C₆⁻ electronic relaxation dynamics probed via time-resolved photoelectron imaging

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Anion time-resolved photoelectron imaging has been used to investigate the electronic relaxation dynamics of C_6^- following excitation of the $\tilde{C}^2 \Pi_g \leftarrow \tilde{X}^2 \Pi_u$ and $2^2 \Pi_g \leftarrow \tilde{X}^2 \Pi_u 0_0^0$ transitions at 607 and 498 nm, respectively. Analysis of evolving photodetachment energy distributions reveals differing relaxation pathways from these prepared states. Specifically, the $\tilde{C}^2 \Pi_a 0^0$ level relaxes on a time scale of 620±30 fs to vibrationally hot (~2.0 eV) anion ground state both directly and indirectly through vibrationally excited levels of the intermediate-lying $\tilde{A}^{2}\Sigma_{g}^{+}$ state that decay with a time scale of 2300±200 fs. In contrast, the $2 \,{}^{2}\Pi_{g} 0^{0}$ level relaxes much more quickly (<100 fs) to vibrationally hot (~2.5 eV) anion ground state directly and with transient population accumulation in the $\tilde{A}^2 \Sigma_g^+$, $\tilde{B}^2 \Sigma_u^+$, and $\tilde{C}^2 \Pi_g$ electronic levels, as determined by spectral and time-scale analyses. This work also presents the experimental observation of the optically inaccessible $\tilde{B}^2 \Sigma_{\mu}^+$ state, which is found to have an electronic term value of 1.41 ± 0.05 eV. © 2004 American Institute of Physics. [DOI: 10.1063/1.1769368]

I. INTRODUCTION

Time-resolved photoelectron spectroscopy (PES) and its variants¹ have been shown to be powerful techniques for the study of ultrafast relaxation dynamics in electronically excited neutral species ranging from diatomics² to biomolecules.³ The application of these methods to similar dynamical processes in negative ions offers the additional advantage of incorporating size selectivity into the experiments, making it possible, for example, to track the evolution of relaxation phenomena with size in mass-selected metal and carbon cluster anions.⁴⁻⁶ Carbon cluster anions are particularly interesting as they support low-lying bound excited electronic states through which radiationless transitions can occur from an initially prepared excited state.⁷ In addition, depending on their size and how they are excited, these clusters undergo both direct photodetachment and thermionic emission.^{8,9} In this paper we present results on time-resolved photoelectron imaging of C₆⁻ in which we elucidate relaxation pathways subsequent to excitation of single vibronic levels, and further characterize the conditions under which this species undergoes thermionic emission.

Carbon cluster anions have been thoroughly characterized spectroscopically and via electronic structure calculations.^{10,11} Studies of these species and their neutral counterparts burgeoned in the 1980s and 1990s, reflecting an interest in identifying the carriers of the diffuse interstellar bands,⁷ the astronomically observed visible and near infrared absorptions of the interstellar medium, and understanding how the geometry of stable carbon structures evolves with size into the nanoscale regime.^{12,13} These molecular anions

Since this work was done, the advantages of photoelectron imaging (PEI) in negative ion experiments have been ^{a)}Author to whom correspondence should be addressed. Fax: 510-642-3635. demonstrated by Bordas,²⁰ Sanov,²¹ and co-workers, and we

are known to have linear equilibrium geometries at sizes n<10, and numerous bound electronic states below threshold,

a consequence of the relatively high electron affinities of

their neutral counterparts^{14,15} and their energetically dense

est in this work, has been characterized by a combination of

matrix absorption,^{16,17} resonant two-photon detachment,⁸ and

ab initio studies.^{18,19} An electronic energy diagram for C_6^{-1} is

given in Fig. 1, labeled with best-available level energetics

and shorthand electronic configurations for all states relevant

to this study. The dominant molecular orbital for the

 $C_6^{-} \tilde{X}^2 \Pi_u$ ground state is $\dots 6\sigma_g^2 1 \pi_u^4 6 \sigma_u^2 7 \sigma_g^2 1 \pi_g^4 2 \pi_u^3$,

while nominal configurations of the energetically lowest ex-

cited states of the anion, $\tilde{A}^2 \Sigma_g^+$, $\tilde{B}^2 \Sigma_u^+$, $\tilde{C}^2 \Pi_g$, and

 $2\,{}^{2}\Pi_{o}$, all within 3 eV of the anion ground state, arise from

 $2\pi_u \leftarrow 7\sigma_g$, $2\pi_u \leftarrow 6\sigma_u$, $2\pi_u \leftarrow 1\pi_g$, and $4\pi_g \leftarrow 2\pi_u$ exci-

tations from the ground state, respectively. All optically al-

lowed electronic transitions exhibit well-resolved vibrational

structure, enabling one to monitor relaxation pathways start-

ing from single vibronic levels of excited electronic states of

 C_6^{-} in time-resolved experiments. We previously studied the

internal conversion dynamics of C6- following excitation

through the $\tilde{C}^2 \Pi_e \leftarrow \tilde{X}^2 \Pi_\mu 0_0^0$ transition in a time-resolved

PES experiment with a magnetic bottle electron energy

analyzer.⁶ This work showed that the initially excited

 $\tilde{C}^2 \Pi_g 0^0$ level decayed with a time constant of 730 fs to the

 $\tilde{X}^2 \Pi_u^\circ$ ground state and the $\tilde{A}^2 \Sigma_g^+$ and/or $\tilde{B}^2 \Sigma_u^+$ levels,

which subsequently relaxed to the ground state on a time

The electronic spectroscopy of C_6^- , the species of inter-

electronic orbital structures.

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scale of 3.0 ps.



FIG. 1. C_6^{-}/C_6 electronic state energetics. Configurations reference ground states. Energetics are taken from best-available data: (a) Ref. 16, (b) Ref. 19, (c) Ref. 8, (d) Ref. 29, and (e) Ref. 30. EA(C_6) = 4.180 eV (Ref. 15). Arrows indicate one-electron-allowed photodetachment correlations.

have incorporated this detection technique into our timeresolved experiments.^{22,23} PEI offers higher electron energy resolution than our magnetic bottle analyzer and yields timeresolved photoelectron angular distributions (PADs) as well. Here, we present a study of the internal conversion dynamics of C₆⁻ following excitation of its $\tilde{C}\,^2\Pi_g \leftarrow \tilde{X}\,^2\Pi_u$ and $2\,^2\Pi_g \leftarrow \tilde{X}\,^2\Pi_u\,0_0^0$ transitions using femtosecond timeresolved photoelectron imaging (TRPEI). The aim of this work was to clarify the channels through which relaxation occurs from the $\tilde{C}\,^2\Pi_g\,0^0$ state, and to contrast these pathways and time scales with those arising through relaxation from the higher-lying $2\,^2\Pi_g$ state.

