

Alignment of a Molecular Anion via a Shape Resonance in Near-Threshold Photodetachment

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One-color–two-photon photodetachment of HOCO^- at $E_{h\nu} = 1.60$ eV accompanied by a measurement of the photoelectron angular distribution (PAD) is used to illustrate a novel approach to the alignment of a molecular anion. A quantitative analysis of the PAD reveals this alignment process is associated with a temporary anion formed by a p -wave shape resonance and the PAD in the two-photon signal is a result of interfering s - and d -partial waves within the atomic approximation. The extracted intensity and phase shift of the partial waves are consistent with the Wigner threshold law for photodetachment.

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Molecular orientation and alignment have long been recognized as key factors determining the probability of bimolecular, molecule-surface, and molecule-electromagnetic field interactions. In the past few decades, the control of molecular alignment has been a major research focus, with the ultimate goal of manipulation of chemical reactivity [1,2]. However, previous studies generally focused on neutral molecules, with few experimental efforts that target negative ions. This Letter illustrates the alignment of a molecular anion via a shape resonance in near-threshold photodetachment for the first time. The phenomenon reported here may prove to be general for molecular anions in which the dominant photodetachment channel above threshold produces free electrons with a nonzero angular momentum. The work should be of general interest as it may open new avenues for the study of electron-neutral interactions and the manipulation of chemically important transient neutral species produced by the photodetachment of anion precursors [3].

Several approaches have been applied to the alignment and orientation of neutral molecules. A hexapole [4] or strong homogeneous electrostatic field [5] can create oriented molecules with large dipole moments. Recently, alignment of general classes of molecules has been reported using a strong laser field on the induced dipole moment [6,7]. An alternative laser control approach utilizes resonant optical transitions with polarized light [8]. Since the transition dipoles in the molecular frame (MF) have specified directions, an anisotropic excited-state molecular ensemble can be generated by the interaction with electromagnetic radiation, leaving the remaining ground-state molecules with an anisotropic distribution as well. Although this type of alignment is not as strong as that achieved by the nonresonant strong laser field, it only requires moderately intense laser pulses and has the advantage of quantum-state selectivity. As a result, it has been widely applied in the study of photoionization dynamics and rotational wave packet revival [9–13]. The application of this technique to the alignment of molecular

anions, however, has seen limited success owing to the paucity of bound excited states in anions. In this Letter, we demonstrate a novel approach to align a molecular anion through a shape resonance near the photodetachment threshold.

In the atomic approximation for photodetachment, the effective potential between a photoelectron and the molecular core can be approximated by a radial form $V_{\text{eff}}(r) = V(r) + l(l+1)\hbar^2/2\mu r^2$ [14], where the first term, $V(r)$, represents the weak electron-neutral attractive potential, the second term describes a centrifugal barrier, l is the angular momentum quantum number for the photoelectron partial wave, and μ is the reduced mass. Unlike the dominant Coulomb attraction between the departing electron and cation core in the photoionization of neutral molecules, $V(r)$ in anion photodetachment decays faster than r^{-2} when r increases. Consequently, when low-energy photoelectrons are produced in near-threshold photodetachment, s -wave photoelectrons ($l = 0$) dominate, while electrons with $l > 0$ are trapped by the centrifugal barrier, forming a temporary anion with the excess electron weakly bound to the neutral core. The lifetime of such a shape resonance can vary from $\sim 10^{-15}$ to $\sim 10^{-10}$ s [15]. In a molecular anion, V_{eff} is expected to depend on the MF instead of being a purely central potential. Therefore, with a short-pulsed laser or two laser pulses, the alignment of a molecular anion can be realized through a shape resonance with an excitation photon near the photodetachment threshold, and be detected by photodetachment of the temporary anion using a second photon and measuring the resulting laboratory-frame (LF) PAD.

This approach was applied in the present study to align a polyatomic anion, HOCO^- . Previously the one-photon detachment of HOCO^- at $E_{h\nu} = 4.80$ eV and 3.21 eV has been used to probe the potential energy surface of the bimolecular reaction $\text{OH} + \text{CO} \leftrightarrow \text{HOCO} \rightarrow \text{H} + \text{CO}_2$ [16,17]. Two planar isomers were reported for both the anionic and neutral HOCO , with *ab initio* calculations predicting adiabatic electron affinities (AEA) of 1.30 and

1.43 eV for *trans*- and *cis*-HOCO, respectively [16]. In the current work, the energy-resolved PAD from one and two-photon detachment of HOCO^- at $E_{h\nu} = 1.60$ eV was obtained, showing evidence for the alignment of HOCO^- by photoabsorption near the detachment threshold. The observed two-photon LF-PAD provides valuable insights into the photodetachment dynamics.

