Time-resolved relaxation dynamics of Hgₙ⁻ (11≤n≤16, n=18) clusters following intraband excitation at 1.5 eV

Jan R. R. Verlet, Arthur E. Bragg, and Aster Kammrath
Department of Chemistry, University of California, Berkeley, California 94720

Ori Cheshnovsky
School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, 69978 Israel

Daniel M. Neumark
Department of Chemistry, University of California, Berkeley, California 94720
and Chemical Sciences Division, Lawrence Berkeley National Laboratories, California 94720

(Received 6 August 2004; accepted 2 September 2004)

Electron-nuclear relaxation dynamics are studied in Hgₙ⁻ (11≤n≤16, n=18) using time-resolved photoelectron imaging. The excess electron in the anion uniquely occupies the p band and is excited intraband by 1.53 eV pump photons; the subsequent dynamics are monitored by photodetachment at 3.06 eV and measurement of the photoelectron images as a function of pump-probe delay. The initially excited state decays on a time scale of ~10 ps, and subsequent relaxation dynamics reveal a smooth evolution of the photoelectron spectra towards lower electron kinetic energy over 50–100 ps. Qualitatively, the relaxation process is captured by a simple kinetic model assuming a series of radiationless transitions within a dense manifold of electronic states. All the clusters studied showed similar dynamics with the exception of Hg₁₁ in which the initially prepared state does not decay as quickly as the others. © 2004 American Institute of Physics. [DOI: 10.1063/1.1809573]

I. INTRODUCTION

Ultrafast dynamics in molecules and in condensed phases have been studied intensely over the last two decades. ¹,² Clusters have also received considerable attention, as their size-dependent properties address the gap between the discrete nature of isolated atoms or molecules and the continuous band structure associated with the condensed phase.³–⁵ For large metallic aggregates, dynamics are reflective of the bulk with perturbations due to quantum confinement and the large fraction of surface atoms. However, even very small metal clusters can reveal properties and dynamics normally associated with extended systems. Alkali metal clusters such as Naₙ with fewer than ten atoms have been shown to exhibit collective plasmon excitations in their electronic absorption spectra.⁶ Photoelectron spectroscopy (PES) of transition metal cluster anions such as Vₙ⁻ clusters show signatures of the bulk electronic band structure beginning in the range 13≤n≤17.⁷ Manifestations of bulk phenomena are also seen in the dynamics of small transition metal clusters. Ultrafast electronic relaxation dynamics on time scales of tens of femtoseconds have been observed in transition metal clusters with as few as three atoms using time-resolved PES and are attributed to electron-electron scattering, a phenomenon normally associated with bulk metals.⁸–¹³ In contrast, electronic structure in Hgₙ anions clusters evolves over a much larger size range, with cluster sizes in the range of n=400 required before band structure characteristic of a metal is observed,¹⁴ while results for much smaller anion clusters suggested the presence of electron-hole recombination and Auger decay subsequent to electronic excitation.¹⁵ These intriguing results motivate the work described here in which the electronic relaxation dynamics of size-selected Hgₙ⁻ are investigated with time-resolved photoelectron imaging.

The evolution of electronic structure with size in Hgₙ clusters has attracted considerable interest. The Hg atom has a closed shell configuration, 5d¹⁰6s², and its dimer forms a van der Waals molecule, bound by only 70 meV.¹⁶ Further aggregation forms Hgₙ clusters where the s states evolve into a filled band, containing 2n electrons, whereas the higher-lying p states form an empty p band. However, as more atoms are added to the cluster, hybridization of the s-type orbitals with the p-type orbitals causes covalent character to be established in the bond. There is a body of experimental¹⁷–²¹ and theoretical²²,²³ work indicating that the transition from van der Waals to covalent bonding occurs in the range of 13≤n≤20 atoms. Clusters larger than this are much like a semiconductor with a band gap separating the valence and conduction bands.

Upon further aggregation, Hgₙ⁻ undergoes a nonmetal to metal transition as the full s band merges with the empty p band. Photoelectron-photoion coincidence measurements on neutral Hgₙ suggest that clusters as small as n=60 exhibit electronic structure characteristic of bulk metals.²⁴ More direct insight into this issue was provided by negative ion PES experiments on Hgₙ⁻ clusters by Busani, Folkers, and Cheshnovsky,¹⁴ in which the extra electron uniquely occupies the bottom of the p band, corresponding to the lowest unoccupied molecular orbital (LUMO) of the neutral. The PE spectra of these clusters show a peak corresponding to detachment of this p electron, which is well separated from the broad detachment of the s-band electrons. The gap be-
be
tween the two reflects the band gap of the neutral cluster and has been extrapolated to establish the metal-nonmetal transition to occur around 400 atoms. This work and more recent higher resolution studies\textsuperscript{25} have also yielded vertical binding energies (VBEs) for a wide size range of Hg\textsubscript{n} clusters.

Dynamical processes in Hg clusters have received less attention. Time-resolved fragmentation and ionization experiments\textsuperscript{26} showed evidence for coherent wave packet dynamics at early times, and for the production of multiply charged fragments at laser intensities as low as 10\textsuperscript{11} W/cm\textsuperscript{2}. Busani et al.\textsuperscript{15} have measured wavelength-dependent PE spectra of Hg\textsubscript{n} anions and found evidence for $p\rightarrow s$ excitation, followed by electron-hole recombination and ejection of a photoelectron via Auger decay.