We find that the $\tilde{C} \,{}^2 \Pi_g \, 0^0$ state undergoes internal conversion to the $\tilde{X} \,{}^2 \Pi_u$ state by direct and indirect pathways; the improved instrumental resolution shows that the indirect pathway involves transient population of the $\tilde{A} \,{}^2 \Sigma_g^+$ state but not the $\tilde{B} \,{}^2 \Sigma_u^+$ state. Initial decay of $\tilde{C} \,{}^2 \Pi_g \, 0^0$ occurs on a time scale of 620 ± 30 fs, while population of the $\tilde{X} \,{}^2 \Pi_u$ and $\tilde{A} \,{}^2 \Sigma_g^+$ states rises on a comparable time scale and the $\tilde{A} \,{}^2 \Sigma_g^+$ state transient subsequently decays on a 2300±200 fs time scale. In contrast, decay of the $2 \,{}^2 \Pi_g \, 0^0$ level and subsequent population of the vibrationally hot ground and electronically excited transient states occur within the experimental pump-probe cross-correlation width ($t_{decay} < 100 \, \text{fs}$), where all intermediate-lying states—the $\tilde{A} \,{}^2 \Sigma_g^+$, $\tilde{B} \,{}^2 \Sigma_u^+$, and $\tilde{C} \,{}^2 \Pi_g$ states—participate as transient levels. The transient feature associated with the $\tilde{B} \,{}^2 \Sigma_u^+$ state provides the first experimental measurement of its term energy. Regardless of which



FIG. 2. Anion TRPEI apparatus. Ion source/mass spectrometer components: PV—pulsed valve; PD—pulsed discharge; E, A, G—Wiley-McLaren TOF focusing electrodes; D—ion deflectors; and Einz—Einzel Lens. Numbering indicates sequential participation in anion photoelectron VMI as explained in the text.

electronic state of C_6^- is prepared initially, the electron kinetic energy distribution after several picoseconds is dominated by photoemission from highly vibrationally excited ground state anions.

II. EXPERIMENT

A detailed schematic of our anion time-resolved photoelectron imaging apparatus is shown in Fig. 2. Anions are generated in a pulsed source, mass separated by time-offlight (TOF), and photoexcited and photodetached by femtosecond laser pulses. The resulting photoelectrons are collected and analyzed with a collinear velocity-map imaging (VMI) electron optical system, yielding both electron kinetic energy (eKE) and angular distributions.

In more detail, C_6^- was generated by passing a pulsed expansion (500 Hz, 350 µm pinhole, 25-35 psi backing pressure) of a 1% C₂H₂:1.5% CO₂ mix in argon carrier through a pulsed discharge (PD).²⁴ A 1200 eV electron beam provided a stabilizing charge source for negative ion formation within the discharge. Negative ions were injected orthogonally into a time-of-flight mass spectrometer at a beam energy of 1700 eV. Ions passed through a grounded aperture (1) and "rereferencing" tube (2) en route to the laser interaction region (3). Ions of interest were mass gated by briefly raising (2) from its normal voltage of either -2500 or -4000 V (depending on the pump wavelength) to 0 V and subsequently returning it to the original voltage once the chosen ions had entered; this permitted transmission of C₆⁻ while blocking ions differing by one mass unit (i.e., C₆H⁻) or more. Source ion distributions and gated ion signal were monitored by a retractable 1 in. chevron microchannel plate (MCP) detector (6).

The far end of (2), capped with an aperture, serves as the repeller electrode in our three-element photoelectron VMI assembly (3), which is based on the design of Eppink and Parker.²⁵ The other two elements are the extractor and grounded aperture electrodes that are held at static potentials. Ions interact with the femtosecond laser pulses—inducing excitation and photodetachment—between the repeller and extractor electrodes. Sharpest photoelectron images were obtained with an extractor-to-repeller potential ratio of 70%

for the current electrode geometry and location of the interaction region within the lens.

Photoelectrons are accelerated toward a 70 mm diameter chevron MCP detector (4), coupled to a P20 phosphor screen (Burle), located 60 cm from the laser-interaction region. With imaging lens potentials (repeller/extractor voltages) of $-2500 \text{ V/}-1750 \text{ V} (\tilde{C}^2 \Pi_g \leftarrow \tilde{X}^2 \Pi_u) \text{ and } -4000 \text{ V/}-2800$ V $(2^{2}\Pi_{e} \leftarrow \tilde{X}^{2}\Pi_{\mu})$, detachment signal filled 50%-70% of the detector area. A 500 Hz pulsed "gain gate" of $<1-2 \ \mu s$ duration limited signal collection about the arrival time $(\sim 300 \text{ ns interaction-to-detector})$ of the photoelectrons. Phosphor emission was ported from vacuum through a fiberoptic bundle, allowing a Dalsa-1M30 charge coupled device (CCD) camera (Uniforce), outfitted with an AF Nikkor 35 mm lens (Nikon), to capture images at a 50 Hz repetition rate (5); each frame integrated the signal of nine consecutive laser shots and was retriggered on the tenth. The camera collected images in a 2×2 pixel binning mode (effectively, 512) \times 512 pixels) in order to increase camera frequency and overall collection speed.

An electron energy resolution of $\Delta E/E \le 5\%$ is routinely obtained following atomic anion photodetachment with broad-bandwidth (20 meV) laser pulses. Photoelectron VMI yields 100% photoelectron collection while eliminating the "Doppler broadening" that results in a significant degradation of resolution when a magnetic bottle analyzer is used in conjunction with a fast ion beam,²⁶ and therefore obviates the need to employ pulsed deceleration fields often used in magnetic bottle anion PES experiments. Moreover, the collinear arrangement used here largely eliminates resolution loss due to the energy spread of the ion beam in a TOF mass spectrometer.²⁷

Pump and probe frequencies used in this experiment were generated from the 790 nm, 1 mJ (500 Hz), 90 fs full width at half maximum (FWHM) chirped-pulse amplified output of a Ti:Sapphire femtosecond oscillator (Clark-MXR NJA-5, CPA-1000) through various frequency conversion schemes. The 607 nm pump pulse (15 μ J, ~100 fs) used to excite the $\tilde{C}^2 \Pi_a \leftarrow \tilde{X}^2 \Pi_u$ resonance was generated by second harmonic generation (BBO type-I) of the infrared signal produced from a fundamental-pumped optical parametric amplifier (TOPAS, Light Conversion). The 498 nm pump pulse (25 μ J, ~100 fs) used to excite the $2^{2}\Pi_{a} \leftarrow \tilde{X}^{2}\Pi_{\mu}$ transition was generated through sum-frequency mixing of a \sim 1350 nm OPA signal with the Ti:Sa fundamental (BBO type-II). A 264 nm probe pulse (15–20 μ J, ~120 fs) was generated by tripling the fundamental output and was delayed with respect to the pump pulse through use of a computer-controlled translation stage. A 50 cm lens focused the collinearly recombined beams within the spectrometer interaction region. The lens position was readjusted for each color scheme to maximize two-color photodetachment signal with respect to probe-only (one-photon 264 nm) detachment. For both transitions, time zero was determined from the pump-induced half fall of direct UV (one-photon 264 nm) ground state detachment signal.

