Auger recombination and excited state relaxation dynamics in Hg_n^- (n=9–20) anion clusters

Graham B. Griffin,[1] Oli T. Ehrler,[1] Aster Kammrath,[2] Ryan M. Young,[1] Ori Cheshnovsky,[3] and Daniel M. Neumark[1,4,a)]
[1]*Department of Chemistry, University of California, Berkeley, California 94720, USA*
[2]*Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA*
[3]*School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel*
[4]*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

(Received 21 March 2009; accepted 14 May 2009; published online 17 June 2009)

Using femtosecond time-resolved photoelectron imaging, electron-hole pairs are created in size-selected Hg_n^- anion clusters (n=9–20), and the subsequent decay dynamics are measured. These clusters eject electrons via Auger decay on time scales of 100–600 fs. There is an abrupt increase in the Auger decay time for clusters larger than Hg_{12}^-, coinciding with the onset of the transition from van der Waals to covalent bonding in mercury clusters. Our results also show evidence for subpicosecond excited state relaxation attributed to inelastic electron-electron and electron-hole scattering as well as hole-induced contraction of the cluster. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3149562]

The potential application of semiconductor quantum dots (QDs) in the construction of efficient solar cells[1] has stimulated interest in their photophysics, particularly the relaxation processes that occur when single or multiple electron-hole (e-h) pairs are created by photon absorption at energies above the band gap. For example, the proposed phenomenon of multiple exciton generation, in which the absorption of a single high energy photon creates multiple e-h pairs, provides a possible means for increasing the conversion efficiency of solar cells. The existence of multiple e-h pairs is inferred from multiexponential decay in transient absorption experiments[2–6] based on the idea that an e-h pair can recombine via an Auger-like process, with the resulting energy release exciting other charge carriers within the system.[7] This process continues until only a single e-h pair remains, which can then decay only radiatively. A recent experiment, however, has questioned whether a single photon can generate multiple e-h pairs,[8] while another[9] has cast doubt on the notion of Auger decay in multiexciton systems.

These controversies result in part because QDs are generally not produced as isolated species but typically are coated with surface-capping groups that can affect e-h dynamics.[10,11] Here, we describe experiments performed on mercury cluster anions. These clusters demonstrate key features of semiconductor QDs, most notably size-tunable band gaps, without the complications associated with surface capping.

Mercury clusters are of interest in cluster science because their electronic structure evolves significantly with size.[12,13] Atomic mercury is divalent, with a $6s^2$ subshell and relatively high-lying empty $6p$ orbitals. A series of experimental[10–13] and theoretical[11–14] studies shows that van der Waals (vdW) bonding dominates for neutral clusters up to $n \sim 13$, while larger clusters exhibit semiconductor-like covalent bonding with well-separated filled $6s$ and empty $6p$ bands.

In mercury cluster anions, Hg_n^-, the excess electron resides at the bottom of the p band, as shown in Fig. 1(c). Photoelectron spectra of mass-selected Hg_n^- anions directly yield the s-p band gap, E_g.[14] These spectra showed that E_g drops steadily with size until it reaches zero, signifying the onset of metallic bonding, at $n \sim 400$. More recent photoelectron spectra[15] of these species showed that excitation of a $6s$ electron into the $6p$ band created an e-h pair (valence electron configuration $6s_h 6p_e^2$) that decayed by an Auger process, in which the energy released by $6p$ electron–$6s$ hole recombination ejected the other $6p$ electrons from the cluster.

We have investigated electronic relaxation dynamics in Hg_n^- using time-resolved photoelectron imaging (TRPEI),[16] in which femtosecond pump and probe pulses are used to electronically excite and photodetach size-selected clusters. Two types of experiments have been performed thus far. In *intraband* excitation experiments, Hg_n^- clusters (n=7–18, E_g=2.8–2.1 eV) were excited with $h\nu_{\text{pump}} < E_g$, resulting in the excitation of the lone p electron within the p band. Time constants of 2–34 ps were found for subsequent relaxation through the closely spaced electronic energy levels of the p band. We recently reported preliminary TRPEI experiments on Hg_{13}^- at $h\nu_{\text{pump}} > E_g$,[17] exciting an electron from the $6s$ to $6p$ band in order to monitor relaxation dynamics subsequent to *interband* excitation. This work showed that Auger decay occurred within 490 fs.

