Complete kinematic measurement of three-body reaction dynamics: Dissociative photodetachment of \( \text{O}_6^- \) at 532 nm

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Measurement of the translational energy partitioning in the three-body dissociative photodetachment of \( \text{O}_6^- \) \((\text{O}_6^- + h\nu \rightarrow \text{O}_2 + \text{O}_2 + \text{O}_2 + e^-)\) at 532 nm is reported. Using photoelectron and photofragment translational energy spectroscopies in coincidence, a complete kinematic measurement of the three-body dissociation of neutral \( \text{O}_6 \) is obtained. Vibrationally resolved product translational energy distributions are observed. The results provide insights into the structure, binding energy, and dissociation dynamics of \( \text{O}_6^- \) and \( \text{O}_6 \) and illustrate a new approach to the study of three-body reaction dynamics. © 1998 American Institute of Physics.

In recent years, there has been an increased interest in developing a more detailed experimental and theoretical understanding of three-body chemical reactions.\textsuperscript{1,2} Significant experimental progress has been made in studies of the dissociation of multiply charged cations and other high energy systems.\textsuperscript{3–5} Detailed experimental studies of the dynamics of three-body reactions of neutral species, however, have been limited to excited-state photodissociation reactions leading to either prompt or sequential dissociation processes. These experiments have in general relied on measurements of the uncorrelated asymptotic properties of the photofragments such as momentum and quantum state.\textsuperscript{1,6–11} The overall three-body dynamics has then been inferred from the data using theoretical guidance to determine the forces at the transition state for dissociation. In our laboratory, we have sought to develop a technique to study three-body dissociation processes on the electronic ground state for neutral systems. The approach we have taken is one developed in our laboratory and previously applied to two-body dissociation processes, photoelectron–photofragment coincidence spectroscopy.\textsuperscript{12} In these experiments, photodetachment of a precursor negative ion and energy analysis of the photoelectron is used to prepare a neutral complex with a known internal energy that subsequently dissociates. Use of a fast precursor negative-ion beam and a new multiparticle detector allows collection of the three photofragments in coincidence, providing a direct measure of the translational energy and angular distributions of the photofragments in a three-body dissociation.

In this communication, we describe the application of this technique to the study of the three-body dissociation reaction initiated by dissociative photodetachment (DPD) of the \( \text{O}_6^- \) cluster anion. Photodetachment of anions can produce a neutral complex far from the equilibrium geometry, and the repulsive energy in the cluster can lead to a rapid dissociation. To determine the energetics and dissociation dynamics of such short lived neutral clusters, a measurement of the photoelectron kinetic energy alone is insufficient—it is necessary to measure the photoelectron kinetic energy in coincidence with the translational energy release.\textsuperscript{12}

The homogeneous cluster anions of \( \text{O}_2 \), of which \( \text{O}_4^- \) and \( \text{O}_6^- \) are the simplest, are known to exhibit a rich photochemistry, undergoing both photodissociation and photodetachment with visible photons.\textsuperscript{13,14} In the case of \( \text{O}_4^- \), energetic considerations indicate that at 532 nm (2.33 eV), DPD produces a free electron and two ground state \( \text{O}_2 \) \((^{3}\Sigma_g^-)\) molecules. Mass spectrometric studies have shown that \( \text{O}_6^- \) is stabilized relative to \( \text{O}_4^- \) by 0.11 eV,\textsuperscript{15} thus DPD of \( \text{O}_6^- \) at 532 nm will yield a free electron and three ground state \( \text{O}_2 \) molecules. Recent work on \( \text{O}_4^- \), both in gas-phase,\textsuperscript{16,17} and matrix isolation\textsuperscript{18} studies, has indicated that the excess electron is delocalized over both \( \text{O}_2 \) moieties in a planar \( D_{2h} \) structure with a \( ^2A_u \) electronic ground state. In a previous study of \( \text{O}_6^- \), Johnson and co-workers\textsuperscript{13} observed a significant enhancement of photodissociation at long wavelengths (1064 nm) relative to \( \text{O}_4^- \). It has been suggested that this is due to a charge-transfer-to-solvent interaction between an \( \text{O}_4^- \) core and the “solvating” \( \text{O}_2 \).\textsuperscript{13} The present experiments focus on the DPD of \( \text{O}_6^- \) at 532 nm, and as shown below, reveal a vibrationally resolved translational energy distribution as well as new photodissociation channels unobserved in \( \text{O}_4^- \).