Data were typically acquired for $50\,000-100\,000$ laser shots (100–200 s) at each pump-probe delay, generally resulting in the collection of $150\,000-200\,000$ photoelectrons

for each delay with 15%–25% of these electrons arising from excited state detachment. Higher quality images (cf. Fig. 5) at selected delay times were acquired over 200 000– 300 000 laser shots, with up to 500 000 photoelectrons collected. Each two-color image has an associated "probe-only" (one-photon 264 nm) image, collected for a third of the number of laser shots used for the two-color image, that was used to normalize image-to-image signal fluctuations. Normalization of two-color signal collected in different sets of scans was accomplished through image collection at a fixed longtime delay where two-color signal no longer evolves. Background collection was interleaved with data acquisition for proper ion and laser background subtraction in both twocolor and normalizing (probe-only) images.

All images have been four-way symmetrized in order to account for inhomogeneities in detector and CCD sensitivity. Three-dimensional (3D) velocity distributions were reconstructed using the basis set expansion (BASEX) forward convolution method developed by Reisler and co-workers.²⁸ Photoelectron kinetic energy distributions were obtained through velocity-energy transformation and radial integration of the $\phi=0$ slice of reconstructed 3D detachment distributions. Photoelectron angular distribution anisotropy parameters, $\beta_n(\epsilon)$, were acquired by projecting the 3D slice onto an even series of associated Legendre polynomials $[P_n(\cos \theta)]$ appropriate for an *m*-photon photodetachment process induced within the cylindrically symmetric experimental arrangement used here-collinear laser propagation, mutually parallel laser polarizations and detector plane; see Sec. IV D for more details.

III. RESULTS

Three types of photoelectron (PE) images were taken as part of this investigation: (i) one-color, one-photon probeonly images at 264 nm, (ii) one-color, resonant multiphoton detachment (RMPD) images at 607 and 498 nm, in which the photon energy is resonant with either the $\tilde{C} \,{}^2\Pi_g \leftarrow \tilde{X} \,{}^2\Pi_u$ or $2 \,{}^2\Pi_g \leftarrow \tilde{X} \,{}^2\Pi_u$ band origins, and (iii) two-color, pump-probe images with pump wavelengths of 607 or 498 nm and a probe wavelength of 264 nm. The assignment of the $2 \,{}^2\Pi_g$ $\leftarrow \tilde{X} \,{}^2\Pi_u$ band at 498 nm by Maier¹⁶ has been questioned,¹⁹ but we believe it to be correct (see Sec. V) and will proceed in this section under that assumption.

Figure 3(a) shows the one-photon PE image of C_6^- obtained at 264 nm. A slice through the reconstructed 3D velocity distribution is displayed in Fig. 3(b), while the photoelectron spectrum is shown (solid) in Fig. 3(c). The PE spectrum, previously measured and analyzed at higher resolution,²⁹ exhibits three peaks at electron kinetic energies (eKE) of 0.52, 0.36, and 0.27 eV [labeled 1, 2, and 3, respectively, in Figs. 3(b) and 3(c)] corresponding to the $\tilde{X}^{3}\Sigma_{g}^{-}$, $\tilde{a}^{1}\Delta_{g}$, $\tilde{b}^{1}\Sigma_{u}^{+} + e^{-} \leftarrow \tilde{X}^{2}\Pi_{u}$ photodetachment transitions, respectively. The improvement in energy resolution relative to our previously measured Doppler-broadened spectrum⁶ obtained with a magnetic bottle [dashed overlay in Fig. 3(c)] is apparent. The angular distributions of the photoelectrons at these energies are relatively isotropic [cf. Figs. 3(a) and



FIG. 3. One-photon photodetachment of C_6^- at 264 nm: PE image and BASEX-inversion—(a) and (b), respectively; (c) C_6^- PE spectrum obtained from (b)—(a) magnetic-bottle PE spectrum (264 nm) of C_6^- is overlaid (dashed). Numbers explained in text.

3(b)]—the anisotropy parameters β_2 for these transitions [see Eq. (6)] were measured as 0.18±0.02, 0.13±0.05, and -0.02 ± 0.07 , respectively.

RMPD images of C_6^- collected at 607 and 498 nm are shown in Figs. 4(a) and 4(b), respectively, while PE spectra (smoothed) obtained from these images are shown in Figs. 4(c) and 4(d). The images at the two wavelengths are dominated by bright central spots. RMPD at 607 nm, resonant with the $\tilde{C}\,^2\Pi_g \leftarrow \tilde{X}\,^2\Pi_u$ band origin, requires a minimum of three photons (i.e., [1+n], n>2) for electron detachment. The resulting PE spectrum peaks at zero eKE and drops off monotonically with increasing eKE. At 498 nm, RMPD via the $2\,^2\Pi_g \leftarrow \tilde{X}\,^2\Pi_u\,0_0^0$ transition yields a PE spectrum similar to that seen at 607 nm, though extending to higher eKE and exhibiting a small maximum at eKE ~550 meV. Absorption of at least three photons is required to observe signal beyond eKE=0.80 eV.

Selected two-color pump-probe photoelectron images of

 C_6^- following excitation of the $\tilde{C}\,^2\Pi_g \leftarrow \tilde{X}\,^2\Pi_u\,0_0^0$ transition are displayed in Fig. 5. The contribution from probe-only photodetachment (i.e., Fig. 3) has been subtracted from the images in order to highlight detachment signal arising from the initial and nascent relaxing states; negative intensities have been minimized in subtraction. For both transitions investigated a parallel pump/probe laser polarization scheme was employed, with a common polarization parallel to the detector plane and corresponding to the vertical direction in all images, as indicated. In both cases, the images are quite isotropic and contract with increasing pump-probe delay, exhibiting two-color, two-photon photodetachment signal well beyond the image centers, in contrast to the one-color RMPD images in Fig. 4.

Time-resolved PE kinetic energy distributions obtained from unsubtracted photoelectron images at both pump wavelengths are displayed in Figs. 6 and 7, with associated pumpprobe delays indicated. These spectra exhibit two-photon contributions from pump-probe photodetachment and onephoton contributions from probe-only photodetachment of ground state C_6^- ; the latter has the same form as in Fig. 3(c) and appears in Figs. 6 and 7 as three sharp features between 0.25 and 0.5 eV. This probe-only signal is depleted at very short pump-probe delay times (cf. Fig. 6, 70 fs); its apparent recovery at longer times is mainly due to the build up of underlying two-photon signal at low eKE. There is also a contribution to the PE spectra from pump-induced RMPD processes (Fig. 4), as can be seen in Fig. 8, which compares pump-probe spectra at long delay times with spectra in which the probe laser comes well before the pump laser.