In the work reported here, the dynamics in Hg_n^- clusters following interband excitation are probed as a function of cluster size using TRPEI. We observe two spectral features exhibiting different dynamics that elucidate the nature of the relaxation that occurs prior to e-h recombination. Moreover,

a)Author to whom correspondence should be addressed. Tel.: 510-642-3502. FAX: 510-642-3635. Electronic mail: dneumark@berkeley.edu.

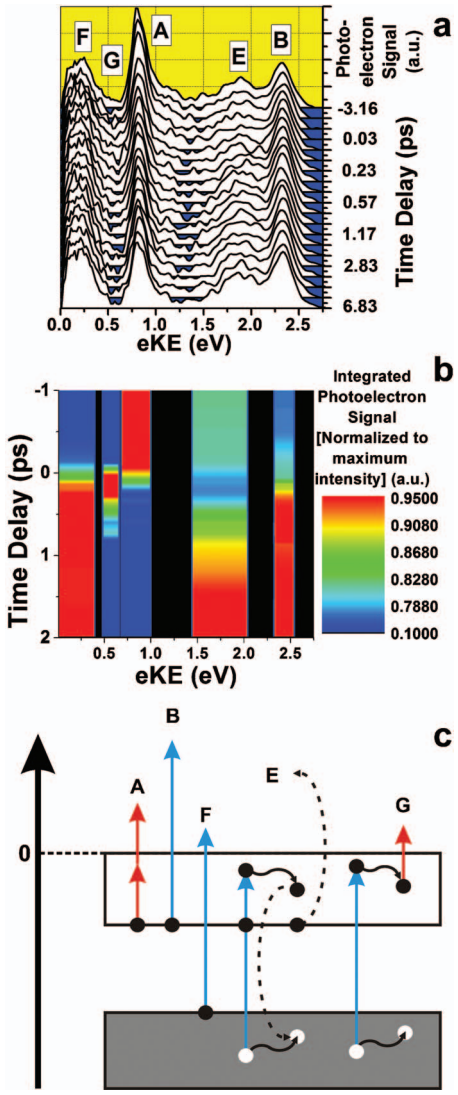

FIG. 1. (Color) (a) Time-resolved photoelectron spectrum of Hg_{19}^- pumped at 4.65 eV and probed at 1.55 eV, with time delay varying from −3.17 to +6.83 ps. (b) Integrated photoelectron signal for each feature presented on a linear time scale and a false color intensity scale chosen to clearly display the observed dynamics. (c) Diagram of the photodetachment processes observed in this experiment. Solid red (blue) arrows correspond to probe (pump) photons, curved solid black arrows correspond to electron dynamics prior to detachment, and dotted black arrows correspond to *e-h* recombination. White (black) circles correspond to holes (electrons).

we find an abrupt increase in the Auger decay time constant at the cluster size corresponding to the onset of the vdW → covalent transition and interpret this result in terms of increased electron and/or hole delocalization in the excited cluster.

The TRPEI instrument has been described in detail previously.[18] Hg_n^- clusters were generated in a pulsed supersonic expansion under conditions similar to our previous work on this system.[17,19,20] Ions were mass-selected by time of flight[21] and then photoexcited with 80–100 fs pump and probe pulses at 4.65 and 1.55 eV, respectively. At each pump-probe delay, photodetached electrons were collected using a collinear velocity-map imaging setup[22] and analyzed using standard methods[23] to yield electron kinetic energy (eKE) and angular distributions.

