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# Ultrafast Probing of Core Hole Localization in N<sub>2</sub>

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Although valence electrons are clearly delocalized in molecular bonding frameworks, chemists and physicists have long debated the question of whether the core vacancy created in a homonuclear diatomic molecule by absorption of a single x-ray photon is localized on one atom or delocalized over both. We have been able to clarify this question with an experiment that uses Auger electron angular emission patterns from molecular nitrogen after inner-shell ionization as an ultrafast probe of hole localization. The experiment, along with the accompanying theory, shows that observation of symmetry breaking (localization) or preservation (delocalization) depends on how the quantum entangled Bell state created by Auger decay is detected by the measurement.

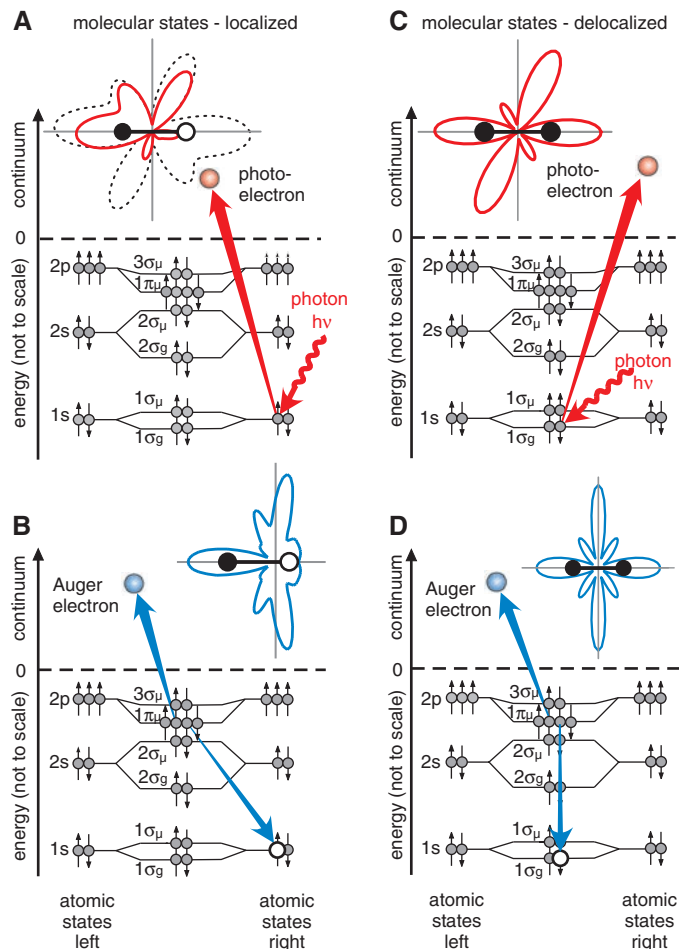
Valence electrons in molecules owe their binding force to their delocalization over two or more sites. By contrast, the orbital density of inner-shell electrons is confined near individual nuclei. The overlap of these wave functions from neighboring atoms is almost negligible (1). Still, the electronic structure of molecules with equivalent sites is generally calculated using symmetry-adapted delocalized wave functions for inner- as well as outer-shell electrons. In N<sub>2</sub>, for example, the spatial distributions of the innermost electrons are usually described by 1σ<sub>g</sub> and 1σ<sub>u</sub> molecular orbitals, which are both delocalized over the two nuclei. For full shells, the quantum mechanical indistinguishability of the electrons renders the question of localization or delocalization meaningless. For a single hole created in an inner shell, however, the question is relevant.

Bagus and Schäfer (2), following a proposal of Snyder (3), found that allowing for a localization of the hole in a Hartree-Fock-type calculation lowers the total energy of the O<sub>2</sub><sup>+</sup>(1s<sup>-1</sup>) ion, yielding better agreement with experiment. However, it is now known that with more accurate approaches than Hartree-Fock, it is always possible to obtain accurate energies without the assumption of localized orbitals (4). Thus, the question of whether a localized hole is formed by photoionization of the K shell is left unanswered by quantum chemistry (5–7). Experimentally, the question is similarly controversial (8).