The two-color signal following excitation of the $\tilde{C}^2 \Pi_g \leftarrow \tilde{X}^2 \Pi_u$ transition at 607 nm (Fig. 6) is consistent with our previous study,⁶ though all features are now better resolved. Signal extending to ~2.5 eV is observed at the earliest delays, decaying by 1 ps. A sharp feature at ~0.85 eV is prominent at 70 fs, growing further by 1 ps, and subsequently decaying. Beyond 4 ps, no further evolution occurs. The pump-probe signal appears mainly as the difference between the black and gray curves in Fig. 8, i.e., as an unstructured shoulder between 0.55 and 1.0 eV.

Pump-probe spectra obtained by excitation of the $2 {}^{2}\Pi_{g} \leftarrow \widetilde{X} {}^{2}\Pi_{u}$ transition at 498 nm (Fig. 7) show new photodetachment features. A very short-lived, low-intensity feature, marked by a + in Fig. 7, is observed between 2.5 and 3.0 eV during the initial probe-only depletion. Subsequently, a pair of resolved peaks centered at 0.88 and 1.08 eV, observed initially near time zero, continue to grow until ~150 fs, after which they decay at comparable rates. At long times, the two-photon signal is similar in nature to that seen at 607 nm, though extending to somewhat higher eKE.

IV. ANALYSIS

A. Spectral assignments and time-scale analyses

The energetics and configurations of C_6^- doublet electronic states below 3 eV are summarized in the lower half of Fig. 1. As pointed out in Sec. I, the term energies of these states were taken from a combination of experimental^{8,16,17} and theoretical^{18,19} studies. Amongst these states, only the



FIG. 4. One-color femtosecond resonant multiphoton detachment (fs-RMPD) of C_6^- . Images and smoothed spectra, respectively: (a) and (c) 607 nm; (b) and (d) 498 nm.

 $\tilde{B}^{2}\Sigma_{u}^{+}$ state is optically inaccessible via one-photon absorption, and it is the only state whose term energy has not been determined experimentally. The electron affinity (EA) of linear C₆ has been determined to be 4.180 eV using anion zero electron kinetic energy spectroscopy.¹⁵

A C₆ (neutral) energy-level diagram, labeled with shorthand electronic configurations, is given in the upper portion of Fig. 1. Numerous excited states lying below the energetic neutral—anion detachment limit $(h\nu_{\text{probe}}+h\nu_{\text{pump}}-\text{EA})$ imposed in this experiment have been mapped and characterized with a combination of anion PE spectroscopy at 5.82 eV (Ref. 29) and multireference doubles configuration interaction (MRD-CI) calculations.³⁰ As discussed previously,⁶ assignments of some of the higher-lying neutral excited states from the experimental PE spectrum²⁹ of C₆⁻ have been revised in light of electronic structure calculations³⁰ performed after the experiment.

Anion photodetachment from either ground or excited states is expected to be dominated by one-electron photode-tachment transitions. The anion and neutral molecular orbital configurations in Fig. 1, based on the calculations by Botschwina¹⁸ and Peyerimhoff,^{19,30} show which neutral

states are thereby accessible from each anion state. While photodetachment from the anion ground state can access all neutral levels shown in Fig. 1, this is not the case for the anion excited states. The dashed arrows in Fig. 1 show the lowest neutral state accessible from each anion excited state. The neutral $1 \,{}^{3}\Pi_{u,g}$ states are the lowest that are accessible from the anion $\tilde{A} \,{}^{2}\Sigma_{g}^{+}$ and $\tilde{B} \,{}^{2}\Sigma_{u}^{+}$ states, while the $1 \,{}^{1}\Pi_{u,g}$ and $\tilde{X} \,{}^{3}\Sigma_{g}^{-}$ states are the lowest-lying neutral levels accessible from $\tilde{C} \,{}^{2}\Pi_{e}$ and $2 \,{}^{2}\Pi_{g} \,C_{6}^{-}$, respectively.

The one-photon absorption and photodetachment spectra of C_6^- from its ground state are generally dominated by $\Delta \nu = 0$ transitions for all transitions observed,^{8,16,17,29} indicating relatively small differences in nuclear geometry between the ground and excited anion/neutral states. If the anion and neutral vibrational frequencies are similar, $\Delta \nu = 0$ photodetachment transitions for even moderately vibrationally excited ions should occur close to eKE_{0-0} , the kinetic energy corresponding to photodetachment transition between anion and neutral vibrationless levels. This value can be determined using the energies in Fig. 1 according to Eq. (1),



FIG. 5. TRPEI— $\tilde{C} \leftarrow \tilde{X}$: experimental images obtained using a 607 nm+264 nm pump-probe scheme. Laser polarizations are mutually parallel, parallel to the detector, and are vertical, as indicated. Direct one-photon UV photodetachment contributions have been subtracted.



FIG. 6. TRPE spectra measured following $\tilde{C} \leftarrow \tilde{X}$ excitation. An arrow indicates the maximum allowable eKE with the color scheme employed.

$$eKE_{0-0} = h \nu_{probe} - EA_{C_6} + {}^X T^0_{C_6} - {}^Y T^0_{C_6}, \qquad (1)$$

in which ${}^{X}T_{S}^{0}$ represents the electronic term value for species *S* in its *X*th electronic state. Table I lists eKE_{0-0} values computed from the referenced anion and neutral term values provided in Fig. 1; these eKE_{0-0} values are used below to guide assignment of observed photodetachment features.

B. $\tilde{C}^{2}\Pi_{q}0^{0}$ relaxation dynamics

In Fig. 6, the earliest transient signal is the broad feature centered at 1.5 eV. This feature lies in the eKE range at which one anticipates detachment from the $\tilde{C}^2 \Pi_g$ state of C_6^- to the $1 \ {}^1\Pi_{u,g}$ states of C_6 (see Table I), and is assigned (as before⁶) to photodetachment from the initially prepared



FIG. 7. TRPE spectra measured following $2 \leftarrow \tilde{X}$ excitation. An arrow indicates the maximum allowable eKE with the color scheme employed. + marks a high eKE (2.5–3.0 eV) feature seen near time zero; * marks a low-intensity feature seen after time zero between 1.25 and 2.5 eV.



FIG. 8. "Pump-probe" photodetachment (black) following excitation at (a) 607 nm ($\Delta \tau_{\text{pu-pr}}$ =43.7 ps) and (b) 498 nm ($\Delta \tau_{\text{pu-pr}}$ =18.7 ps) vs "probebefore-pump" (gray, dotted) photodetachment.

 0^0 level of the $\tilde{C}\,^2\Pi_g$ state. The sharp, transient feature at 0.85 eV is where the 1 ${}^3\Pi_{u,g} \leftarrow C_6^- \tilde{A}\,^2\Sigma_g^+$ photodetachment transition is anticipated (cf. Table I). This feature is present between 70 fs and 1 ps, indicating that the $\tilde{A}\,^2\Sigma_g^+$ state serves as an intermediate in the overall relaxation dynamics. No evolution of the pump-probe signal occurs beyond ~4 ps; at these long delays, pump-probe signal is most evident on the high eKE side of the probe-only signal between 0.5 and 1.0 eV (see Fig. 8), and is attributed to highly vibrationally excited C_6^- in its ground $\tilde{X}\,^2\Pi_u$ electron state formed by internal conversion from the $\tilde{A}\,^2\Sigma_g^+$ and $\tilde{C}\,^2\Pi_g$ states.