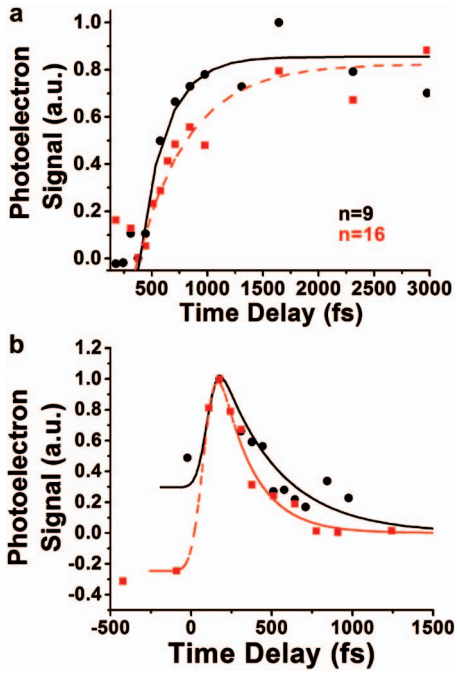

FIG. 2. (Color) Integrated intensity of features (a) E and (b) G for Hg_9^- (black circles) and Hg_{16}^- (red squares), normalized on a 0–1 scale. Fit lines for the data are displayed for both cluster sizes (black lines for Hg_9^- and red lines for Hg_{16}^-.)

Figure 1(a) shows time-resolved photoelectron spectra of Hg_{19}^- as a waterfall plot, displaying five distinct features. The integrated time-dependent signal from each feature is presented in Fig. 1(b). Assignments of the features in Figs. 1(a) and 1(b) are indicated in Fig. 1(c). Features A, B, and F are from direct detachment by either two probe photons (A) or one pump photon (B and F). Feature G is at the expected eKE for probe pulse detachment of transient *p*-band electrons created by the pump pulse. Feature E is the Auger peak, resulting from decay of the $6s_h^*6p_e6p_e^*$ anion excited state to the closed-shell ground state of neutral Hg_n+e^-, akin to the excited state autodetachment seen in small negative ions.[24]

Features A, B, and F change in intensity only around zero time delay owing to depletion effects induced by either the pump or probe pulses.[17] Features E and G are the only features that show nontrivial dynamics extending beyond the ~150 fs cross correlation of the pump and probe pulses [see Fig. 1(b)].

Figure 2 shows the results of gated integration of features [Fig. 2(a)] E and [Fig. 2(b)] G for Hg_9^- and Hg_{16}^-, illustrating representative dynamics of each feature. Feature E can be fitted to an exponential recovery with time constant τ_E, while feature G can be fitted to the convolution of an exponential decay (τ_G) with a Gaussian line shape accounting for the experimental cross correlation. The corresponding time constants for all clusters studied here are summarized in Fig. 3. For clusters with $n \leq 12$, the two time constants τ_E and τ_G are the same, within error bars, but τ_E rises abruptly from 290 fs for $n=12$ to 480 fs for $n=13$, while τ_G shows a less noticeable size dependence.

The overall similarity of τ_E and τ_G, particularly for $n \leq 12$, suggests that both are sensitive to the lifetime of the pump-excited $6p^*$ electron with respect to Auger decay. Prior

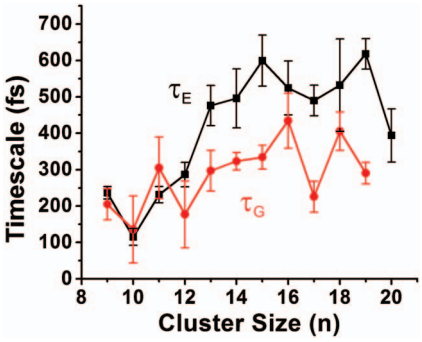

FIG. 3. (Color) Fitted time scales for recovery of Auger electron signal [feature E (black)] and pump-probe transient decay [feature G (red)]. Time scales are the mean of two to six separate experiments at each cluster size with the standard error for measurements at each cluster size displayed as error bars.

to Auger decay, the probe laser can eject this electron, producing a photoelectron at the eKE of feature G and depleting the Auger feature E, but once Auger decay occurs, the probe laser has no effect on feature E. Hence, feature G decreases in intensity over time as the transient excited state population decreases, and depletion of Auger signal induced by the probe laser is reduced for the same reason.

The decay times τ_E are more than a factor of 10 shorter than the electronic relaxation times observed in our intraband experiments.[19,20] In those experiments, the excited $6p$ electron can only relax by a sequence of radiationless transitions between closely spaced (by ~0.1 eV) electronic states within the p band,[12] with each transition channeling electronic energy into the vibrational degrees of freedom in the cluster. The shorter lifetimes in the interband experiments reflect the availability of additional decay pathways.

