisotropy in the intermediate state. We shall, therefore, approximate  $\langle i|D_{\mu_0}|0\rangle$  by

$$\langle i|D_{\mu_0}|0\rangle = (-1)^{J_i - M_{J_i}} \begin{pmatrix} J_i & 1 & J_0 \\ -M_{J_i} & \mu_0 & M_{J_0} \end{pmatrix}. \quad (5)$$

The bound-free matrix element can be written as

where

$$r_{fi}^{(\lambda\mu)}(R) = \langle \psi_{kl\lambda}(\mathbf{r}'; R) | r Y_{1\mu}(\hat{r}') | \phi_i(\mathbf{r}; R) \rangle. \quad (8)$$

We now prove the selection rule defined in Eq. (2). First, note that  $N_i$ ,  $N_+$ , and  $l$  are all integers. For linear molecules  $r_{fi}^{(\lambda\mu)} = r_{fi}^{\lambda-\mu}$  because of the  $\sigma_v$  symmetry. If the state  $|i\rangle$  and the ionic state are both  $\Sigma$  states, we have

$\Lambda_+ = \Lambda_l = 0$ , which in turn implies  $\lambda_l = 0$  and

$$N_+ + N_l + N_r = \text{even} \quad (9a)$$

Since  $\lambda_l = 0$ ,  $\mu = \lambda$ . It can then be shown, using the properties of 3- $j$  symbols,<sup>24</sup> that the summation inside the square brackets in Eq. (6) vanishes unless

$$N_l + 1 + l = \text{even} \quad (9b)$$

Combining Eqs. (9a) and (9b) yields

$$N_+ - N_l + 1 + l = \text{even} \quad (10)$$

Note that this selection rule follows from the part of  $\langle f | D_{\mu_0} | i \rangle$ , which depends on angular momentum projections along the internuclear axis, namely, the quantity inside the square brackets in Eq. (7). It does not depend on how the state  $|i\rangle$  is created and is, therefore, applicable to single-photon ionization out of a  $\Sigma$  state as well as to  $(M+1)$  REMPI via a  $\Sigma$  state leaving the ion in a  $\Sigma$  state. Bonham and Lively<sup>25</sup> have alluded to a particular case ( $\Delta N$  even for ionization out of the  $\Sigma_g$  state) of Eq. (10) in their single-photon ionization studies.

Finally, we would like to point out that the energy denominator in Eq. (3) can be suppressed, as we are interested in relative branching ratios. It follows from the definitions of  $\langle f | D_{\mu_0} | i \rangle$  and  $\langle i | D_{\mu_0} | 0 \rangle$  that  $d\sigma/d\Omega$  can be expressed in terms of Legendre polynomials as

$$\frac{d\sigma}{d\Omega} = \beta_0 + \beta_2 P_2(\cos\theta) + \beta_4 P_4(\cos\theta) \quad (11)$$

For comparison with the data of Wilson *et al.*,<sup>12</sup> who collected photoelectrons along the direction of light polarization, we will calculate

$$\frac{d\sigma}{d\Omega}(\theta=0) = \beta_0 + \beta_2 + \beta_4 \quad (12)$$

The molecular parameters needed to calculate the relative branching ratios are the bound-free matrix elements  $r_{fi}^{\lambda\mu}$  and the scattering phase shifts. The Rydberg nature of the  $A^2\Sigma^+$  state implies that ionization out of the  $v_l=0$  vibrational level will be dominated by the Franck-Condon factor for the  $v_+ = 0$  level of the ion. Therefore, we calculate  $r_{fi}^{\lambda\mu}$  at the equilibrium separation of the  $A$  state (2.0095 a.u.). The  $A$ -state self-consistent-field (SCF) wave function has been calculated using a  $32\sigma 22\pi$  Slater basis set including  $n=3, 4, 5$  Rydberg functions. The basis set was obtained by deleting the  $\delta$  and  $\phi$  functions from an earlier basis set used in the calculation of the optical Stark effect<sup>26</sup> and absorption cross section<sup>27</sup> in the  $X \rightarrow A$  two-photon transition in NO. The  $\delta$  and  $\phi$  functions make no contribution in an SCF calculation. We have also replaced the two  $4f\sigma$  functions in that basis with diffuse  $3s\sigma$  functions with exponents 0.338 and 0.294, and have changed the exponent of the  $N5s\sigma$  function from 0.390 to 0.221. The continuum wave function was obtained using the iterative Schwinger variational technique.<sup>28</sup> The differential cross section is then calculated using Eqs. (3), (5), and (6). For the  $X^2\Pi \rightarrow A^2\Sigma^+$  excitations we used  $J_0=21.5$ ,  $N_l=22$ , and  $J_l=22.5$ . The branching ratios for excitation through a given branch ( $R$  branch in this case) change very little with  $J$  for such high values of  $J$ .