It thus appears that the overall relaxation dynamics involve three electronic states of C_6^- : the initially prepared $\tilde{C}^2 \Pi_g$ vibrationless level, the $\tilde{A}^2 \Sigma_g^+$ state, and the $\tilde{X}^2 \Pi_u$ state. We can gain more quantitative insight into these dynamics by integrating the signal associated with each state as a function of pump-probe delay. In order to monitor the $\tilde{C}^2 \Pi_g$ state population, the integrated intensity between 1.25 and 2.50 eV is plotted as a function of temporal delay in Fig. 9(a), and fit to Eq. (2),

$$\widetilde{C}(t) = c_1 \exp\{-t/\tau_{\widetilde{C}}\} + c_0, \qquad (2)$$

with a lifetime $\tau_{\tilde{C}}$ of 620±30 fs. Transient $\tilde{A}^2 \Sigma_g^+$ population and subsequent decay are clocked according to the evolution

TABLE I. eKE₀₋₀ values for photodetachment of C₆⁻ from low-lying electronic states with 264 nm (4.70 eV), calculated with Eq. (1) from the text and best-available electronic anion and neutral term values (references for values listed in Fig. 1 caption). Parenthesized values give eKE₀₋₀ for 498 nm [1+1] photodetachment through 2 $^{2}\Pi_{g}$. Italicized values give electron kinetic energies following nominally disallowed, multielectron-active photodetachment transitions.

Low-lying excited electronic states of C_6^-									
		$2 \ ^2\Pi_g^a$	$ ilde{C} {}^2\Pi^c_g$	$\widetilde{B}^{2}\Sigma_{u}^{+b}$	$\widetilde{A}^{2}\Sigma_{g}^{+a}$	$\tilde{X}^2 \Pi_u$			
Accessible electronic states of C ₆	$\widetilde{X}^{3}\Sigma_{g}^{-1}$	3.02 (0.80)	2.56			0.52			
	$\tilde{a}^{1}\Delta_{g}^{1}$	2.84 (0.63)	2.40			0.35			
	$1 \ {}^{1}\Sigma_{g}^{+2}$	2.74 (0.53)	2.30			0.25			
	$1 \ {}^{3}\Pi^{1}_{g,u}$	•••	1.71	0.99	0.83	•••			
	$1 \ ^{1}\Pi^{1}_{g,u}$		1.46	0.74	0.58				

of signal between 0.80 and 1.05 eV, encompassing the peak centered at 0.85 eV. Gated integration of this window versus pump-probe delay is plotted in Fig. 9(b) and has been fitted with Eq. (3),

$$\widetilde{A}(t) = a_2 \exp\{-t/\tau_{\widetilde{A}}\} - a_1 \exp\{-t/\tau_{\widetilde{C}}\} + a_0, \qquad (3)$$

in which $\tau_{\tilde{A}}$ corresponds to the population lifetime of the intermediate-lying state. With $\tau_{\tilde{C}}$ fixed to 620 fs, $\tau_{\tilde{A}}$ was determined to be 2300±200 fs. Finally, the ground state population was obtained by integrating the signal from 0.50 to 0.75 eV; this is plotted in Fig. 9(c) and fit to Eq. (4),

$$\widetilde{X}(t) = x_0 - x_2 \exp\{-t/\tau_{\widetilde{A}}\} - x_1 \exp\{-t/\tau_{\widetilde{C}}\},$$
(4)

in which the time scales have been fixed to those found above, as both relaxation pathways are anticipated to end with population of highly vibrationally excited levels of the ground state.

The time constants in Eqs. (2)–(4) are listed in Table II. The time scales and overall dynamical picture for relaxation of the $\tilde{C} \,{}^2\Pi_g$ vibrational origin are similar to those obtained in our earlier study of C_6^- , but the transient state can now be definitively assigned as the $\tilde{A} \,{}^2\Sigma_g^+$ state owing to the higher energy resolution in the TRPEI experiment.

One point not addressed in the above analysis is the branching of the initial relaxation between the $\tilde{A}^2 \Sigma_g^+$ and $\tilde{X}^2 \Pi_u$ states. The relative photodetachment cross sections from these two states are unknown, so the branching cannot be assessed quantitatively. However, decay of the $\tilde{A}^2 \Sigma_g^+$ state is *not* accompanied by a significant increase in the $\tilde{X}^2 \Pi_u$ state signal, i.e., $x_2 \ll x_1$ when fit to Eq. (4). It therefore appears that direct relaxation to the ground state dominates over relaxation via the $\tilde{A}^2 \Sigma_g^+$ state.

C. 2 ${}^{2}\Pi_{a}$ 0⁰ relaxation dynamics

We next consider the TRPE spectra resulting from excitation of the $2\,{}^{2}\Pi_{g}\,0^{0}$ level, starting with the very shortlived, weak feature between 2.5 and 3.0 eV. One would like to assign this to one-photon detachment out of the initially prepared $2\,{}^{2}\Pi_{g}$ state. In fact, detachment from this state to the lowest three neutral levels of C₆ should occur at eKE's in the range 3.02-2.74 eV (see Table I), consistent with such an assignment. One must question whether this feature is a real resonant pump-probe feature, given its low intensity. In fact, a peak at the corresponding eKE is also seen in the RMPD spectrum at 498 nm [Fig. 4(d)]; the small peak at ~550 meV is at the correct eKE for [1+1] detachment out of the 2 ${}^{2}\Pi_{g}$ state at this wavelength when compared to the eKE observed for [1+1'] detachment. Given that one and two-color experiments show essentially the same weak feature, we are confident it is actually present and corresponds to a resonant process.

The next features of interest are the pair of relatively sharp transient peaks at 0.88 and 1.08 eV. These are also seen at the earliest delay times but persist longer than the feature from the 2 ${}^{2}\Pi_{g}$ state. The two peaks are quite close to the eKE values expected for transitions from the $\tilde{A} {}^{2}\Sigma_{g}^{+}$ and $\tilde{B} {}^{2}\Sigma_{u}^{+}$ states to the 1 ${}^{3}\Pi_{g,u}$ states of C₆; according to Table I, the two $\Delta v = 0$ transitions should occur at 0.83 and 0.99 eV, respectively. There are also smaller features at slightly lower eKE's that may arise through transitions from the two anion states to the higher-lying 1 ${}^{1}\Pi_{g,u}$ states, but this correspondence is less definitive. Finally, the long-time signal is attributed to photodetachment from the vibrationally excited $\tilde{X} {}^{2}\Pi_{u}$ state of C₆⁻.