In this paper, we explore electronic relaxation dynamics in size-selected Hg\textsubscript{n} ($n = 11\text{--}18$) anions using time-resolved photoelectron imaging (TRPEI), a pump-probe experiment in which one measures the time-evolving photoelectron kinetic energy and angular distribution from electronically excited clusters. The utility of this and related techniques in following nonradiative dynamics in molecules and clusters has been amply demonstrated.\textsuperscript{27,28} We focus on intraband relaxation dynamics of these clusters. Using a 100 fs pump pulse, we excite the single $p$ electron, initially in the lowest molecular orbital of the $p$-band, to an excited state within this band lying below the detachment limit. We then probe the resulting nonstationary state using a delayed probe of similar duration, which detaches the electron, and by imaging of the photoelectrons obtain their kinetic energy and angular distributions as a function of pump-probe delay, enabling us to track the relaxation dynamics of the excited $p$ electron.

This experiment offers several noteworthy features. First, since the anion clusters are charged species, they can be (and are) mass-selected prior to spectroscopic investigation, removing any ambiguity as to the size of the cluster. Second, the pump photon energy, 1.5 eV, is less than the $s$-$p$ band gap, so the electronic excitation only involves excitation of a single $p$ electron and for the same reason, dipole-dipole induced interband excitations cannot be involved in the relaxation dynamics. This situation differs from the electronic spectroscopy of neutral and positively charged metal cluster anions.\textsuperscript{12,13} There are significant variations in the excitation dynamics occur on a time scale of tens of picoseconds, whereas the pump photon energy, 1.5 eV, is less than the band gap, so the electronic excitation only involves excitation, removing any ambiguity as to the size of the cluster.

Finally, as was demonstrated in our recent studies of C\textsubscript{6}\textsubscript{11}, TRPEI not only yields lifetimes for the initially excited species but also allows continuous tracking of the relaxation dynamics through multiple electronic states.

The key results in this work are that the intraband relaxation dynamics occur on a time scale of tens of picoseconds, considerably slower than was observed in small transition metal cluster anions.\textsuperscript{12,13} There are significant variations in the relaxation rates with cluster size, with Hg\textsubscript{811} showing a particularly long-lived initially excited state. We attribute the observed dynamics to sequential radiationless transitions between close-lying excited electronic states, essentially the cluster analog of electron-phonon coupling; electron-electron scattering effects seen in previous TRPES experiments on metal cluster anions are largely absent here because the $p$ band, in which all the dynamics occur, is singly occupied.

Furthermore, other decay channels such as interband excitation are blocked as the band gap is greater than the photon energy. The observed dynamics reflect pure electron-nuclear relaxation, comparable to electron-phonon relaxation in the bulk.

II. EXPERIMENT

The experiment has been described in detail elsewhere and only an overview and specifics are presented here.\textsuperscript{30,32} The main components of the vacuum system are shown in Fig. 1 where the main difference is that we use a pulsed valve designed for the generation of mercury cluster anions. Mercury clusters are produced by coexpanding 40 psi of Ar and the vapor pressure of Hg at 220 °C into vacuum using an Even-Lavie pulsed solenoid valve\textsuperscript{33} operating at 40 Hz. The expansion is intersected by a pulsed electron beam forming cluster anions through secondary electron attachment. These are then extracted perpendicularly into a Wiley-MacLaren time-of-flight mass spectrometer and mass-selected using an electrostatic switch 1.2 m downstream.\textsuperscript{34} This mass gate is also used as a re-referencing tube and acts as the first plate of the velocity map imaging (VMI) lens.\textsuperscript{35} VMI projects each velocity vector of the ejecting photoelectrons onto a specific point on a two-dimensional (2D) plane. On this focal plane, a 70 mm diameter dual multichannel plate coupled to a phosphor screen yields a visual readout of each event, which is captured using a charge-coupled device (CCD) camera. Typically each laser shot produces between 10 and 20 photoelectrons (depending on cluster size) and images are accumulated over 15,000–20,000 laser shots.

Pump and probe pulses are derived from a commercial Ti:Sapphire oscillator and chirped pulse regenerative amplifier (Clark MXR, NJA-5, and CPA1000). The output from the amplifier is recompressed to give 100 fs pulses around 800 nm. In one-color experiments, we use either this laser pulse at a photon energy of 1.57 eV, or frequency-doubled/tripled light at 3.15/4.58 eV. In two-color experiments, the fundamental at 1.53 eV is split into two parts: a pump and probe beam. The pump is frequency-doubled in BBO yielding 90 $\mu$J/pulse around 3.06 eV. The remainder is used for the probe (50 $\mu$J/pulse) and is directed onto a motorized delay stage generating a relative pump-probe delay and subsequently recombin ionization effects in previous TRPES experiments on metal cluster anions are largely absent here because the $p$ band, in which all the dynamics occur, is singly occupied.
try, thus allowing for the reconstruction of this 3D cloud from its measured 2D projection, which we do using a variation of the BASEX (Basis-Set Expansion Abel Transform) routine.36 PE spectra are generated by angular integration of a slice through the center of the 3D reconstruction and conversion from velocity to energy space. The kinetic energy resolution is typically 5%, some of which is from the ~20–25 meV bandwidth of our pulses. Photoelectron angular distributions (PADs) are immediately available from the data. Generally, the anisotropy of a PAD is defined by an anisotropy parameter β2, which we obtain by radially integrating the inverted image over the feature of interest.

Finally, we can monitor fragmentation of mass-selected clusters following pump-only irradiation. This is accomplished by detecting ions on a retractable dual multichannel plate (see Fig. 1), which intersects the ion beam path some 30 cm beyond the laser interaction region. Parent and daughter ions emerge with different speeds from the static electric field of the VMI lens and thus are temporally separated en route to the retractable detector (see inset, Fig. 1) In this manner, the existence and extent of cluster fragmentation is determined. Unfortunately, no temporal information about the fragmentation process is gained.