The experimental details have been described elsewhere [16,17], and will only be briefly reviewed here. The HOCO^- anions were generated in a supersonic expansion of a gas mixture (7% CO, 6% N_2O , 17% CH_4 , and 70% N_2) crossed by a 1 keV electron beam. The anion beam was then accelerated to 10 keV, and mass selected by time of flight. The HOCO^- ($m/e = 45$) beam was crossed by the fundamental (772 nm, $E_{h\nu} = 1.60$ eV) of a Ti:sapphire laser (Clark-MXR CPA-2000, 1.8 ps FWHM, 1 kHz). The laser power density in the photon-ion interaction volume was estimated to be $\sim 6 \times 10^{10}$ W/cm².

Photoelectrons ejected over the 4π sr solid angle were collected by a space focusing electron optics assembly [11] and recorded on an event-by-event basis with a time- and position-sensitive detector parallel to the plane of the ion and laser beams, yielding angle-resolved photoelectron kinetic energy (*eKE*) distributions. The electron detector was calibrated by photodetachment of O^- at $E_{h\nu} = 1.60$ eV (*eKE* = 0.14 eV, FWHM = 0.06 eV). The neutral fragments produced by photodetachment were registered by another time- and position-sensitive detector, allowing coincidence studies of the dissociative photodetachment of HOCO^- that will not be considered further in this Letter.

Figure 1(a) shows the angle-integrated $P(e\text{KE})$ spectrum. Two narrow peaks (I) at 0.01 eV and (II) at 0.09 eV, along with a broad peak (III) ranging from ~ 0.4 eV to ~ 1.9 eV are observed. A comparison between peak (III) and the $P(e\text{KE})$ obtained in a previous study at $E_{h\nu} = 3.21$ eV shows great similarity [17]. Noting the maximum *eKE* in the one-photon detachment at $E_{h\nu} = 1.60$ eV should be 0.30 eV for *trans*- and 0.17 eV for *cis*- HOCO^- using previously calculated AEAs [16], the energetic photoelectrons in peak (III) can only result from two-photon detachment of HOCO^- . This was further verified by reducing the laser power by $\sim 60\%$. Assuming no competition between one- and two-photon processes, the signal intensities $I_{1h\nu}$ and $I_{2h\nu}$ are proportional to the first and second order of the laser power, respectively, so the intensity ratio $I_{2h\nu}/I_{1h\nu}$ is also expected to drop by 60%. In this experiment, the intensity of peak (III) compared to the sum of peaks (I) and (II) dropped by over 70%, consistent with the two-photon process “bleaching” the one-photon signal. The fine structure resolved in the near-threshold one-photon detachment [peaks (I) and (II)] may originate from the coexistence of *cis*- and *trans*- HOCO^- in the ion beam or O-C-O bending vibrations in HOCO. A significant portion of the one-photon signal is seen to extend to