Our observation of fast Auger decay following interband excitation calls to mind experiments on semiconductor QDs, in which multiple e-h pairs created in a single QD recombine much more rapidly than a single e-h pair.[2,7] If multiple e-h pairs are created, one pair can recombine by an Auger-like process, releasing energy into other charge carriers present within the cluster; clearly this channel cannot occur if there is only one e-h pair in the QD. Similarly, in Hg_n^- clusters, the released energy from e-h recombination ejects the second p-band electron into the continuum.

The abrupt rise in τ_E at $n=13$ is intriguing in light of prior experimental[25] and theoretical[26,27] results, indicating the onset of a transition in neutral Hg_n clusters from vdW bonding for $n<13$ to covalent bonding, with larger cohesive energies and increased s-p hybridization, for Hg_{13} and larger clusters.[12] In particular, photoionization efficiency measurements by Brechignac *et al.*[28] showed that the energies of $5d \rightarrow 6p$ autoionizing resonances in neutral Hg_n clusters decreased gradually, with a slope proportional to $1/n$, in clusters up to $n=12$ but then dropped considerably faster for larger clusters. The $1/n$ dependence suggested gradual stabilization of a localized upper state with increasing cluster size, a phenomenon seen in other vdW clusters.[29] However, the more abrupt drop starting at $n=13$ was attributed to greater delocalization in the upper state, owing to the enhanced s-p hybridization.

Our experiments provide a time-domain view of the same phenomenon. For clusters with $n<13$, a shorter τ_E would be expected if the e-h pair created by the pump pulse was localized on some subset of atoms within the cluster. The Auger decay rate is proportional to $|\langle\psi_k\psi_{6s}|r_{12}^{-1}|\psi_{6p}\psi_{6p^*}\rangle|^2$, the Coulomb interaction between the two $6p$ electrons present prior to Auger detachment and the ground state $6s$ electron and outgoing ejected electron (ψ_k) that result after Auger decay.[30] Thus, a reduced e-h Coulomb interaction, which should occur in clusters with more delocalized orbitals, would result in an increased τ_E. Note that the structure of Hg_{13} is predicted to be an icosahedron with a single central Hg atom;[31] such a highly symmetric structure is conducive to delocalized molecular orbitals. The same calculation shows that larger clusters are built on an icosahedral core, which may be the reason why there is little variation in τ_E for $n=13-20$.

A key characteristic of the Auger feature E is that it occurs at lower eKE than peak B, which arises from direct detachment of the electron originally at the bottom of the p band by a pump photon. As pointed out by Busani *et al.*[15] this result implies partial relaxation of the e-h pair created by the pump pulse, in all clusters studied here, prior to recombination and Auger decay. This relaxation must occur within 100–600 fs, the range of values for τ_E in Fig. 3, and is thus over an order of magnitude faster than the relaxation that occurs subsequent to intraband excitation. It therefore must arise from a mechanism other than electron-phonon coupling in the excited state.

This large difference between relaxation times reflects the distinct nature of the excited anion states created in the two types of experiments, as illustrated in Fig. 4(a). In the intraband experiments, the pump pulse creates a $6p_e^*$ state in which only the lone $6p$ electron is excited, and relaxation can occur only by conversion of electronic energy to vibrational energy. In contrast, the $6s_h^*6p_e6p_e^*$ state lies within a much denser manifold of electronic states. It can undergo multiple near-resonant electronic energy transfers to nearby states through inelastic electron-electron and electron-hole scattering, with a smaller energy mismatch (relative to the intraband case) needing to be taken up by vibrational modes of the cluster. Either process results in a decreased $6p_e^*$-$6s_h^*$ energetic separation and thus less energy for ejection of the Auger electron upon recombination. This type of relaxation is similar to that proposed by Efros *et al.*[7] to explain subpicosecond electronic relaxation in CdSe QDs.