III. RESULTS AND ANALYSIS

A. One-color PEI

Figures 2(a)–2(c) show symmetrized PE images collected following one-color detachment of Hg14 at 1.57 eV, 3.15 eV, and 4.58 eV, respectively. Figures 2(d)–2(f) show their corresponding PE spectra. Rings at larger diameter in the images correspond to peaks at higher electron kinetic energy (eKE) in the PE spectra. The vertical binding energy (VBE) and s–p band gap (BG) are 1.87 and 2.2 eV, respectively, for this cluster.14,25 Several physically distinct mechanisms contribute to the one-color PE spectra. Each feature is labeled to indicate its correspondence with the various photodetachment schemes as shown in Fig. 3.

Excitation at 1.57 eV shows an outer ring in the image (the central spot is discussed below) corresponding to peak A, which is about 200 meV wide, in the PE spectrum. This peak is from two-photon detachment of the single electron occupying the lowest molecular orbital of the p band (see Fig. 3). The photoelectron peak is very intense for a two-photon process and suggests resonance enhancement via excited states within the p band. Excitation with 3.15 eV exceeds the VBE of Hg14 and so in Fig. 2(e), a single distinct peak is present (labeled A) corresponding to direct detachment of this p electron with a single photon. Both features labeled A in Figs. 2(d) and 2(e) are centered at 1.3 eV, in accord with the VBE of Hg14–.

Figure 2(e) also shows a broad feature at low kinetic energy (B) and a high-energy shoulder extending to about 2.0 eV (C). These extra features appear because the photon energy, 3.15 eV, is greater than the band gap and can therefore excite electrons from the s to p bands. The high-energy shoulder extending past 2.0 eV shows quadratic laser power dependence. We assign this feature (C) to a resonance enhanced interband two-photon detachment process: excitation of an s electron to a 6s2n–16p2 configuration followed by detachment of the same electron, leaving the neutral in the excited 6s2n–16p1 state. The first step involves excitation from the s band, which is full. All electrons in this band are optically active and those with energies hν-BG below the top of the s band contribute to the photoelectron feature C. The maximum kinetic energy of the photoelectrons for this process is eKEmax=2hν−(EA+BG)−2.2 eV for Hg14–, in accord with the observed PE spectrum.

Feature B is attributed to the ejection of Auger electrons following single-photon absorption. The incident photon excites an electron from the full s band to the p band, creating an electron-hole pair. Thermalization of the electrons and hole is in competition with electron-hole recombination, which is accompanied by ejection of the second p electron in a concerted Auger process.15 This Auger electron contributes to the PE spectra as a low-energy shoulder relative to direct detachment of the p electron.

Detachment with 4.58 eV photons produces PE spectra similar in appearance to those presented by Busani et al.15 for excitation at similar energies. Briefly, features A, B, and C have the same origin as the features in Fig. 2(e) and are depicted in Fig. 3. Photoelectrons contributing to feature
arise from direct one-photon detachment from the s band, leaving the neutral in the excited \(6s^{2n-1}6p^1\) excited state. The VBE for detachment of the s electron is about 4.1 eV. The difference between the onset of this broad feature and detachment of the p electron to the neutral ground state presents a direct measure of the band gap of the neutral.\(^{14}\) Feature D shows quadratic power dependence. It may be an extension of feature C, simply involving two-photon detachment deeper into the s band, or it may be from process D in Fig. 3: excitation of an s electron to a \(6s^{2n-1}6p^2\) configuration of the anion, followed by detachment of the electron at the bottom of the p band, leaving the neutral in the \(6s^{2n-1}6p^1\) excited state.

The PE spectra of Busani et al. were collected using a magnetic bottle, which is relatively insensitive to very low-energy electrons. Imaging, on the other hand, does not suffer from this limitation and very low kinetic energy photoelectrons are collected with high efficiency.\(^{37}\) A peak at zero energy is seen in all three PE spectra. This corresponds to the bright spot in the center of the PE images in Fig. 2(a) and is also present in Figs. 2(b) and 2(c) although, in order to reveal other features in the latter two, saturation at the center has obscured this. These slow electrons probably originate from thermionic emission similar to low-energy electrons observed for \(C_n^-\) clusters.\(^{38,39}\) The time scale of such delayed emission is typically on the order of many nanoseconds\(^{40}\) and is not expected to compete with any of the processes in Fig. 3 nor with decay dynamics described below.

Finally, TRPEI measures PADs from which we extract anisotropy parameters. The PAD at a given eKE may be expressed as\(^{41}\)

\[
I(\theta, \varepsilon) = \frac{\sigma}{4\pi} \left[ 1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta) + \cdots \right],
\]

where \(\theta\) is the angle between the laser polarization and the ejected photoelectrons at energy \(\varepsilon\), \(\sigma\) is the total cross section, and \(P_l(\cos \theta)\) are \(l\)-th order Legendre polynomials weighted by the anisotropy parameters \(\beta_l\). For \(n\)-photon transitions, \(l = 0, 2, \ldots, 2n\). Anisotropy parameters provide insight into the detachment process, and thus the nature of the ground anion state. This is particularly so for single photon transitions, where \(\beta_4\) is omitted. Feature A is perhaps the most informative from this perspective as it involves direct detachment of the ground state anion to the ground state neutral.