Following the procedure in Sec. IV B, signal in selected eKE regions is integrated as a function of time to track energy flow through the various anion electronic states. The results are shown in Fig. 10(a) for long delay times and in Fig. 10(b) for shorter delays. Population was monitored in the $2\,{}^{2}\Pi_{g}$ state by integrating electron signal from 2.50 to 3.00 eV, the $\tilde{B}\,{}^{2}\Sigma_{u}^{+}$ state from 0.99 to 1.20 eV, the $\tilde{A}\,{}^{2}\Sigma_{g}^{+}$ state from 0.78 to 0.95 eV, and the $\tilde{X}\,{}^{2}\Pi_{u}$ state from 0.58 to 0.76 eV. Finally, gated integration between 1.25 and 2.50 eV (centered on the * in Fig. 7) has been performed to identify "trace" accumulation in the $\tilde{C}\,{}^{2}\Pi_{g}$ state; there does appear to be non-negligible time-dependent signal in this region, as shown in Figs. 10(a) and 10(b).

In Fig. 10(b), electron signals associated with the $2 {}^{2}\Pi_{g}$ and $\tilde{C} {}^{2}\Pi_{g}$ states are compared to a 200 fs FWHM Gaussian (dashed line) representing the approximate cross correlation of pump and probe laser pulses. Signal intensity from $2 {}^{2}\Pi_{g}$ is limited to the laser cross correlation, and is estimated to be a sub-100 fs process. Notably, the intensity in the $\tilde{C} {}^{2}\Pi_{g}$, $\tilde{B} {}^{2}\Sigma_{u}^{+}$, and $\tilde{A} {}^{2}\Sigma_{g}^{+}$ states rises on a comparable time scale, reaching a maximum by ~150 fs. For this reason only signal decay has been fit for each integrated spectral window (gray



FIG. 9. Integrated photodetachment intensities vs delay— $\tilde{C} \leftarrow \tilde{X}$: (a) \tilde{C} , (b) \tilde{A} , and (c) vibrationally hot \tilde{X} states; data are overlaid with fitting curves (dashed). Details regarding spectral gate widths and fitting procedures are outlined in the text.

lines) in accordance with Eq. (2). Decay lifetimes for the $\tilde{C}^2 \Pi_g$, $\tilde{B}^2 \Sigma_u^+$, and $\tilde{A}^2 \Sigma_g^+$ state windows decay with first-order lifetimes of 560±70, 1860±140, and 2350±200 fs. Growth of signal intensity within the gate encompassing relaxed ground state detachment features occurs largely

through the bright state decay, with negligible increase thereafter, similar to the rise observed following $\tilde{C}\,^2\Pi_g \leftarrow \tilde{X}\,^2\Pi_u$ excitation (see previous discussion); this observation regarding the relaxed ground state photodetachment signal is highlighted by the overlaid "*s*-curve," which approaches its maximum value by ~150 fs, and indicates that relaxation favors direct decay to the anion ground state. All relaxation time scales are summarized in Table II.

Finally, the transient signal from relaxation of the initially prepared $2\,{}^{2}\Pi_{g}$ locates the $\tilde{B}\,{}^{2}\Sigma_{u}^{+}$ of C_{6}^{-} experimentally for the first time. The transient peak at eKE=1.08 eV is assigned to the $C_{6}\,1\,{}^{3}\Pi_{u,g} \leftarrow C_{6}^{-}\,\tilde{B}\,{}^{2}\Sigma_{u}^{+}$ photodetachment transition. The term value of the $\tilde{B}\,{}^{2}\Sigma_{u}^{+}$ state is then given by

$$T_{\tilde{B}}^{-} = EA + eKE + T_{3\Pi}^{0} - h \nu_{\text{probe}}, \qquad (5)$$

in which $T_{3\Pi}^0$ and $T_{\tilde{B}}^-$ represent the neutral Π and anion \tilde{B} term values, respectively. From Fig. 1, $T_{3\Pi}^0 = 0.849 \pm 0.040 \text{ eV}$ for one or both of the nearly degenerate $1{}^3\Pi_{u,g}$ neutral states. Using $h\nu_{\text{probe}} = 4.70 \text{ eV}$, we find $T_{\tilde{B}}^- = 1.41 \pm 0.05 \text{ eV}$, where the measurement uncertainty has been estimated based on the FWHM of the probe laser bandwidth and the $1{}^3\Pi_{u,g}$ term value uncertainty. This value lies close to values of 1.32 and 1.34 eV previously reported^{18,19} in *ab initio* studies.

D. Angular distributions

The PADs in the pump-probe experiments were fit to the standard expression,³¹

$$I(t;\theta,\epsilon) \propto 1 + \beta_2(\epsilon) P_2(\cos\theta) + \beta_4(\epsilon) P_4(\cos\theta), \qquad (6)$$

where $P_n(\cos \theta)$ represents the *n*th-order Legendre polynomial, θ is the polar angle between the photoelectron recoil vector and the laser polarization direction, and $\beta_n(\epsilon)$ corresponds to the nth PAD anisotropy parameter for photoelectrons generated with kinetic energy ϵ . These were fitted for each angular distribution as a function of pump-probe delay using the spectral gates assigned to each detachment feature. For each detachment transition, the fitted values exhibited noticeable scatter with time, though no statistically significant variation as a function of time. We thus report only the time-averaged values of the anisotropy parameters, which are listed in Table III with anisotropy values (β_2) for direct UV photodetachment of the ground state ion. In all cases measurement uncertainties have been determined from consideration of multiple images/measurements. In all cases the mean β_4 's were ~0.0, and are not considered here. The β_2 param-

TABLE II. Relaxation time scales of bright and nascent populated transient states (left to right) following excitation of the $\tilde{C} \,{}^2\Pi_g \leftarrow \tilde{X} \,{}^2\Pi_u$ and $2 \,{}^2\Pi_g \leftarrow \tilde{X} \,{}^2\Pi_u \, 0^0_0$ transitions. Details of time-scale analyses are given in the text.

Subsequently populated states							
		$2 \ ^2\Pi_g$	${ ilde C}{}^2\Pi_g$	$\widetilde{B}^{2}\Sigma_{u}^{+}$	${\widetilde A}\ ^2\Sigma_g^{+}$		
Initial states	$ ilde{C}^2\Pi_g0^0$		$620\pm30 \mathrm{fs}$		2300±200fs		
	$2 \ ^2 \Pi_g \ 0^0$	<100 fs	$560\pm70 \mathrm{fs}$	1860±140 fs	2350±200fs		



FIG. 10. Integrated intensities vs delay— $2 \leftarrow \tilde{X}$: (a) full range, 2 is plotted with an estimated temporal pulse cross correlation (200 fs FWHM, gray); \tilde{C} , \tilde{B} , and \tilde{A} are plotted with first-order exponential decays (gray); \tilde{X} is plotted with an "*s*-curve" growth function (gray). Fit details are given in the text. (b) Early-delay ($<\sim 1$ ps): 2 and \tilde{C} are plotted with a 200 fs FWHM Gaussian (dashed).

eters are all positive but small (<0.3), corresponding to nearly isotropic PADs and limiting, in this particular instance, their utility towards differentiating overlapping detachment transitions.