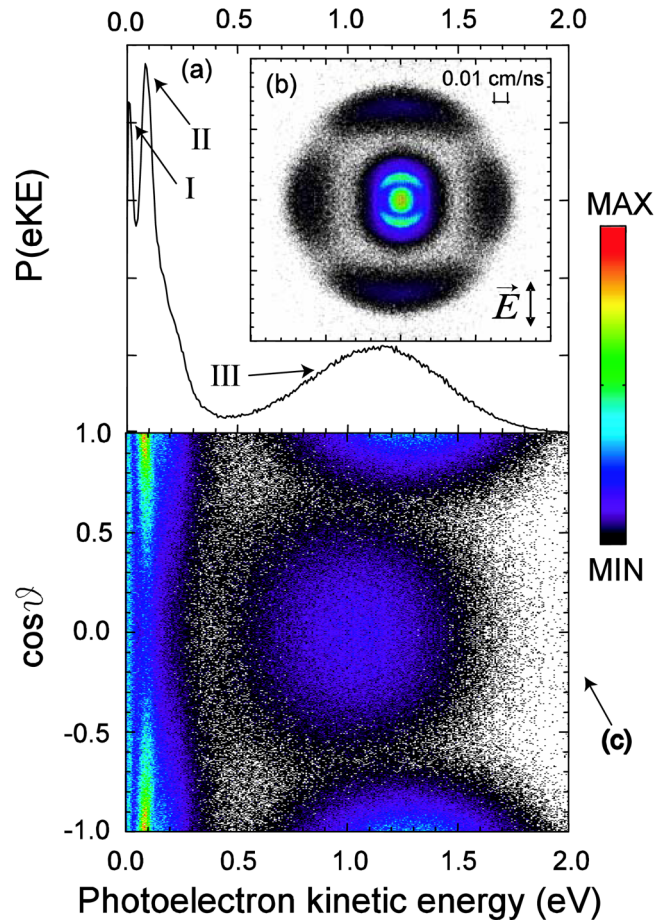


FIG. 1 (color online). (a) The angle-integrated $P(e\text{KE})$ spectrum of photodetachment of HOCO^- at $E_{h\nu} = 1.6$ eV. The peaks (I) and (II) correspond to the one-photon signals and peak (III) corresponds to the two-photon signal. (b) The projection of 3D photoelectron velocities on the 2D electron detector, with the laser \vec{E} vector along the ordinate. (c) The *eKE*-resolved PAD plotted in $P(e\text{KE}, \cos\theta)$, where θ is the electron recoil angle referenced to the laser \vec{E} vector parallel to the direction of ion beam propagation.

~ 0.4 eV, possibly a result of the uncertainty of the predicted AEA values and the presence of vibrationally excited HOCO^- in the parent ion beam as discussed in a previous study [17], though the rotational temperature of the HOCO^- is expected to be low.

The photodetachment dynamics are revealed by the LF-PAD. Figure 1(b) shows the projection of the measured 3D photoelectron velocities on the 2D electron detector, with the laser \vec{E} vector along the ordinate. The isotropic “disc” at the center of the image corresponds to peak (I) in Fig. 1(a), consistent with the *s*-wave photoelectrons expected to dominate in near-threshold anion photodetachment [18]. The two lobes next to the center show that the electrons in peak (II) are ejected along the laser \vec{E} vector, consistent with dominant *p*-wave photodetachment above threshold, as seen previously at higher photon energies [16,17]. The unique fourfold outer ring corresponds to

the two-photon signals. Unlike in the one-photon detachment at $E_{nv} = 3.21$ eV [17], photoelectrons generated by absorbing two 1.60 eV photons have both parallel and perpendicular LF-PAD components. The eKE dependence of the LF-PAD can be viewed in a 2D histogram $P(eKE, \cos\theta)$ as shown in Fig. 1(c), where the intensity of each point represents the number of events corresponding to a certain eKE and the cosine of the electron recoil angle θ relative to the laser \vec{E} vector. In the two-photon signal, the photoelectrons with the perpendicular PAD have a $P(eKE)$ peak around 1.0 eV, shifted away from those with the parallel PAD peaking at ~ 1.2 eV.

A more quantitative understanding of the two-photon photodetachment dynamics can be achieved by fitting the eKE -resolved LF-PAD to the following equation [19]:

$$I(\theta, eKE) = \frac{\sigma(eKE)}{4\pi} [1 + \beta_2(eKE)P_2(\cos\theta) + \beta_4(eKE)P_4(\cos\theta)], \quad (1)$$

where $\sigma(eKE)$ is the total cross section at a certain eKE , P_2 and P_4 are second- and fourth-order Legendre polynomials, β_2 and β_4 represent energy-dependent anisotropy parameters. When β_2 and β_4 are zero, only s -wave photodetachment occurs and an isotropic PAD is observed. In the case of interfering s and d waves [20], β_2 and β_4 are restricted by

$$9\beta_2^2 - 10\beta_2\beta_4 + 30\beta_4^2 - 70\beta_4 \leq 0. \quad (2)$$

The one-photon photodetachment can also be described by Eq. (1) with $\beta_4 = 0$ and β_2 ranging from $-1[I(\theta, eKE) \propto \sin^2\theta]$ to $2[I(\theta, eKE) \propto \cos^2\theta]$ [21].