Figure 4 shows \(\beta_2\) values for feature A, radially integrated over the full width at half maximum, for a range of clusters detached at 3.15 eV. The \(\beta_2\) values show rather erratic behavior up to \(Hg_{15}\), indicating that the nature of the neutral LUMO is changing quite dramatically over this cluster range. Specifically, \(Hg_8\) and \(Hg_9\) show very anisotropic detachment (\(\beta_2 = 1.3\) and 1.4, respectively), whereas \(Hg_{12}\) shows an almost isotropic distribution (\(\beta_2 = 0.1\)). For cluster \(Hg_{15}\) and larger, the \(\beta_2\)’s behave more smoothly and decrease gradually from \(\beta_2 = 0.7\) for \(Hg_{15}\) to \(\beta_2 = 0.6\) for \(Hg_{20}\).

In measuring the values of \(\beta_2\) for the direct detachment feature, we cannot account for the contributions from overlapping features such as B and C. In particular, feature B is unavoidable at 3.15 eV for clusters whose band gap is less than this energy (\(Hg_n, n > 12\)). Feature C is minimized by ensuring that the intensity is sufficiently low.

Finally, we point out that the PAD produced from the Auger electrons (feature B) is isotropic, \(\beta_2 \sim 0.0\), for all the clusters in which this feature was present. This is expected and in accord with the findings of Busani et al.\(^{15}\)

### B. Pump-probe dynamics for \(Hg_n^- (11 \leq n \leq 16, n = 18)\)

Figure 2(a) shows photodetachment occurs via intraband excitation of the p electron to excited electronic states within the band. This result suggests we can perform two-color pump-probe experiments to follow the dynamics within the p band subsequent to intraband excitation, using the scheme shown in the top panel of Fig. 5. Specifically, as the excited electron relaxes, the probe-induced PE spectrum should shift toward lower eKE.

Typical pump-probe PE images and spectra are presented in Figs. 5(a)–5(c) for the \(Hg_{15}\) cluster for pump-probe delays of 0, 8, and 62 ps, respectively. Near \(t = 0\), the PE image shows two major features: an intense, anisotropic ring and a fainter ring at larger diameter. Spectra at later times show the outer ring becoming more diffuse and shrinking in diameter, while the inner ring is unchanged. The corresponding PE spectra show that the inner ring transforms to a sharp peak at eKE=1.15 eV. This feature is from mechanism A seen in the one-color spectra and is labeled as such: a combination of one-photon detachment of the p electron of the probe and two photon detachment by the pump with VBE =1.91 eV for \(Hg_{15}\). Processes B and C [Fig. 2(e)] also contribute. However, the main feature of interest is the outer ring, since this is clearly dependent on the pump-probe delay. At \(t = 0\), it transforms to a relatively narrow feature at eKE =2.7 eV. At 8 ps [Fig. 5(b)], the two-color signal has shifted toward lower eKE and broadened considerably. By 62 ps [Fig. 5(c)], it appears as a shoulder on the high-eKE side of peak A.

A more detailed view of the time-evolving spectra is given in Fig. 6, where we show time-dependent PE spectra progressions at pump-probe delay increments of 6.7 ps for \(Hg_{11}\) (a) and 3.3 ps for \(Hg_{15}\) (b). In order to emphasize the
two-color signal, a probe-before-pump spectrum is subtracted from all the plots. This procedure results in negative signal in the region of peak A (vertical arrow), since the depletion of peak A induced by the pump pulse is absent in the probe-before-pump spectrum. For clarity, all negative intensities are set to zero in Fig. 6.

At $t=0$ ps, the excited $p$ electron produces a photoelectron peak which is very similar in shape and width, about 200 meV at FWHM, to that produced by direct detachment of the electron from the bottom of the $p$ band. For Hg$^{15}$, the signal then gradually shifts towards lower kinetic (higher binding) energy and spreads. At long times, $t>50$ ps, the PES has evolved into a peak centered at $eKE=1.5$ eV, that is, only slightly broader than the $t=0$ peak, and no further dynamics occur. This long-time signal does not merge completely with that of the unexcited cluster but instead extends to higher eKE. The general pattern of spectral evolution in Fig. 6(b) is seen for every cluster studied here except Hg$^{11}$, shown in Fig. 6(a). For this cluster, the initially prepared state persists for significantly longer. At times in excess of 100 ps, there still remains a well-defined photoelectron peak, which has not spread but has simply dropped in intensity. At the same time, some of the signal does shift to lower eKE and reforms a peak at long times, just as in the larger clusters.

We point out that Hg$^{11}$ was the smallest cluster studied here and has the lowest VBE = 1.73 eV, just above the pump photon energy. For smaller clusters, $h\nu_{\text{pump}} > \text{VBE}$ and the PE spectra are dominated by one-photon direct detachment, for which the cross section is apparently so large that any resonant two-color signal is depleted beyond the point where it can be observed. Dynamics in these smaller clusters are discussed in a following publication in which a lower pump photon energy was used.42

C. Relaxation rates

The time evolution in the PE spectra represents relaxation of the initially excited $p$ electron; as this electron loses...
by background subtraction of a probe-pump PE spectrum for the decay of the initially prepared excited state is tracked. Figs. 5 are monitored by integrating signal in the windows shown in Fig. 5 by the vertical dashed lines. For Hg\(_{15}\), the main dynamical features are monitored, as illustrated in the time-dependent PE spectrum. The windows are chosen such that the integrated photoelectron intensity in spectral windows of the high-eKE drops. These dynamics can be clocked by measuring the apparent linearity from 2 ps to about 50 ps and has been observed for all clusters. The average kinetic energy then evolves towards its final value, indicating the end of the observed dynamics.