V. DISCUSSION

Our results on C₆⁻ can be summarized as follows. At a pump wavelength of 607 nm, where the $\tilde{C} \,^2 \Pi_g \leftarrow \tilde{X} \,^2 \Pi_u \, 0_0^0$

TABLE III. Time-averaged photodetachment anisotropy parameters (β_2) obtained following $2 \,{}^2\Pi_g \leftarrow \tilde{X} \,{}^2\Pi_u$ (nonparenthesized) and $\tilde{C} \,{}^2\Pi_g \leftarrow \tilde{X} \,{}^2\Pi_u$ (parenthesized) excitation. Italicized values were measured for one-photon photodetachment from the $\tilde{X} \,{}^2\Pi_u$ ground state.

		Neutral electronic states				
		$\widetilde{X} {}^3\Sigma_g^{-} / \widetilde{a} {}^1\Delta_g / \widetilde{b} {}^1\Sigma_u^{+}$	$1 \ {}^3\Pi_{u,g}$	$1 \ ^1\Pi_{u,g}$		
	$2 \ ^2\Pi_g$	0.16±0.08		•••		
	${ ilde C}{}^2\Pi_g$			0.15 ± 0.05 (0.15 \pm 0.10)		
Anion electronic	$\widetilde{B}^{\ 2}\Sigma_{u}^{\ +}$		0.24 ± 0.06	•••		
states	${ ilde A}\ ^2\Sigma_g^{+}$		$\begin{array}{c} 0.15 \pm 0.06 \\ (0.29 \pm 0.06) \end{array} \dots$			
	$ ilde{X}^2 \Pi_u$	$\begin{array}{c} 0.14 \pm 0.05 \\ (0.18 \pm 0.06); \\ 0.18 \pm 0.02 \\ 0.13 \pm 0.05 \\ -0.02 \pm 0.07 \end{array}$				

transition is excited, the $\tilde{C} \,{}^2\Pi_g$ state undergoes parallel decay to the $\tilde{A} \,{}^2\Sigma_g^+$ and $\tilde{X} \,{}^2\Pi_u$ states with a time constant of 620 fs, while the $\tilde{A} \,{}^2\Sigma_g^+$ state subsequently decays to the $\tilde{X} \,{}^2\Pi_u$ state with a lifetime of 2300 fs. At 498 nm, where the $2 \,{}^2\Pi_g \leftarrow \tilde{X} \,{}^2\Pi_u$ state is excited, the $2 \,{}^2\Pi_g$ state decays on a time scale too fast to measure with our instrumentation. This decay is accompanied by a nearly instantaneous rise in the lower-lying excited states and ground state of C_6^- , with the excited states then decaying to the ground state with time constants ranging from 560 to 2300 fs. At both wavelengths, direct relaxation to the ground state dominates over the indirect pathways through intermediate excited states.

The relaxation mechanism for the 0^0 level of the $\tilde{C}^2 \Pi_a$ state is similar to that put forth in our earlier paper,⁶ though the current study provides more details into the dynamics. The improved resolution of the TRPEI setup shows that relaxation occurs via the $\tilde{A}^2 \Sigma_g^+$ state but not the $\tilde{B}^2 \Sigma_u^+$ state. The origin of this selectivity is of considerable interest, since the initially prepared bright state can be vibronically coupled to either the $\overline{A}^2 \Sigma_g^+$ or $\overline{B}^2 \Sigma_u^+$ states through π_g or π_u bending modes, respectively, both of which are present in C_6^- . While a conical intersection between the $\tilde{C}^2 \Pi_g$ and $\tilde{A}^2 \Sigma_g^+$ states could favor relaxation through the $\tilde{A}^{2}\Sigma_{g}^{+}$ state, the calculated equilibrium geometries¹⁸ of the $\tilde{A}^2 \Sigma_g^+$ and $\tilde{B}^2 \Sigma_u^+$ states are nearly identical and quite close to that of the $\tilde{C}^2 \Pi_a$ state, so it is unlikely that the $\tilde{C}^2 \Pi_{g}$ state undergoes a conical intersection with either the $\tilde{A}^{2} \tilde{\Sigma}_{g}^{+}$ or $\tilde{B}^{2} \Sigma_{u}^{+}$ states anywhere near its minimum energy structure where the 0^0 vibrationless level is localized. On the other hand, the density of vibrational levels isoenergetic to the $\tilde{C}^2 \Pi_{\rho} 0^0$ state is about a factor of 5 higher for the $\tilde{A}^2 \Sigma_g^+$ state than for the higher-lying $\tilde{B}^{2}\Sigma_{u}^{+}$ state.⁶ A feature in the TRPE spectra one fifth the size of the transient $A^{2}\Sigma_{g}^{+}$ state feature would be difficult to observe here, and so this simple density-of-states consideration may explain our results.

The pump-probe experiments at 498 nm pump wavelength provide new insight into a less well-characterized region of the C_6^- electronic absorption spectrum. In a matrix absorption experiment, Maier and co-workers¹⁶ assigned a weak band with an origin at 498 nm (2.49 eV) to the $2 {}^{2}\Pi_{a} \leftarrow \tilde{X} {}^{2}\Pi_{u}$ transition. The only theoretical work on the upper state was carried out by Cao and Peyerimhoff,¹⁹ who calculated vertical transition energies for this and many other electronic transitions in C_6^- . They calculated the $2 \, {}^2\Pi_g$ $-X^2\Pi_u$ transition to lie at 2.84 eV, but found the lowest quartet state of C_6^- , the 1 ${}^4\Pi_g$ state, to lie 2.50 eV above the $\overline{X}^{2}\Pi_{\mu}$ ground state. As a result, they suggested that the experimental band was misassigned and may have been the spin-forbidden $1 \, {}^{4}\Pi_{a} \leftarrow X \, {}^{2}\Pi_{\mu}$ transition. Our results and analysis in Figs. 7 and 10 show that the upper state undergoes extremely rapid radiationless decay (<100 fs) to lowerlying doublet states. Such rapid dynamics would be unprecedented for a spin-forbidden relaxation pathway and support the original experimental assignment of the 498 nm band.

