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# Rotationally resolved photoelectron spectroscopy of the $2\Sigma^-$ Rydberg states of OH: The role of Cooper minima

E. de Beer and C. A. de Lange

Department of Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127,  
1018 WS Amsterdam, The Netherlands

J. A. Stephens, Kwanghsi Wang, and V. McKoy

Arthur Amos Noyes Laboratory of Chemical Physics,<sup>a)</sup> California Institute of Technology, Pasadena,  
California 91125

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Resonance enhanced multiphoton ionization coupled with high-resolution photoelectron spectroscopy (REMPI-PES) provides a unique probe of molecular excited states and their photoionization dynamics.<sup>1-4</sup> Recently we have used a combined photodissociation and REMPI-PES technique<sup>5</sup> to prepare and spectroscopically characterize the  $D^2\Sigma^-(3p\sigma)$  and  $3^2\Sigma^-(4s\sigma)$  Rydberg states of the OH radical.<sup>6,7</sup> OH and other first-row diatomic hydrides are common and important dissociation fragments, and this combination of techniques can be expected to yield new detailed information on highly excited rovibronic states and photoionization dynamics of these molecules.

The Letter reports the first observation of effects of a Cooper minimum on the rotationally resolved photoelectron spectra of a resonantly prepared Rydberg state of a molecule, and demonstrates the significant influence that Cooper minima exert on rotational molecular ion distributions. Illustrated in this work are two situations, one in which the occurrence of a Cooper minimum has a dramatic effect on the rotational ion distribution, and another where Cooper minima do not play a role.

OH  $X^2\Pi(v=0)$  radicals are produced by photolysis of  $H_2O_2$  (80% w/w). It has been found most of the excess energy (64 kcal/mol) goes into translation and a small part (3 kcal/mol) is released as rotational energy.<sup>8</sup> The  $D^2\Sigma^-(v'=0-2)$  and  $3^2\Sigma^-(v'=0)$  Rydberg states were prepared by two-photon absorption from the  $X^2\Pi(v=0)$  ground state in the two-photon energy region between 81 300 and 88 900  $cm^{-1}$ . Wavelength scans which show a multitude of rotationally resolved resonances associated with transitions to these Rydberg states were recorded.<sup>5</sup> Molecular constants for the newly observed  $3^2\Sigma^-(4s\sigma)$  state have been obtained.<sup>5</sup> Photoionization occurs via absorption of a third photon and electron kinetic energy scans employing a sensitive "magnetic bottle" electron spectrometer were recorded for selected resonances. For all observed transitions the ionic vibrational branching ratios show dominant  $\Delta v = v^+ - v' = 0$  behavior, as expected for ionization of Rydberg levels. The high translational energy with which the OH fragments are generated leads to a broadening of the photoelectron signals of  $\sim 30$  meV. Nevertheless, the significant rotational excitation of OH makes it possible to investigate the rotational ion distributions produced upon ionization out of intermediate states with high rotational quantum numbers  $N'$ . Rotationally re-

solved photoelectron spectra have been recorded for ionization via  $D^2\Sigma^-(v'=0-2)$  and  $3^2\Sigma^-(v'=0)$  Rydberg states for  $N' = 8-11$ . The rotational ion distributions can only be resolved for the  $\Delta v = 0$  transitions as signals corresponding to  $\Delta v \neq 0$  are too weak to give adequate statistics. Figures 1(a) and 1(c) show spectra for the  $D^2\Sigma^-(v'=0, N'=9) \rightarrow X^3\Sigma^-(v^+=0, N^+)$  and  $3^2\Sigma^-(v'=0, N'=9) \rightarrow X^3\Sigma^-(v^+=0, N^+)$  transitions, for the  $O_{11}(11)$  rotational branch. For ionization of these Rydberg levels the ion rotational distribution is governed by the propensity rule  $\Delta N + l = \text{odd}$ , where  $\Delta N = N^+ - N'$  is the change of rotational quantum number and  $l$  is a partial-wave component of the photoelectron orbital.<sup>1,2,9,10</sup> For ionization via the  $D^2\Sigma^-$  state we observe strong  $\Delta N = \text{even}$  signals in the photoelectron spectrum, in contrast to the  $\Delta N = \text{odd}$  distribution expected for ionization of a  $3p\sigma$  Rydberg electron in an atomic-like picture, i.e.,  $3p\sigma \rightarrow ks, kd$ . Figure 1(c) shows a rotationally resolved REMPI-PES spectrum for the next member of the Rydberg series, the  $3^2\Sigma^-$  state, which reveals a qualitatively different and much broader distribution of ion rotational levels. In contrast to transitions observed for the  $D^2\Sigma^-$  state, both  $\Delta N = \text{even}$  and  $\Delta N = \text{odd}$  transitions are clearly prominent.

Figures 1(b) and 1(d) show results of *ab initio* calculations of the rotationally resolved photoelectron spectra compared with experiment. In these calculations, the resonant intermediate and electronic continuum final states are treated at a Hartree-Fock level using multiplet-specific ion potentials. The effect of vibrational motion and the alignment induced by the two-photon absorption step are also included in these studies.<sup>10-12</sup> We have also studied the effect of alignment induced in the OH  $X^2\Pi$  fragment via photofragmentation<sup>13</sup> on these rotational distributions and found that this had no influence on the present spectra. Analysis of results for the  $D^2\Sigma^-$  state [Fig. 1(b)] reveals that this rotational distribution arises from a Cooper minimum in the  $3p\sigma \rightarrow k\pi(l=2)$  ionization channel<sup>11,12</sup> near the photoelectron kinetic energies accessed in our experiments. As the photoelectron energy increases from threshold, severe cancellations occur in the  $3p\sigma \rightarrow k\pi(l=2)$  channel, at internuclear distances less than  $\sim 2a_0$ . Since the  $l=2$  continuum wave becomes depleted upon formation of the Cooper minimum, the odd photoelectron waves from the  $3p\sigma \rightarrow k\sigma$  channel predominate. The strong  $\Delta N = 0$