The asymptotic signal levels in Figs. 7(c) and 7(f) are only 0.7–0.8, reflecting the observation that the integrated signal level in the long-time window is less than that in the short-time window. The apparent loss of total population at long times reflects the fact that some of this signal occurs in a region of overall negative intensity resulting from our background subtraction procedure. This effect can be seen more clearly in Fig. 5(c), which is not background-subtracted, showing the shoulder at long times merging with the one-color peak A. Fitting two Gaussian profiles to this long-time PE spectrum does indeed reveal that about 30% is lost to the main feature; the two peaks are separated by 0.28 eV. In any case, the observation that most of the signal at long times is shifted to higher eKE from peak A is significant and discussed in Sec. IV.

As a further means of characterizing the dynamical evolution of the excited electron with time, we have considered the average eKE for the photoelectron feature due to this electron by calculating the first moment of the photoelectron signal with respect to the energy. This is plotted on Fig. 8 for cluster Hg\(_{15}\). The most striking feature of this plot is the apparent linearity from 2 ps to about 50 ps and has been observed for all clusters. The average kinetic energy then evolves towards its final value, indicating the end of the observed dynamics.

In Figs. 7(a)–7(c) and 7(d)–7(f), we show the results of such an analysis for Hg\(_{11}\) and Hg\(_{15}\), respectively, using the photodetector data in Figs. 6(a) and 6(b). Integrated intensities in the high-, intermediate, and low-eKE windows are shown in (a) and (d), (b) and (e), and (c) and (f), respectively; normalization is with respect to the maximum signal in the high-eKE window (top panels). For all clusters, the drop in intensity of the initially prepared state is well fit with an exponential decay with size-dependent time constants given in Table I. As the initially prepared state decays, population migrates into the intermediate window, which grows accordingly and then decays. The signal in the low-energy window, monitoring the long-time dynamics, remains constant at early times [see inset in bottom panel of Fig. 7(c)], as it takes several picoseconds for the population to reach this spectral window. This signal then rises and flattens over a period of several tens of picoseconds after which no more dynamics are observed.

The average eKE for the photoelectron feature due to this electron by calculating the first moment of the photoelectron signal with respect to the energy. This is plotted on Fig. 8 for cluster Hg\(_{15}\). The most striking feature of this plot is the apparent linearity from 2 ps to about 50 ps and has been observed for all clusters. The average kinetic energy then evolves towards its final value, indicating the end of the observed dynamics.

![Figure 7](image1.png) Normalized integrated photoelectron intensity for spectral windows representative of the main dynamical features. (a)–(c) and (d)–(f) represent the population for the initially prepared state, the intermediate regime and the final state for Hg\(_{11}\) and Hg\(_{15}\), respectively.

![Figure 8](image2.png) Average electron-kinetic energy (eKE) of the two-color time-dependent signal for Hg\(_{15}\).

**TABLE I. Lifetimes for initially excited states in Hg\(_n^-\) clusters.**

<table>
<thead>
<tr>
<th>Size</th>
<th>Relaxation time (ps)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>33.9</td>
<td>±0.7</td>
</tr>
<tr>
<td>12</td>
<td>13.5</td>
<td>±0.3</td>
</tr>
<tr>
<td>13</td>
<td>6.6</td>
<td>±0.3</td>
</tr>
<tr>
<td>14</td>
<td>13.8</td>
<td>±0.9</td>
</tr>
<tr>
<td>15</td>
<td>10.3</td>
<td>±0.2</td>
</tr>
<tr>
<td>16</td>
<td>7.5</td>
<td>±0.6</td>
</tr>
<tr>
<td>18</td>
<td>8.0</td>
<td>±0.4</td>
</tr>
</tbody>
</table>
D. Fragmentation

Using the scheme indicated in Fig. 1, we have monitored fragmentation of the mass-selected clusters following interaction with a pump-only beam (1.5 eV). Generally, hot clusters may dispose of excess energy by evaporation if the cluster is bound by weak forces or thermionic emission, when the electron affinity is much less than the energy required to break internal bonding. We may expect evaporation as the mercury clusters considered in this size range are relatively weakly bound due to the van der Waals nature present in the bonding.

For all mass-selected clusters studied, \( \text{Hg}_n^- \) \((n = 11–15, 18)\), we have observed anionic daughter ions. A typical example of a mass spectrum is shown in the inset of Fig. 1 for \( \text{Hg}_{11}^- \), indicating the arrival of two daughter ions prior to the parent ion. For \( \text{Hg}_n^- \) \((n = 11–13)\), we see both \( \text{Hg}_{n-1}^- \) and \( \text{Hg}_{n-2}^- \) daughter ions, where the relative intensity of \( \text{Hg}_{n-2}^- \) increases from the weaker peak to the overwhelmingly dominant peak. In the range \( n = 14–15 \), we observe \( \text{Hg}_{n-1}^- \), \( \text{Hg}_{n-2}^- \), and \( \text{Hg}_{n-3}^- \) daughter ions although for \( \text{Hg}_{14}^- \), the \( \text{Hg}_{n-1}^- \) peak is very small. Finally, for \( \text{Hg}_{18}^- \), we again only observe the loss of up to two atoms to leave \( \text{Hg}_{17}^- \) and \( \text{Hg}_{16}^- \). We stress that the evaporation studies are more designed toward demonstrating the existence of fragmentation as opposed to extracting accurate photofragment branching ratios. In particular, it is possible that the true \( \text{Hg}_{n-1}^- \) daughter ion and even the \( \text{Hg}_{n-2}^- \) daughter are obscured by the rather broad parent peak. Hence, the fragmentation patterns given here represent “lower bounds” on the extent of dissociation; the daughter ions may actually be smaller by one or two Hg atoms.