For K-shell ionization, the latest studies using high-resolution electron spectroscopy seem to support the picture of a delocalized hole. These

experiments resolved the energy splitting between the gerade (g) and ungerade (u) states of the hole (9–11), which was found to be 100 meV

**Fig. 1.** Ultrafast probing of core hole localization by coincident detection of a photoelectron and an Auger electron. **(A and B)** Scenario for the case of a K hole localized at one atom. **(A)** Photoelectron is emitted from the right atom. The red line in the diagram shows the calculated angular distribution for this photoelectron at 9 eV; the light is circularly polarized, propagating into the plane of the figure. The orientation of the molecule is indicated by the barbell. In a standard experiment, where the Auger electron is not detected, one would measure the dotted black angular distribution, which is the sum of the electron emission pattern from the left and right atoms. **(B)** With a time delay of ~7 fs, the core hole decays by emission of an Auger electron (blue). The blue line in the diagram shows the calculated angular distribution of the Auger electron for assumed localization of the hole at the right atom. **(C and D)** Scenario for the case of a delocalized core hole in the 1σ<sub>g</sub> molecular orbital. **(C)** The red line shows a RPA calculation of the photoelectron angular distribution, with electron energy of 9 eV, ejected from the 1σ<sub>g</sub> shell by circularly polarized light. **(D)** Calculated angular distribution of Auger electron from decay of delocalized 1σ<sub>g</sub> hole state. Detecting photoelectrons and Auger electrons in coincidence in the localized scenario reveals broken symmetry, whereas inversion symmetry is preserved in a coincidence experiment for the delocalized scenario.



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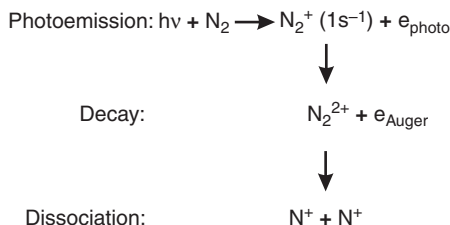
for N<sub>2</sub>. Ehara *et al.* (11) were able to track the photon energy dependence and even the photoelectron angular dependence for the g and u hole states separately, yielding very good agreement with a theory built on symmetry-adapted wave functions (i.e., a delocalized hole). In contrast, recent core hole photoelectron-photoion coincidence experiments on acetylene (HCCH) support the opposite view (12). The photoelectron angular distributions associated with nonsymmetric fragmentation show evidence of a localized core hole.

A puzzling question throughout this discussion is what physical process could possibly be responsible for the apparent break in the inversion symmetry of the system, leading to localization of the electron in the molecule. For molecules such as HCCH with equivalent sites, asymmetric vibrational modes are excited. The vibrational excitation breaks the original symmetry of the molecule and allows a localization of the hole [see, e.g., (13–15)]. For homonuclear diatomics, however, no such asymmetric modes exist and the only remaining means of labeling left

and right sides is by the charge states of the ions created by fragmentation. For  $H_2$  ionization followed by asymmetric dissociation to a neutral H atom and a proton, we have recently shown that the symmetry of the photoelectron can be broken if intermediate doubly excited states are involved (16). The case discussed here is much more fundamental because even the ion charge states are symmetric. The  $N_2$  ultimately fragments into two indistinguishable  $N^+$  ions, both in their electronic ground state. Does this mean that the symmetry must be conserved?

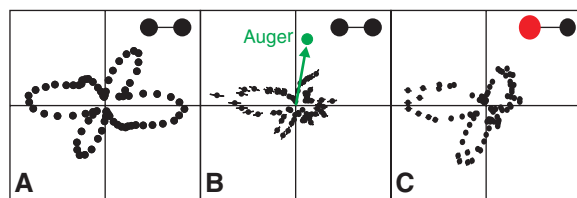
We used a distinct approach to address this question. A core-ionized molecule is not stable. The core hole decays, in many cases by emission of an Auger electron. In the Auger decay, an electron from an outer shell fills the core hole while a second outer-shell electron is emitted, carrying the excess energy. This decay can be thought of as a measurement: The photoabsorption is a pump step, and the Auger decay acts as an ultrafast probe step delayed by the lifetime of the hole (~7 fs). The Auger electron carries information about the hole that was filled. In our coincidence experiment we read out this information.

The experimental idea is sketched in Fig. 1 together with our calculated distributions (see below), assuming either a localized hole (Fig. 1, A and B) or one of the two possible delocalized core holes (Fig. 1, C and D). Clearly, the Auger and photoelectron angular distributions in the body-fixed frame of the molecule are different in the two cases. However, if (as in all previous experiments) the two electrons are not detected in coincidence, then, even with the localized assumption, emission from the left and right atoms would be equally probable, and the experiment would yield a distribution characterized by the inversion symmetry shown by the black dashed line in Fig. 1A (the sum of the red curve and its inverse image). An identical result would be ob-



**Scheme 1.**

**Fig. 2.** Photoelectron angular distribution in the molecular frame for circularly polarized light. The photon propagation direction is into the plane of the figure. The orientation of the molecular axis is indicated by the barbells. The photoelectron energy is 9 eV. (A)  $N_2$  K-shell ionization integrated over all Auger electron angles. (B) Subset of data in (A), where the Auger electron is emitted at  $80^\circ$  to the molecular axis, as indicated by the arrow. (C) Distribution of photoelectrons emitted from the carbon K shell of CO (black end of the barbell).



tained by summing the delocalized  $1\sigma_g$  (Fig. 1, C and D) and  $1\sigma_u$  core hole contributions. By tracking both electrons, however, the localized case might be expected to show an asymmetric pattern for the photoelectron, if the Auger electron is detected (for example) on the left. In contrast, with the delocalized assumption (Fig. 1, C and D), all coincident electron distributions will always show inversion symmetry. In reality, both situations are realized, depending on the angles of the photoelectron and Auger electron emissions. This is possible because of the quantum nature of the two entangled electrons, which form a Bell state.