The $\beta_2(eKE)$ and $\beta_4(eKE)$ distributions are obtained by fitting the observed PAD using Eq. (1). The results are summarized in Fig. 2. At low eKE , β_4 fluctuates around zero, consistent with one-photon photodetachment and no apparent anion polarization by the electric field of laser. When $eKE \leq 0.04$ eV, β_2 is nearly zero. The β_2 values then rapidly increase to 0.9 at $eKE \sim 0.09$ eV, which corresponds to the peak (II) in Fig. 1(a). There is another minimum at $eKE = 0.13$ eV where $\beta_2 \sim 0.6$, followed by a slow increase of β_2 to a maximum of ~ 0.9 . The positive β_2 values ranging from 0 to 1 in the one-photon detachment imply a mixing of s - ($l = 0$) and p - ($l = 1$) partial wave continuum electrons in the atomic approximation, with the low-energy p -wave photoelectrons suppressed by the centrifugal barrier, causing $\beta_2 \sim 0$ at small eKE . The rapid increase of β_2 above $eKE = 0.04$ eV should be related to the height of the centrifugal barrier for $l = 1$. Since p -wave electrons may tunnel through the centrifugal barrier, it is reasonable to assign 0.04 eV as a lower limit for the height of the p -wave centrifugal barrier.

When the two-photon process dominates at $eKE \geq 0.40$ eV, β_4 increases to an unusually large positive value for a molecular anion, indicating significant alignment of

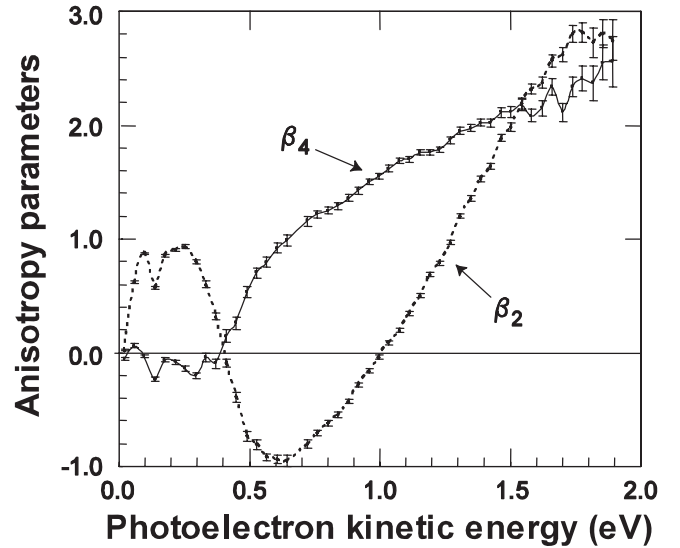


FIG. 2. The $\beta_2(eKE)$ and $\beta_4(eKE)$ functions obtained by fitting the experimental LF-PAD with Eq. (1), including 1 σ error bars.

the temporary HOCO^- anion. Since there is no centrifugal barrier for s -wave photoelectrons and a picosecond laser was used in the present study, the most likely mechanism is that when HOCO^- absorbs the first photon, s -wave photoelectrons as well as the fast p -wave photoelectrons escape the molecular core, while slow p -type electrons are temporarily trapped by the centrifugal barrier and detached by a second photon. This mechanism is also consistent with the observation that the increased two-photon signal comes at the expense of the one-photon signal. In the absence of absorption of a second photon during the 1.8 ps laser pulse, the temporary anion produced by the shape resonance can later decay by electron tunneling through the centrifugal barrier. Thus, the observed alignment of HOCO^- presented here is assigned to a sequential two-photon process using the temporary anion formed by an $l = 1$ shape resonance as the intermediate state, and is expected to have an angular distribution proportional to $\cos^2\theta$ relative to laser \vec{E} vector as suggested by the previous time-resolved photoionization experiments [12]. According to the $\Delta l = \pm 1$ atomic selection rule, photodetachment of the p -type electrons will result in an interference of s - and d -wave free electrons. This atomic approximation is seen to be valid in the molecular case under investigation as Eq. (2) holds well for the measured β_2 and β_4 values in an eKE range up to 1.7 eV, possibly because of the relatively large size of the excess electron orbital with respect to the molecular core in the temporary anion. In fact, the patterns shown in Fig. 1(c) are similar to those reported in a previous above-threshold two-photon photodetachment study of atomic H^- using a strong laser field, which solely involves mixing s - and d -partial wave photoelectrons [22]. When $eKE > 1.7$ eV, the experimental β_2 and β_4 no