IV. DISCUSSION

In this section, we first consider qualitative aspects of the TRPE spectra and the electronic structure of the mercury clusters studied here. The shifting of the two-color photoelectron peak towards lower KE is interpreted in terms of electronic relaxation of the initially prepared state, with the excited electron ultimately ending up at or near the bottom of the \( p \) band from whence it came. We then propose a simple kinetic model based on sequential radiationless transitions among the electronic states of the \( p \) band that reproduces the main features of our results. This electronic relaxation is accompanied by vibrational excitation of the cluster, resulting in vibrationally hot clusters at the longest delay times probed in the experiment. At very short delay times, rapid shifts of the KE are attributed to wave packet motion on the initially excited multidimensional potential energy surface. At the longest delays, we take into account the effects of the vibrational heating on the PES and consider the possibility of ultrafast evaporation. Cluster size effects are discussed in terms of the observed relaxation rates for the range of clusters studied. In particular \( \text{Hg}_{11}^- \) relaxes significantly slower than the other clusters.

A. Overall relaxation dynamics

TRPES allows one to track excited state anion dynamics by correlating the KE following probe detachment to the energetics of the system under investigation. The photoelectron KE may be expressed as

\[
eKE = h\nu_{\text{probe}} - \text{EA} + E_{\text{anion}} - E_{\text{neutral}},
\]

where EA is the size-dependent electron affinity of cluster \( \text{Hg}_n^- \), \( E_{\text{anion}} \) is the total internal (electronic + vibrational) energy of the cluster following pump excitation, and \( E_{\text{neutral}} \) corresponds to the internal energy of the neutral formed by photodetachment. Note that the neutral clusters are formed in their ground electronic state; the first excited state, corresponding to a \( 6s^2n-16p^1 \) configuration, is not energetically accessible by one-photon detachment at 3.06 eV.

In the absence of fragmentation or photon emission, \( E_{\text{anion}} \) is constant with time. However, energy partitioning between electronic and vibrational degrees of freedom will evolve following pump-induced electronic excitation within the \( p \) band. The photoelectron spectrum at a given pump-probe delay time then represents a Franck-Condon mapping of the anion vibronic wave function \( \Psi^{(-)}(t) \) onto the ground electronic state of the neutral cluster. More specifically, one expects that electronic energy is converted into vibrational energy over time. Thus, while electronic relaxation tends to shift the photoelectron KE toward lower values, the accompanying vibrational heating partially compensates for this via vibrational hot band transitions. This latter effect depends on the geometry change between the various anion electronic states and the neutral ground state. If the geometry changes are small, then vibrational heating has minimal effect on the PE spectra because the cluster vibrational modes are largely inactive; as a result, their time evolution can be interpreted rather straightforwardly in terms of electronic relaxation.

There is considerable evidence that this scenario is indeed the case for Hg clusters. PE spectra from direct, \( p \)-band detachment are only 200 meV wide [Fig. 2(e), for example], indicating small geometry changes between the anion and neutral ground state. The pump-probe spectra at \( t = 0 \) are similarly narrow, showing that the geometries of the initially excited state and neutral ground state are similar. Finally, although the TRPE spectra exhibit considerable spreading at intermediate times, a relatively narrow peak is seen at the longest times, when the vibrational energy should be maximal. Hence, the overall observed dynamics reflect primarily the time-dependent electronic energy of the excited cluster.

There are many instances in the literature in which TRPES has been used to follow the dynamics of radiationless transition in molecules. In such experiments the manifold of electronic states is relatively sparse; as a result, features in the PE spectra are readily assigned to individual electronic states, from which state-specific lifetimes may be extracted. In contrast, for the mercury clusters studied here, the density of electronic states participating in the dynamics is much higher, and the evolution of the time-dependent PE spectra suggests bulklike continuous relaxation for the excited electron back to its ground state. However, the assumption of a continuum of electronic states is an oversimplification. There are \( 3n \) electronic states for cluster \( \text{Hg}_n^+ \) in the \( p \)
band. The width of the band is cluster-dependent and ranges between about 4.0 eV for Hg$_{11}$ and 4.6 eV for Hg$_{18}$, implying an average density of states (DOS) ranging between 8 states/eV and 12 states/eV, respectively. The observed initial state lifetimes (Table I) imply homogeneous linewidths (<1 meV) that are much smaller than the spacing between electronic states (~100 meV), so in the size range under consideration, the $p$ band is best considered as a dense but discrete set of electronic states.

**B. Kinetic modeling of TRPE spectra**

In this section, we put forth a simple kinetic model for the TRPE spectra based on the ideas enumerated above. For simplicity, we consider the electronic states within the $p$ band to be distributed evenly, reflecting an average electronic DOS as mentioned before. Electronic excitation introduces 1.5 eV of energy into the system, which defines the initial conditions. We may then calculate the evolution of the electronic energy with time using kinetic rate equations of the form

$$\frac{dN_i}{dt} = \sum_{j<i} k_{ij}N_j - \sum_{j>i} k_{ji}N_i,$$

where we have labeled the states involved as $i=1,2,3,...$ in descending energy order. $N_i$ and $N_j$ represent the population probability in state $i$ and $j$, respectively, and these states are coupled together through rate constants $k_{ij}$. The first term accounts for population contributing to state $i$ from higher lying electronic states, $j$; the second term allows for population to be removed from state $i$, which is transferred to lower-lying electronic states, $j$. The rate constants, $k_{ij}$, depend on the energy gap between state $i$ and $j$, such that