A schematic of the detection geometry is shown in Fig. 1. The photoelectron–photofragment spectrometer is described in detail elsewhere\textsuperscript{19} and will only be briefly described here. Anions are made and cooled in a pulsed free jet expansion of \( \text{O}_2 \) intersected by a 1 keV electron beam. The anions are accelerated to an energy of 4 keV and mass selected by time of flight. Anions at \( m/e = 96 \) are intersected...
by a 120 μJ/pulse, 100 ps full width at half-maximum (FWHM), linearly polarized 532 nm laser beam. In these experiments, the electric vector of the laser was fixed parallel to the ion beam direction. Photoelectrons traverse a nominal 50 mm field-free flight path and impinge on one of two 100-mm-diam detectors, both centered perpendicular to the laser electric vector on opposite sides of the ion beam. The two time- and position-sensitive photoelectron detectors comprise the photoelectron spectrometer and have an effective angular acceptance of 21% of 4π sr. Using the time and position information, the electron recoil angle and actual flight path are calculated, allowing correction for the large Doppler shift associated with the ion beam as a function of angle. The center-of-mass electron kinetic energy (eKE) resolution is ΔE/E (FWHM)=5% at 1.3 eV as determined by measurements of the O$_2^-$ photoelectron spectrum at 532 nm.

Photofragments recoil out of the beam over a 104 cm flight path between the laser interaction region and the photofragment detector. Residual ions and ionic photofragments are electrostatically deflected away from the detector. The photofragment detector consists of four quadrants, each capable of recording the time and position of arrival of up to two photofragments. This microchannel-plate-based detector uses a crossed delay-line format for the anode, with each delay line instrumented to record two photofragments per shot as long as they are separated by a delay-line length of ~25 ns. There is effectively no dead area within the 40 mm active diameter of this detector, since an event arriving on a quadrant boundary will excite two quadrants, and can be subsequently analyzed and assigned to one of them by an analysis of the event charge. The time and position of arrival of the photofragments together with conservation of momentum determine the recoil angles, photofragment mass ratios, and the total center-of-mass translational energy release (E$_T$) for the three molecular photofragments. Due to the small recoil of one of the O$_2$ products in the case of O$_6^-$, the product mass resolution of the apparatus is low (m/Δm≈2). Energetic considerations, however, dictate that three-body DPD processes for O$_6^-$ at this wavelength must yield 3O$_2$+e$^-$. The translation energy resolution of the apparatus is <8% ΔE/E at 0.8 eV, as determine by studies of the photodissociation of O$_3^-$ at 532 nm. The angular acceptance is a full circle covering 100% of 4π sr given the beam energy and the kinematics of this reaction.

Each event is required to consist of a single electron and three neutral photofragments. Conservation of momentum allows discrimination against false photofragment coincidences while correlation of the electron and photofragments is determined by the spectrometer efficiency and the count rate. These experiments were carried out at repetition rate of 500 Hz and the observed quadrupole coincidence rate of 0.1 Hz yields ~5% false coincidences.

The O$_6^-$ data at 532 nm have been analyzed for both two- and three-body dissociation pathways, and the only dissociation pathway observed is O$_6^-$+hν→3O$_2^+$+e$^-$. This is in accord with our studies of O$_4^-$, which show that no stable O$_4$ is produced. To examine the partitioning of translational energy among the photoelectron and the three photofragments produced in the DPD of O$_6^-$, it is useful to examine the photoelectron–photofragment correlation spectra, N(eKE, E$_T$), as shown in Fig 2. This shows a two-dimensional histogram of the correlation between eKE and E$_T$. The spectra along the eKE and E$_T$ axes are found by integrating over the complementary variable and are the photoelectron and photofragment translational energy release spectra that are measurable in conventional noncoincidence spectrometers. The limit A corresponds to the maximum kinetic energy among the four particles (3O$_2$+e$^-$), given the 0.11 eV stability of O$_3^-$ relative to O$_3^+$+O$_2$ inferred from these experiments and mass spectrometric studies by Hiraoka.