The results of our calculations for the rotational branching ratios are presented in Fig. 1. Reasonable overall agreement is seen between theory and experiment. Theoretical calculations using the length and the velocity forms of the dipole moment operator and the experimental results of

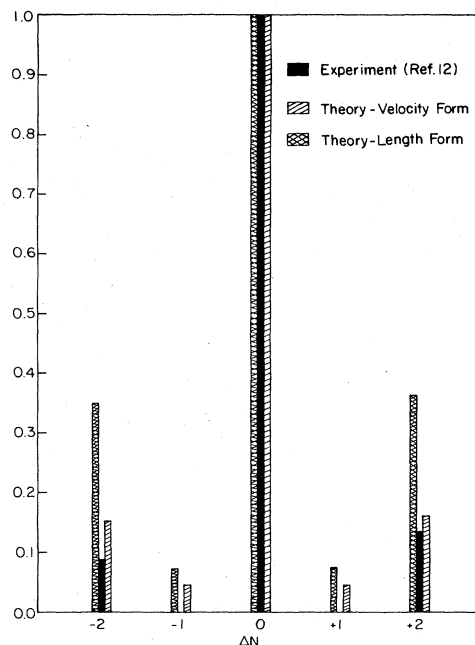


FIG. 1. Comparison of calculated rotational branching ratios with experimental results of Ref. 12.

Wilson *et al.*<sup>12</sup> are normalized to unity for the  $\Delta N=0$  transition. The length and velocity form results are within 5% of each other for this transition. The discrepancy between the length and velocity form results in the  $\Delta N \neq 0$  peaks arise due to numerical roundoff errors. As observed, the  $\Delta N=0$  peak is the strongest with the  $\Delta N = \pm 2$  peaks being the next largest in intensity. Our calculations, however, yield nonzero intensities for  $\Delta N = \pm 1$  transitions. We believe that, in the results of Wilson *et al.*,<sup>12</sup> these peaks are buried under the strong central peak because of insufficient resolution (6–10 meV for the effusive NO beam used in Ref. 12). The observed discrepancy between theory and experiment in the  $\Delta N = \pm 2$  peaks can be attributed to possible correlation effects and experimental limitations such as signal averaging, etc.

The suppression of the  $\Delta N = \pm 1$  transition in the photoionization of the  $A^2\Sigma^+$  state seems rather surprising since, according to Eq. (2), a heteronuclear molecule such as NO should exhibit a  $\Delta N = \pm 1$  peak. As we show in the analysis below, the reduction in the intensity of this peak is due to the apparent gerade character of the diffuse  $6\sigma$  orbital in the  $A^2\Sigma^+$  state. The analysis also reveals the molecular nature of the ionization process and the pitfalls associated with simple atomiclike analyses.

It is well known that the  $A^2\Sigma^+$  state is a Rydberg state with the  $6\sigma$  orbital being a  $3s\sigma$  Rydberg orbital. Indeed, a single-center expansion of the  $6\sigma$  orbital about the center of mass reveals that the wave function has 94%  $s$  character, 0.3%  $p$  character, and 5%  $d$  character. Moreover, these expansion coefficients also indicate that the state is predominantly a gerade state. This is a result of the diffuse nature of the  $6\sigma$  orbital. Photoionization out of this "gerade"-type  $3s\sigma$  orbital ejects the electron into an "ungerade"-type  $k\sigma$  and  $k\pi$  continua. From an "atomic" point of view, one might expect that the ejected electron will be in a  $p$  wave. This has been postulated recently<sup>17</sup> in analyzing (1+1) REMPI signals via this state. Our calculations show that