$$k_{ij} = \frac{1}{e^{\Delta E_{ij}/k_B T} - 1},$$

where $k$ is a rate constant and $\Delta E_{ij}$ is a scaled energy gap, given by $(j-i)^{\alpha}E_{av}/0.110$, where $E_{av}$ is the average spacing between adjacent energy levels for Hg$_p$, and 0.110 eV is the average energy spacing for all the clusters studied here. $\Delta E_{av}$ and the overall average of 0.110 eV are estimated from the calculations by Pastor and Benneman, which show that the $p$-band width scales approximately as $n^{1/3}$, so that $\Delta E_{av} \approx n^{-2/3}$. Initial conditions at $t=0$ are $N_i = 1$, and $N_{j>1} = 0$, where state 1 lies 1.5 eV above the bottom of the band.

In Fig. 9(a), we show the time-dependent populations of Hg$_{15}$ for excitation at 1.5 eV, an average DOS of 10 states/eV, and where we have chosen $k_{1,i+1}$, the radiationless transition rate between adjacent levels, to be 0.1 ps$^{-1}$. The origin of the spreading is immediately recognizable in Fig. 9(a): population rapidly migrates into a number of excited states before being totally relaxed. As a number of states at a given time during the decay process have appreciable population, the electron has effectively spread over a range of energy levels.

We may convert the time-dependent populations to a PE spectrum progression, as a direct comparison with our experiment, by simply convoluting the time-dependent populations with a Gaussian with a full width at half maximum of 200 meV. This width was set to reflect the direct detachment observed experimentally. The PES progression is shown in Fig. 9(b) and shows remarkable qualitative agreement with Fig. 6(b) considering the simplicity of the model. At early time, a well-defined peak is observed, which rapidly spreads and shifts to lower eKE. Relaxation is complete by 60 ps, by which time only the lowest electronic level of the $p$ band is populated. The dynamics may be further characterized by considering the average eKE with time of the excited electron, directly comparable to Fig. 8, where the average eKE is shown for the relaxation in Hg$_{15}$. This has been shown in Fig. 9(c), where again, the model reproduces the most prominent feature of the experimentally observed average eKE—the linearity as the electron cascades towards the bottom of the band.

The question arises as to whether this model can be modified to reproduce the anomalous results found for Hg$_{11}$ in which the initially excited state appears to persist for a much longer time than for the larger clusters studied here. In fact, we found that by reducing $k_{ij}$, where $i=1$, by a factor of 6 relative to the other rate constants yielded the calculated PE spectrum progression shown in Fig. 9(d). Comparing this result with the experimentally observed TRPEI spectra for Hg$_{11}$ in Fig. 6(a) reveals excellent overall qualitative agreement. The initially excited state acts as a bottleneck and once population leaves this excited state, it reaches the initial ground state quickly.

There are, however, two aspects of the experimental spectra not reproduced by our kinetic model. These are considered in the following sections.
Given that we have argued that there are only small changes in equilibrium geometry, resulting in small Franck-Condon factors for off-diagonal (i.e., hot band) transitions, it would seem that vibrational heating cannot explain the long-time shifts. However, mercury clusters are weakly bound clusters with very low frequencies; calculations by Flad et al. yield an average frequency of 34 cm$^{-1}$ (4.2 meV) for Hg$_6$, for example. Hence, each mode has significant vibrational excitation, and the resulting large amplitude motion is quite likely to render inadequate the standard Franck-Condon picture of photoelectron spectroscopy based on separable harmonic oscillators.

The shifted PE spectra at long times may also be a signature of evaporation, because the VBEs of Hg$_n$ clusters generally drop as the cluster becomes smaller. Excitation at 1.5 eV is certainly sufficient for evaporation of multiple Hg atoms. We observe fragmentation using the scheme illustrated in Fig. 1. Moreover, the average cohesive binding energy per atom in the anion clusters, $E_{coh}^{'}(n)$, can be estimated from the relation

$$E_{coh}^{'}(n) = E_{coh}^{(0)}(n) + VBE/n,$$  

where $E_{coh}^{(0)}(n)$, the corresponding value for neutral Hg clusters, has been measured and calculated. Equation (4) yields $E_{coh}^{'}(n) = 0.25$ eV for Hg$_{13}$, for example. The question here is one of kinetics. In other words, does at least some evaporation happen on the ~100 ps time scale probed in these experiments, and can such a process be distinguished from vibrational heating?

There is in fact evidence for evaporation on this timescale based on the trends in long-time shifts vs cluster size. A plot of VBE vs $n$ for Hg$_n$ clusters shows a significant decrease in slope starting around $n = 10$. As a result, for example, the loss of three Hg atoms from Hg$_{11}$ results in a decrease in the VBE by 0.36 eV, while evaporation of three atoms from Hg$_{15}$ drops the VBE by only 0.12 eV. These energetic trends are in accord with the experimental size-dependent shifts, and the degree of evaporation required to produce these shifts is to some degree consistent with the fragmentation results discussed in Sec. III D. Thus, while vibrational heating accompanying electronic relaxation can be responsible for some of the shift in the long-time PE spectra, there is reasonably strong evidence that evaporation of two to three atoms occurs on the time scale of the pump-probe experiment; this evaporation is reflected as a perturbation on the electronic relaxation dynamics that dominate the time-dependent PE spectra.