The dominant feature observed in Fig. 2 arises from the three-body DPD process [O$_6^- + h\nu \rightarrow 3O(X^3\Sigma_g^-) + e^- \] (eKE, E$_T$) correlation spectrum for O$_6^-$ at 532 nm. The energetic limit A for the process O$_6^- + h\nu \rightarrow 3O(X^3\Sigma_g^-) + O_2(X^3\Sigma_g^-) + O_2(X^3\Sigma_g^-) + e^-$ is shown. The contours are linearly scaled and the marked features are discussed in the text.
by I. These ridges are very similar to the features previously observed in the DPD of \( \text{O}_4^+ \) at 532 nm.\(^\text{16}\) In the DPD of \( \text{O}_4^+ \), a series of five diagonal ridges were observed in the photoelectron–photofragment correlation spectrum, corresponding to direct DPD on a series of vibrationally adiabatic repulsive curves correlating to ground electronic state \( \text{O}_2^+(v = 0) + \text{O}_2(v = 0) \), \( \text{O}_2^+(v = 0) + \text{O}_2(v = 1) \), and so forth. In the \( \text{O}_6^- \) spectrum, these diagonal bands are shifted to a lower eKE and \( E_T \), due to the 0.11 eV stability of \( \text{O}_6^- \) relative to \( \text{O}_4^+ + \text{O}_2 \).\(^\text{15}\) In the correlation spectrum, internal energy of the photofragments appears as a displacement along the diagonal between the origin and the limit \( A \). The separation of the ridges along the diagonal is \( \approx 0.19 \) eV, consistent with the vibrational spacing of the \( \text{O}_2 \) photofragments. Thus, as in the case of \( \text{O}_4^+ \), these features are assigned to the correlated product state distribution of the \( \text{O}_2 \) products.

These diagonal features in the correlation spectrum arise from direct DPD of a bound anion on a repulsive electronic state of the nascent neutral complex. The eKE is determined by the photon energy and the vertical energy difference between anion and neutral, while \( E_T \) for a given DPD event contains additional information concerning the repulsive energy in the neutral complex relative to the dissociation asymptote. Energy conservation dictates that all events that lie within a single ridge have a well-defined total kinetic energy (\( E_{\text{tot}} = \text{eKE} + E_T \)). Within a given ridge, however, there is a range of energy partitioning between the electron and photofragments that is determined by the Franck–Condon overlap between a bound coordinate in the anion and the dissociation coordinate.

There are two other important features in Fig. 2. Feature II, the vertical row of spots at \( E_T = 0.7 \) eV, results from a photodissociation process \( \text{O}_6^- + h\nu \rightarrow \text{O}_2^1(\Delta_g, v = 0) + \text{O}_2^2(\Pi_g, v = 0) + \text{O}_2^3(\Sigma_g^+) \). The analogous process \( \text{O}_2^1 + h\nu \rightarrow \text{O}_2^2(\Delta_g, v = 0) + \text{O}_2^3(\Pi_g, v = 0) \) was previously observed, at \( E_T = 0.8 \) eV. The lower \( E_T \) observed in the photodissociation of \( \text{O}_6^- \) is consistent with the 0.11 eV stability of \( \text{O}_6^- \) relative to \( \text{O}_4^+ + \text{O}_2 \). These features are observable in this experiment (that only detects neutral photofragments) due to photodetachment of the nascent \( \text{O}_6^- \) photofragments by a second photon, yielding the well-known photoelectron spectrum of \( \text{O}_2^1(v = 0) \)\(^\text{13,23}\) as the vertical row of spots. Finally, feature III is a second photodissociation process, not observed in \( \text{O}_4^+ \) at 532 nm; \( \text{O}_2^1 + h\nu \rightarrow \text{O}_2^2(\Pi_g, v > 3) + \text{O}_2^3(\Sigma_g^+) + \text{O}_2^3(\Sigma_g^-) \). The peaks visible in the photoelectron spectrum appear at energies of 0.09, 0.19, and 0.30 eV, consistent with autodetachment of \( \text{O}_2^1(v = 4, 5, 6) \) to \( \text{O}_2(v = 0) + e^- \). Observation of maximum \( \Delta v \) autodetachment of \( \text{O}_2^1 \) was discussed by Schultz and co-workers,\(^\text{24}\) and is thought to derive from the high centrifugal barrier faced by the autodetaching \( \ell = 2 \) diatomic photoelectron. Higher-resolution photoelectron spectra from this laboratory have shown that the peak for \( \text{O}_2^1(v = 7) \) autodetachment is also observed at 0.41 eV.\(^\text{25}\) A consideration of the energetics indicates that this process can only occur if no \( \text{O}_2^3(\Delta_g) \) is produced in this photodissociation channel.