These electronically inelastic processes also reduce the kinetic energy of the electrons contributing to feature G, which arises from the detachment of the $6p_e^*$ electron by the probe pulse. Feature G represents the probe-induced signal that can be distinguished from the more intense, adjacent peaks, and thus really measures the excited state population within a fairly narrow energy window. If the initially excited $6p_e^*$ electron loses too much energy, it will be obscured by peak F, resulting in the apparent disappearance of feature G prior to Auger decay. Hence, rapid loss of electronic energy by the $6p_e^*$ electron may account for the observation that $\tau_G<\tau_E$ for clusters with $n>12$.

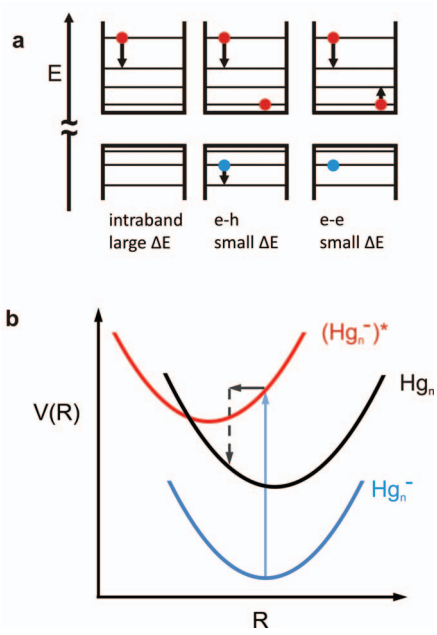

FIG. 4. (Color) (a) Qualitative diagram of relaxation pathways in electronically excited Hg_n^- anions. Relaxation following intraband excitation (left) occurs by sequential radiationless transitions involving the conversion of electronic to vibrational energy. For interband excitation, inelastic electron-electron (right) and electron-hole (center) scattering enables relaxation via a small energy defect taken up by cluster vibrational modes. Note that energy levels are drawn closer together near the band gap for the 6*p* and 6*s* bands, consistent with our earlier pump-probe experiments (Ref. 19). (b) Schematic potential energy curves for Hg_n^- (blue ground state, red $6s_h^*6p_e6p_e^*$ excited state) and Hg_n^0 (black) plotted vs *R*, the average nearest neighbor distance. Bond lengths in the neutral ground state should be slightly longer than in the anion (Ref. 32). The solid black arrow indicates nuclear motion on the anion excited state, while the dashed black arrow shows electron-hole recombination via Auger decay.

Excited state nuclear dynamics may also contribute to *e-h* relaxation. Calculations by Kitamura[27] on the ground and excited states of *neutral* Hg_n clusters show that the hole induces a significant contraction of the nearest neighbor distances in the excited state, on the order of 0.5 Å in Hg_{13}, for example. A similar situation should hold for the excited anion electronic states with a 6*s* hole. The resulting nuclear dynamics are indicated in Fig. 4(b). The initially prepared $6s_h^*6p_e6p_e^*$ state can relax rapidly via contraction around the hole, as shown, prior to recombination and Auger decay, resulting in a lowered eKE for the ejected electron.

Overall, we observe subpicosecond Auger decay dynamics in the $6s_h^*6p_e6p_e^*$ excited states of Hg_n^- created by interband *s-p* excitation. These excited states undergo ultrafast nuclear and electronic relaxation prior to electron-hole recombination and Auger decay, over an order of magnitude faster than electronic relaxation in the $6p_e^*$ states created by intraband excitation. Various aspects of the interband dynamics seen here have been invoked to explain relaxation of multiple and/or highly excited electron-hole pairs in semiconductor QDs with E_g comparable to the clusters studied here. It thus appears that Hg_n^- clusters represent a valuable model system for gaining new insights into QD photophysics.

This research was supported by the National Science Foundation under Grant No. CHE-0649647. Additional support was provided by the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, under Grant Nos. 2000-333 and 2004-401. O.T.E. is grateful to the Alexander von Humboldt Foundation (Germany) for the award of a Feodor-Lynen fellowship.