E. Size-dependent relaxation rates

The relaxation rates (ps$^{-1}$) for of the initially prepared excited state in the $p$ band obtained from the time scales in Table I are shown in Fig. 10. The solid line shows how the rate constants would scale if they depended only on the cluster DOS. Here we have fixed $k$ in Eq. (3) so that initial decay rate $k_{i,i+1}$ matches the experimental decay rate for Hg$_{15}$. This value of $k$ is then used for all clusters, with the initial decay rates determined by the average energy gap between
The experimental data in Fig. 10 show an overall increase in rate with \( n \) but oscillate significantly above and below the solid line, possibly with decreasing amplitude as \( n \) increases. This result indicates that the vibronic coupling responsible for the decay of the initially excited state is quite sensitive to the number of atoms in the cluster. In other words, the size regime studied here is such that addition of each atom markedly changes the cluster properties. This conclusion is supported by the size-dependent anisotropy parameters \( \beta_2 \) for detachment from the ground anion state shown in Fig. 4. These exhibit substantial variation with \( n \), indicating that the character of the molecular orbital from which detachment occurs is quite sensitive to the cluster size. Again, we may expect a smoother trend for larger clusters, as here the extra atom will impose a lesser perturbation on the cluster. Interestingly, the cluster revealing the most rapid relaxation is the anion of \( \text{Hg}_{13}^- \), which, if considered purely geometrically or electronic shell motifs present for this particular cluster. We do not, however, rule out the possibility of a polarization-supported state near threshold.  

For \( \text{Hg}_{11}^- \), excitation at 1.53 eV promotes the electron to right below the detachment limit at 1.73 eV. Note that this value corresponds to the central peak position in the photoelectron spectra and has a width of \( \sim \)200 meV at half maximum. We may be accidentally exciting an image-charge bound state, or a state stabilized by induced dipoles within the cluster. The polarization-ability of \( \text{Hg} \) clusters is very large due to the very large atomic polarizability of atomic \( \text{Hg} \) (5.7 Å\(^3\) compared to 4.0 Å\(^3\) for \( \text{Xe} \)) and collectively due to the van der Waals contributions to the bonding. Polarization-bound states are diffuse states and will consequently have a poor overlap with the molecular orbitals of the cluster causing a dramatic reduction in the rate. Such polarization bound states have, however, not been observed in \( \text{Hg}_n^- \) but experiments to do so are underway.  

Finally, we contrast our observations with similar experiments in metallic clusters. Pontius et al.\(^5\)\(^\text{–12}\) performed a series of anion TRPE spectroscopy experiments on small transition metal clusters. Two distinct time scales are seen for \( \text{Ni}_n^- \) and \( \text{Pd}_n^- \) (\( n = 4, 7 \)): a ultrafast sub-100 fs decay due to electron-electron scattering and, once the electron bath has thermalized, a second somewhat slower electron-nuclear relaxation occurring on a 1 ps time scale for \( \text{Pd}_n^- \) clusters. We see no evidence for electron-electron scattering in our experiment, a reasonable result since we are dealing with a singly occupied electronic band. The electron-nuclear coupling in the \( \text{Hg}_n^- \) clusters is slower than in the transition metal clusters, most likely because of the high density of electronic states in the latter owing to the open-shell \( d \) atoms. The time scales seen in our experiments are intermediate between those seen in TRPE studies of \( \text{Al}_{n-15}^- \) (200–500 fs),\(^\text{49} \) and \( \text{Au}_{n-15}(~1 \text{ ns}) \),\(^\text{50} \) two families of clusters with closed \( d \)-shell atoms. While these general trends can be rationalized in terms of electronic state densities, a quantitative understanding of these orders-of-magnitude variations in excited state lifetimes is clearly lacking. We hope this growing body of results stimulates a serious theoretical effort to gain more fundamental insights into the factors governing excited state dynamics of these clusters.

V. SUMMARY

Time-resolved photoelectron imaging was used to investigate the dynamics of \( \text{Hg}_n^- \) (\( n = 11–18 \)) cluster anions following intraband excitation at 1.5 eV of the lone electron occupying the \( p \) band. These experiments yield the lifetime of the initially excited state and allow one to track the subsequent relaxation dynamics in considerable detail. The excited state lifetimes vary from 6.6 to 33.9 ps, with the \( n = 11 \) lifetime being considerably longer than that of any of the other clusters. The \( p \) band in these anions is a dense but discrete manifold of electronic states, and the time-evolving PE spectra can be modeled as a series of radiationless transitions between nearby states, leading to an electronically relaxed but vibrationally hot cluster. The PE spectra at long times show evidence for evaporation of a small number of \( \text{Hg} \) atoms occurring on a time scale of \( \sim 100 \) ps. The relaxation dynamics and photoelectron angular distributions show a strong dependence on cluster size, indicating that we are still in a size regime where the addition of each atom significantly affects the properties of the cluster. The size range under study here corresponds to the transition between van der Waals and covalent bonding in \( \text{Hg} \) clusters, and it will clearly be of interest to determine how moving further into the covalent regime will affects trends in the dynamics of these clusters. Dynamical studies following interband (i.e.

![FIG. 10. Relaxation rates for decay of initially excited state for \( \text{Hg}_n^- \) in the size range 11\( \leq n \leq 18 \). Open circles correspond to the experimentally observed time scales and solid squares and solid line indicate the rates determined from kinetic model, where representative electronic DOS were used (see text).](image-url)
(s→p) excitation at higher pump energies will also be of interest. These extensions of the work presented here will be carried out in the near future.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under Grant No. DMR-0139064. Additional support from the US-Israel Binational Science Foundation is gratefully acknowledged.

25 O. Cheshnovsky (private communication).
48 O. Cheshnovsky (Unpublished).