In Fig. 3 the \( E_{\text{tot}} \) spectra for \( \text{O}_4^+ \) (from Ref. 16) and \( \text{O}_6^- \) are shown in the lower and upper frames, respectively. These spectra are generated from the correlation spectra by historgramming \( E_{\text{tot}} = \text{eKE} + E_T \) for each event. The shift of the threshold \( A \) in the \( \text{O}_6^- \) spectrum is due to the stability of \( \text{O}_6^- \) relative to \( \text{O}_4^+ + \text{O}_2 \). The diagonal ridges of Fig. 2 now appear as resolved peaks in the \( \text{O}_6^- \) data. The spectrum shows that the DPD of \( \text{O}_6^- \) is characterized by an increase in the relative intensities of the peaks corresponding to vibrationally excited \( \text{O}_2 \) relative to \( \text{O}_4^+ \). There is also evidence of increased rotational excitation at higher vibrational energies, as shown by the shift of the peaks and reduction in resolution at lower \( E_{\text{tot}} \). The fact that these peaks are resolved indicates that the rotational distribution in the photofragments, even in the case of \( \text{O}_6^- \), is narrow and generally less than a vibrational quantum. Remarkably, the dynamics observed in DPD of \( \text{O}_4^+ \) are largely preserved in \( \text{O}_6^- \).

The low observed rotational excitation indicates that, like \( \text{O}_4^+ \), there is a restricted range of product angular momenta produced in the dissociation of the nascent \( \text{O}_6^- \) neutral. This result is consistent with either a weakly bound ion–dipole complex, in which the third \( \text{O}_2 \) is merely a spectator, or perhaps a molecular \( \text{O}_6^- \) anion with a reasonably high symmetry. The observed product vibrational distribution is not consistent with either extreme limit, however, at least within the framework of the simple local-mode Franck–Condon simulation previously used in the analysis of the \( \text{O}_4^+ \) \( E_{\text{tot}} \) spectrum. In this calculation, the probability for each energetically allowed combination of vibrational states is calculated as a product of the individual diatom Franck–Condon factors, taking into account the degeneracy for a given set of product vibrational states. A good fit to the \( \text{O}_4^+ \) \( E_{\text{tot}} \) spectrum, shown by the solid line in Fig. 3, was generated by calculating the overlap of the vibrational wave functions of two perturbed \( \text{O}_2 \) moieties \( (r_e = 1.272 \ \text{Å}, \ \omega_e = 1335 \ \text{cm}^{-1}) \) with two free \( \text{O}_2(3\Sigma_g^-) \) molecules. In the limit of a weak interaction between \( \text{O}_2 \) and \( \text{O}_4^+ \), a similar distribution would be expected for \( \text{O}_6^- \). An examination of Fig. 3 shows that the \( \text{O}_4^+ \) distribution predicts lower vibrational excitation than observed in \( \text{O}_6^- \). An alternative possibility for \( \text{O}_6^- \) is that all three short O–O bonds are equal,
with $r_c = 1.255 \text{ Å}$, one third of the difference between $\text{O}_2$ and $\text{O}_3^-$. This fit, shown on the $\text{O}_6^-$ spectrum, does not reproduce the correlated product vibrational distribution. A better fit to the data will require more information on the structure of $\text{O}_6^-$ and the dynamics of the three-body dissociation of $\text{O}_6$.

In conclusion, we report the first complete kinematic description of a three-body DPD process. These results show that while the DPD dynamics of $\text{O}_6^-$ are remarkably similar to $\text{O}_4^-$, a more marked change is observed in the photodissociation dynamics. The low rotational excitation in the products permits the observation of vibrationally resolved translational energy distributions and argues for either an $\text{O}_2^-$ core bound electrostatically to a third $\text{O}_2$ or perhaps, a highly symmetric structure for $\text{O}_6^-$. Studies of the photodestruction dynamics at other wavelengths and theoretical calculations of the $\text{O}_6^-$ structure are under way to resolve this question. In future studies, the time scale for three-body dissociation will be addressed by examination of the photoelectron–photofragment and photofragment–photofragment angular correlations, and this technique will be extended to important systems including the three-body association reaction responsible for the formation of ozone: $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$.

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1 Recent experiments on three-body dissociation are extensively reviewed in: C. Maul and K. H. Gericke, Int. Rev. Phys. Chem. 16, 1 (1997).