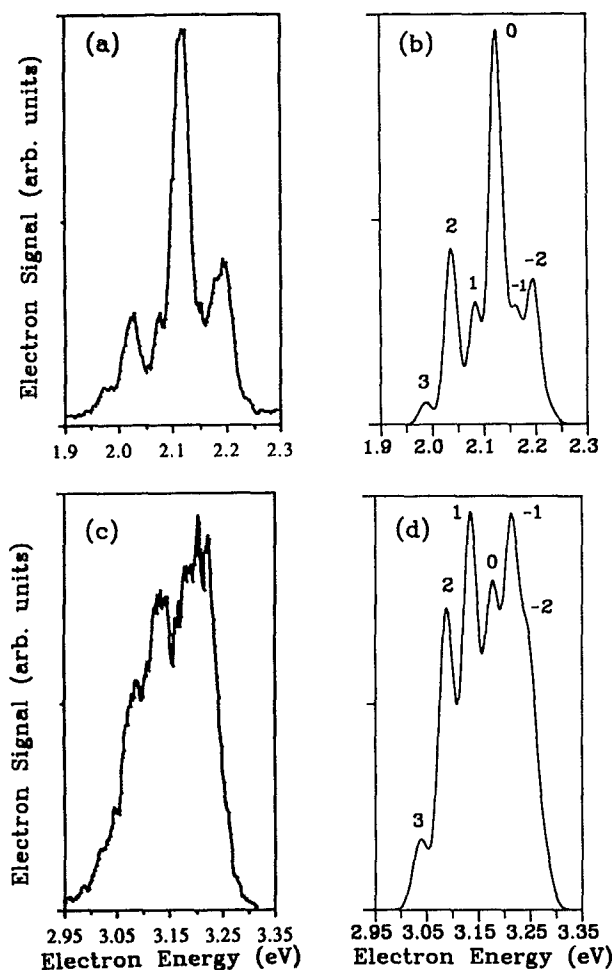


FIG. 1. Experimental and calculated rotationally resolved photoelectron spectra for (2 + 1) REMPI of OH. (a) Observed spectra for the  $D^2\Sigma^-$  state,  $v' = 0 \rightarrow v^+ = 0$ ,  $O_{11}(11)$  rotational branch; (b) calculated  $D^2\Sigma^-$  ( $3p\sigma$ ) photoelectron spectra, assuming a Gaussian line shape with a FWHM of 30 meV; (c) observed spectra for the  $3^2\Sigma^-$  state,  $v' = 0 \rightarrow v^+ = 0$ ,  $O_{11}(11)$  rotational branch; (d) calculated  $3^2\Sigma^-$  ( $4s\sigma$ ) photoelectron spectra, assuming a Gaussian line shape with a FWHM of 35 meV. The labeling of peaks in the calculated spectra indicates the change of rotational quantum number  $\Delta N = N^+ - N'$ .

peak is associated mainly with the  $l = 1$  ( $p$  wave) component of the photoelectron orbital. At  $R_e = 2.043a_0$  the " $3p\sigma$ " Rydberg wave function is 63.3%  $p$  and 34.9%  $s$  character, and the  $3s\sigma \rightarrow kp\sigma$  component contributes substantially to the total transition moment. The continuum  $l = 3$  ( $f$  wave) is also important, and contributes principally to the weaker  $\Delta N = \pm 2$  peaks of Fig. 1(a). The presence of these additional continuum waves reflects angular momentum coupling induced by the strongly anisotropic molecular field. The agreement between the experimental [Fig. 1(a)] and theoretical [Fig. 1(b)] photoelectron spectra is encouraging. The observed skewing of the  $\Delta N = -2$  over  $\Delta N = 2$  transitions is not repro-

duced by theory. For the present (2 + 1) REMPI experiments via these Rydberg states, the  $a^1\Delta$  ionic state is energetically open, and electronic channel coupling in the continuum final state could perturb the observed rotational distributions. This seems likely since ionization channels exhibiting Cooper minima are inherently weak, and even weak channel interaction may influence the spectra. Note that some partial rotational state selectivity in Fig. 1(a) has been achieved due to the presence of the Cooper minimum, a result predicted previously for the  $\text{NO } H^2\Sigma^+$  Rydberg state.<sup>14,15</sup>

Experimental and theoretical results for photoionization of the  $3^2\Sigma^-$  ( $v' = 0$ ) state are shown in Figs. 1(c) and 1(d). In contrast to the  $D^2\Sigma^-$  state, the photoelectron spectra reveal a broader spectral distribution for rotational transitions  $\Delta N = 0, \pm 1, \pm 2, \pm 3$ . The appearance of this spectrum arises from greater  $l$  mixing in the higher Rydberg orbital (54.3%  $s$  and 42.7%  $p$  at  $R = 2.043a_0$ ) and much weaker Cooper minima for photoionization from this state.<sup>12</sup>

Cooper minima in the REMPI-PES spectra of diatomic molecules were first predicted for the  $D^2\Sigma^-$  Rydberg state of OH.<sup>11,12,16</sup> The close connection between Cooper minima and rotational state selection in molecular REMPI-PES was identified using the example of NO.<sup>14,15,17</sup> The generality and implications of Cooper minima in molecular REMPI-PES are just emerging, and the present work provides the first experimental evidence of these features in molecular REMPI-PES.

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