this assumption is incorrect and the photoelectron, experiencing the noncentral field of the  $\text{NO}^+$  molecule, is scattered into a state of coupled  $l$  waves. This can be best illustrated through the single-center expansion of  $\phi_l(\mathbf{r}';R)$  and  $\psi_{kl\lambda}(\mathbf{r}';R)$  in Eq. (8b). The bound-free matrix element  $r_{ff}^{l\mu}(R)$  can be rewritten as

$$r_{ff}^{l\mu}(R) = \sum_{l',l_0} \langle \psi_{kl'\lambda}(r,R) Y_{l'\lambda}(\hat{r}') | r Y_{l\mu}(\hat{r}') | \phi_{l_0}(r,R) Y_{l_0^0}(\hat{r}') \rangle. \quad (13)$$

For central potentials,  $l'=l$  while  $l' \neq l$  terms can be quite large for noncentral molecular potentials. Since the  $6\sigma$  state is predominantly of  $s$  type,  $\phi_{l_0}$  is largest for  $l_0=0$  and this implies that the  $l'=1$  term will be the dominant term. This "p-wave" electron experiences the nonspherical molecular potential and is scattered into  $l \neq 1$  channels. In fact, we observe that the  $f$  wave ( $l=3$ ) dominates the  $k\sigma$  channel at this energy. The relative magnitudes of  $|r_{ff}^{l\mu}(R)|^2$  are 0.033, 0.059, 0.060, 0.202, and 0.004 for  $l=0-4$  in the  $k\sigma$  channel, and are 0.386, 0.001, 0.102, and 0.003 for  $l=1-4$  in the  $k\pi$  channel. These values also illustrate the ungerade character of the probed ionization channel. This feature together with Eq. (2) explains the suppression of  $\Delta N \mp 1$  peaks in Fig. 1. The dominance of the  $f$  wave in the  $k\sigma$  channel is believed to be the influence of a shape-resonance-like feature. Recent calculations<sup>29</sup> have demonstrated a shape resonance in this channel at a photoelectron kinetic energy of 5 eV. Our present calculations differ, apart from ionizing out of the  $A$  state, from those of Ref. 29 in two aspects. The internuclear separation is 2.0095 a.u., while in Ref. 29 it was 2.173 a.u. and the core wave functions used here closely resemble the completely relaxed ionic core wave functions due to the Rydberg character of  $6\sigma$  orbital. Both of these effects tend to shift the resonance

to higher energies and broaden it.<sup>30</sup> We believe this feature is still influencing the  $f$  wave at 1.5-eV kinetic energies in the present calculation. If the  $p$  wave were dominant, the  $\beta_4 P_4(\cos\theta)$  term would be negligible in the angular distribution expression of Eq. (11). Our calculated values for  $\beta_0, \beta_2, \beta_4$  for the  $\Delta N=0$  branch are  $\beta_0=1$  (normalized),  $\beta_2=1.628$ , and  $\beta_4=-0.386$ . A measurement of the full angular distribution for this transition would be useful in confirming these predictions.

The rotationally unresolved, fixed-nuclei, photoionization cross sections for the  $\sigma$  and  $\pi$  channels are 0.354 and 0.974 Mb, respectively. These are again in disagreement with conclusions of Booth, Bragg, and Hancock,<sup>17</sup> who estimate almost complete  $p\sigma$  photoionization. On the other hand, the total cross section (1.328 Mb) agrees reasonably well with the measured<sup>7</sup> (partially rotationally resolved) cross section of  $(0.7 \pm 0.09)$  Mb. Detailed theoretical analysis of the laser-induced fluorescence spectrum and the REMPI spectrum observed by Booth *et al.*,<sup>17</sup> as well as the saturation behavior studied by Zacharias, Schmiedl, and Welge,<sup>7</sup> are currently under way, and the results will be published elsewhere.<sup>31</sup>

In conclusion, we have presented *ab initio* calculations and a detailed analysis of the rotational branching ratios resulting from  $(1+1)$  REMPI of NO via the  $A^2\Sigma^+$  state. Calculated ratios are in reasonable agreement with the measured values of Wilson *et al.*<sup>12</sup> More importantly, the analysis underscores the complexities of the molecular nature of the photoionization process and the necessity of generating accurate molecular continuum wave functions to understand the related dynamics.

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