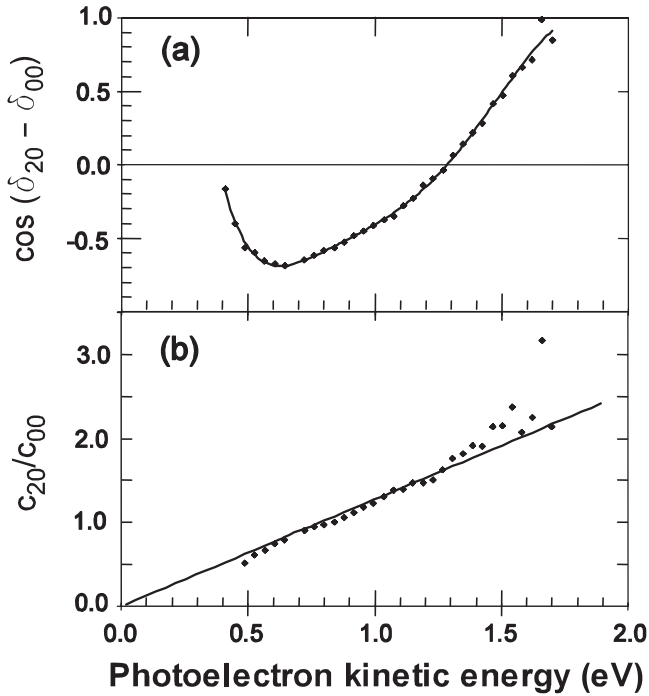


FIG. 3. (a) Cosines of the phase-shift difference, $\cos(\delta_{20} - \delta_{00})$, and (b) the ratios of the radial transition coefficients, c_{20}/c_{00} vs. eKE for continuum s - and d -wave photoelectrons produced in the two-photon process. The solid line in (a) is obtained by fitting the data with a sixth order polynomial. The solid line in (b) shows the linear relationship of c_{20}/c_{00} with eKE that is consistent with the Wigner threshold law for photodetachment.

longer satisfy Eq. (2) as a result of larger measurement uncertainties at high eKE .

Quantitatively, the PAD in the two-photon detachment can be decomposed into photoelectron partial waves as

$$I(\theta, \phi) \propto |\psi_e|^2, \quad \psi_e = \sum_{lm} c_{lm} e^{i\delta_l} Y_{lm}(\theta, \phi), \quad (3)$$

where the coefficient c_{lm} is determined by the radial component of the dipole transition and has a non-negative real value, δ_l is a phase shift, and $Y_{lm}(\theta, \phi)$ is the corresponding spherical harmonic [19]. With a linearly polarized laser, only $m = 0$ contributes, and assuming only s - and d -partial wave contributions, a ratio of c_{20}/c_{00} , as well as a phase difference ($\delta_{20} - \delta_{00}$) with an uncertain sign, can be determined for each set of β_2 and β_4 by comparing Eqs. (1) and (3) [19,20]. Figure 3 shows c_{20}/c_{00} and $\cos(\delta_{20} - \delta_{00})$ as functions of eKE . An interesting observation is that the experimental c_{20}/c_{00} values are linearly proportional to eKE up to ~ 1.3 eV, in good agreement with the Wigner law for near-threshold photodetachment: $\sigma_l = |c_l|^2 \propto (eKE)^{l+1/2}$ [18]. This is consistent with the interference of s - and d -partial waves generated by photodetachment of the temporary anion supported by the $l = 1$ shape resonance leading to the molecular alignment im-

plied by the eKE -dependent LF-PAD of the two-photon signal.

In conclusion, the two-photon detachment of HOCO^- at $E_{h\nu} = 1.60$ eV shows that it is possible to use a shape resonance near the photodetachment threshold to align a molecular anion. In this study, the excitation and probe laser pulses have the same linear polarization. Further experiments using different polarization geometries or two-color pump and probe lasers may yield more insights into the photodetachment dynamics [19], along with direct measurements of the photofragment angular distributions to quantify the alignment. Additionally, time-resolved PAD measurements may help characterize the resonance lifetimes that play an essential role in this type of alignment, and the time-evolution of the alignment as a result of molecular rotation that tests the sensitivity of the PAD to the alignment [12,19]. This phenomenon may prove to be general for molecular anions dominated by p - or higher l -wave photodetachment above threshold.

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