[1] W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos, Science **295**, 2425 (2002).
[2] V. I. Klimov, A. A. Mikhailovsky, D. W. McBranch, C. A. Leatherdale, and M. G. Bawendi, Science **287**, 1011 (2000).
[3] R. D. Schaller, V. M. Agranovich, and V. I. Klimov, Nat. Phys. **1**, 189 (2005).
[4] A. J. Nozik, Chem. Phys. Lett. **457**, 3 (2008).
[5] G. Nair, S. M. Geyer, L. Y. Chang, and M. G. Bawendi, Phys. Rev. B **78**, 125325 (2008).
[6] M. B. Ji, S. Park, S. T. Connor, T. Mokari, Y. Cui, and K. J. Gaffney, Nano Lett. **9**, 1217 (2009).
[7] A. L. Efros, V. A. Kharchenko, and M. Rosen, Solid State Commun. **93**, 301 (1995).
[8] G. Nair and M. G. Bawendi, Phys. Rev. B **76**, 081304 (2007).
[9] A. Pandey and P. Guyot-Sionnest, J. Chem. Phys. **127**, 111104 (2007).
[10] P. Guyot-Sionnest, B. Wehrenberg, and D. Yu, J. Chem. Phys. **123**, 074709 (2005).
[11] A. Pandey and P. Guyot-Sionnest, Science **322**, 929 (2008).
[12] G. M. Pastor and K. H. Bennemann, in *Clusters of Atoms and Molecules*, edited by H. Haberland (Springer-Verlag, Berlin, 1994), p. 86.
[13] B. Issendorff and O. Cheshnovsky, Annu. Rev. Phys. Chem. **56**, 549 (2005).
[14] R. Busani, M. Folkers, and O. Cheshnovsky, Phys. Rev. Lett. **81**, 3836 (1998).
[15] R. Busani, R. Giniger, T. Hippler, and O. Cheshnovsky, Phys. Rev. Lett. **90**, 083401 (2003).
[16] A. Stolow, A. E. Bragg, and D. M. Neumark, Chem. Rev. (Washington, D.C.) **104**, 1719 (2004).
[17] G. B. Griffin, A. Kammrath, O. T. Ehrler, R. M. Young, O. Cheshnovsky, and D. M. Neumark, Chem. Phys. **350**, 69 (2008).
[18] A. V. Davis, R. Wester, A. E. Bragg, and D. M. Neumark, J. Chem. Phys. **118**, 999 (2003).
[19] A. E. Bragg, J. R. R. Verlet, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, J. Chem. Phys. **122**, 054314 (2005).
[20] J. R. R. Verlet, A. E. Bragg, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, J. Chem. Phys. **121**, 10015 (2004).
[21] W. C. Wiley and I. H. McLaren, Rev. Sci. Instrum. **26**, 1150 (1955).
[22] A. T. J. B. Eppink and D. H. Parker, Rev. Sci. Instrum. **68**, 3477 (1997).
[23] V. Dribinski, A. Ossadtchi, V. A. Mandelshtam, and H. Reisler, Rev. Sci. Instrum. **73**, 2634 (2002).
[24] U. Hefter, R. D. Mead, P. A. Schulz, and W. C. Lineberger, Phys. Rev. A **28**, 1429 (1983).
[25] H. Haberland, H. Kornmeier, H. Langosch, M. Oschwald, and G. Tanner, J. Chem. Soc., Faraday Trans. **86**, 2473 (1990).
[26] M. E. Garcia, G. M. Pastor, and K. H. Bennemann, Phys. Rev. Lett. **67**, 1142 (1991).
[27] H. Kitamura, Eur. Phys. J. D **43**, 33 (2007).
[28] C. Brechignac, M. Broyer, P. Cahuzac, G. Delacretaz, P. Labastie, J. P. Wolf, and L. Woste, Phys. Rev. Lett. **60**, 275 (1988).
[29] S. Leutwyler and J. Bosiger, Chem. Rev. (Washington, D.C.) **90**, 489 (1990).
[30] R. S. Berry, J. Chem. Phys. **45**, 1228 (1966).
[31] N. Gaston, P. Schwerdtfeger, and B. von Issendorff, Phys. Rev. A **74**, 043203 (2006).
[32] Y. Wang, H.-J. Flad, and M. Dolg, Int. J. Mass Spectrom. **201**, 197 (2000).