The relaxation dynamics of the $2 \,{}^{2}\Pi_{g} 0^{0}$ level exhibit parallels and differences relative to the $\tilde{C} \,{}^{2}\Pi_{g}$ state. In both cases, the decay time of the initially prepared state matches, to within experimental resolution, the rise time of populations in the lower-lying doublet states. However, the lifetime of the $2 \,{}^{2}\Pi_{g}$ state is significantly shorter than that of the $\tilde{C} \,{}^{2}\Pi_{g}$ state; we can only place an upper bound of ~100 fs on its decay time and the associated rise times in the lowerlying states. The $2 \,{}^{2}\Pi_{g}$ state relaxes via both the $\tilde{A} \,{}^{2}\Sigma_{g}^{+}$ and $\tilde{B} \,{}^{2}\Sigma_{u}^{+}$ states; the state-selective effect observed following $\tilde{C} \,{}^{2}\Pi_{g} \leftarrow \tilde{X} \,{}^{2}\Pi_{u}$ excitation is absent. Finally, Table II shows that the decay times for the $\tilde{C} \,{}^{2}\Pi_{g}$ and $\tilde{A} \,{}^{2}\Sigma_{g}^{+}$ transients are essentially the same at the two pump wavelengths. This result indicates that the additional ~0.5 eV of vibrational energy available to both states at 498 nm has little effect on their lifetimes.

A detailed explanation of the 2 ${}^{2}\Pi_{g}$ state relaxation dynamics is difficult in the absence of more information about its electronic structure and equilibrium geometry. Cao¹⁹ characterizes the 2 ${}^{2}\Pi_{g} \leftarrow \tilde{X} {}^{2}\Pi_{u}$ transition as a 4 $\pi_{g} \leftarrow 2 \pi_{u}$ molecular orbital (MO) promotion. As a result (see Fig. 1), the MO occupancies of the 2 ${}^{2}\Pi_{g}$ state differ from those of the $\tilde{A} {}^{2}\Sigma_{g}^{+}$, $\tilde{B} {}^{2}\Sigma_{u}^{+}$, and $\tilde{C} {}^{2}\Pi_{g}$ states by two electrons, which would normally result in weak coupling and hence slow radiationless transitions. The very rapid relaxation to these states may result from significant configuration interaction between the 2 ${}^{2}\Pi_{g}$ and $\tilde{C} {}^{2}\Pi_{g}$ states.

The time scales extracted from the pump-probe experiments for relaxation to the ground state are of use in understanding the fs-RMPD photoelectron spectra in Fig. 4. The monotonically decreasing signal towards higher eKE [except for the small maximum at 0.55 eV in Fig. 4(d)] is suggestive of the cluster analog of thermionic emission. This emission process involves the statistical evaporation of an electron from a cluster in which excitation energy has been randomized amongst all internal degrees of freedom.^{32–34} This phenomenon has been observed in resonant multiphoton excitation of carbon cluster anions using nanosecond lasers⁸ and single photon detachment of metal cluster and larger carbon cluster anions,^{9,20,35} and has been implicated in the autodetachment dynamics of excited dimeric-core $(OCS)_n^-$ and $(CS_2)_n^-$ clusters.^{36–38}

In the previous ns-RMPD experiments on C_6^- , the observation of thermionic emission was explained in terms of sequential absorption and thermalization events.⁸ In the proposed mechanism, resonant excitation of the $\tilde{C}^2 \Pi_g \leftarrow \tilde{X}^2 \Pi_u$ transition is followed by internal conversion to the ground state. The vibrationally hot ion subsequently absorbs additional photons, relaxing vibronically between absorption events, until a sufficient number of photons (three total at 607 nm) have been absorbed for electron emission to be energetically feasible. This mechanism requires that internal conversion is rapid on the time scale of the nanosecond laser pulse.

The observation of thermionic emission in fs-RMPD spectra is consistent with the ultrafast internal conversion dynamics observed in two-color time-resolved investigations, as it implies that the time constant for internal conversion is comparable to the laser pulse duration of ~ 100 fs. At 498 nm, internal conversion to the ground state is sufficiently rapid to satisfy this condition. At 607 nm, however, internal

conversion to the ground state occurs with a time constant of 620 fs, considerably longer than the laser pulse, implying that the sequential absorption/thermalization mechanism is less efficient at this wavelength. Indeed, the intensity of the RMPD signal at 607 nm is considerably lower than at 498 nm at comparable laser pulse energies, despite a significantly larger absorption cross section at 607 nm. Additionally, while only two photons at 498 nm are needed to detach an electron, the eKE distribution in Fig. 4(d) extends well beyond the energetic limit for two-photon absorption (0.80 eV), indicating a substantial amount of three-photon absorption. This observation implies that after two photons at 498 nm have been absorbed, the time constant for thermionic emission must be comparable to or longer than the laser pulse width, thus facilitating absorption of a third photon prior to electron emission.

VI. CONCLUSIONS

Time-resolved photoelectron imaging has been used to characterize the relaxation dynamics of C_6^- electronically excited through the $\tilde{C}^2 \Pi_g \leftarrow \tilde{X}^2 \Pi_u 0_0^0$ and $2^2 \Pi_g$ $\leftarrow \tilde{X}^2 \Pi_u 0_0^0$ transitions. Relaxation from the $2^2 \Pi_g 0^0$ level is substantially faster than the $\tilde{C}^2 \Pi_{\rho} 0^0$ level (<100 fs versus 620 fs). The increased resolution available for this investigation relative to a previous study⁶ yields a more detailed assignment of the electronic states participating in the ensuing electronic relaxation pathway. In both cases, parallel relaxation pathways are observed; the initially excited state relaxes directly to the ground state and also to lower-lying excited states, which then relax more slowly to the ground state. The direct pathway dominates for both initially excited states. The indirect pathway for relaxation from the $C^2 \Pi_g 0^0$ state involves only the $\tilde{A}^2 \Sigma_g^+$ state; no population in the close-lying $\tilde{B}^{2}\Sigma_{\mu}^{+}$ state is seen at any time. In contrast, the indirect pathway from the $2 \,{}^{2}\Pi_{g} \, 0^{0}$ level results in transient population of all lower-lying excited doublet states. In particular, a transient feature assigned to the $\tilde{B}^2 \Sigma_{\mu}^+$ state yields the first experimental term value for this state, 1.41 ± 0.05 eV. Finally, one-color, resonant multiphoton detachment at the pump wavelengths corresponding to the two electronic transitions yields PE spectra characteristic of thermionic emission, consistent with a previously proposed model⁸ in which sequential absorption and relaxation cycles lead to a vibrationally hot anion cluster from which the excess electron evaporates.

This study highlights the advantages of anion TRPEI relative to older time-resolved anion PES methods. This technique may be further applied to investigate electronic relaxation dynamics following excitation of analogous species, such as "odd-numbered" carbon clusters and the hydrides of these species, in which electronic states are more sparse,⁷ perhaps leading to divergent dynamics from those observed. Yet this technique may be applied more generally than to the case of relaxation following excitation between discrete molecular levels. For example, as mentioned in the Introduction, TRPES has been applied to the study of relaxation dynamics in transition metal cluster anions, revealing

near-bulk relaxation time scales reflective of high electronic state densities. However no time-resolved studies have directly observed, in progression, the consequence of a gradual transition from molecular to "bulklike" properties on the electronic relaxation dynamics of size-selected clusters. Such a study would provide a much desired link to understand the evolution of material properties with increased degree of aggregation and is one of our current research goals.

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