The photoinduced process can be described more completely as a three-step model (Scheme 1). First, the absorption of a photon ejects a photoelectron from the K shell of  $N_2$ , creating a hole in the  $1s$  shell  $N_2^+(1s^{-1})$ . We directly measure the trajectory of this electron with respect to the molecular axis in our experiment. The energy of the photoelectron (9 eV in this case) is determined by the excess photon energy. Second, the  $N_2^+(1s^{-1})$  decays to  $N_2^{2+}$  by emission of a fast Auger electron (around 370 eV), which is also measured in coincidence. Finally, the  $N_2^{2+}$  dissociates into two  $N^+$  ions with a kinetic energy release (KER) in the region of 4 to 20 eV. The question of core hole localization concerns the character of a short-lived transient state of  $N_2^+(1s^{-1})$ .

Parity describes the behavior of a system's wave function under inversion through the center of the molecule. If the system is in a quantum state of well-defined gerade or ungerade parity, all observables are fully symmetric under inversion, because they are obtained from the squared modulus of the wave function. A hole localized on one of the  $N_2$  atoms implies that the wave function is not a pure symmetry eigenstate but rather a coherent superposition of gerade and ungerade states.

The process we measure begins with the  $N_2$  molecule in its ground state, which has  $1\Sigma_g$  symmetry. After absorption of the photon, simple selection rules dictate that the system consisting of  $N_2^+$  and the photoelectron must have ( $\Sigma$  or  $\Pi$ ) ungerade symmetry. After the Auger decay, the new system consisting of  $N_2^{2+}$ , the photoelectron, and the Auger electron must also have ungerade symmetry, because Auger decay cannot change the overall parity of the system. Auger decay can, however, populate states of  $N_2^{2+}$  of any symmetry or parity. In our data reduction, we

select the decay to the  $1\Sigma_g^+(1\pi_u^{-2})$ ,  $1\Delta_g(1\pi_u^{-2})$ , and  $3\Pi_g(1\pi_u^{-1}, 2\sigma_u^{-1})$  states of  $N_2^{2+}$  for further analysis [see (17) for the assignment of states]. All these states have gerade parity, but the total system must have ungerade parity, as explained above. Consequently, the photoelectron and Auger electron must have opposite parity to each other, one gerade and the other ungerade.

To analyze our findings theoretically, we exploit a two-step model in which we describe the steps of photoionization and subsequent Auger decay by the product of a dipole amplitude  $\langle \Psi_{1\sigma_{g,u}}^+ \psi_{k_p}^- | d | \Psi_0 \rangle$  describing the former, and of a Coulomb matrix element  $\langle \Psi_f^{2+} \psi_{k_a}^- | V | \Psi_{1\sigma_{g,u}}^+ \rangle$  describing the latter. The subscript  $f$  refers to the final state of  $N_2^{2+}$ . We choose gerade and ungerade molecular states  $\Psi_{1\sigma_{g,u}}^+$  for the intermediate, core-ionized singly charged ion, and coherently sum the amplitudes corresponding to these intermediate core hole states before computing the probabilities for producing the various  $N_2^{2+}$  final states.

Using a completely coherent superposition of two pathways to the final state via the  $1\sigma_u^{-1}$  and  $1\sigma_g^{-1}$  intermediate states would be correct only if the two states were energetically degenerate or if the pathways could not be distinguished by the energy of the photoelectron. The core  $g/u$  energy splitting of 100 meV in  $N_2$  (9, 11) is comparable to the natural widths of the  $2\Sigma_g^+(1\sigma_g^{-1})$  and  $2\Sigma_u^+(1\sigma_u^{-1})$  states, which are lifetime-limited. Therefore, the states cannot be fully resolved in principle and their amplitudes must be added coherently. With this assumption, the cross section for coincident detection of a photoelectron into the solid-angle element  $d\Omega_{k_p}$  and an Auger electron into  $d\Omega_{k_a}$  is given by

$$\frac{d\sigma}{d\Omega_{k_a} d\Omega_{k_p}} = \sum_f \left\langle \Psi_f^{2+} \psi_{k_a}^- | V | \Psi_{\sigma_g}^+ \right\rangle \left\langle \Psi_{\sigma_g}^+ \psi_{k_p}^- | d | \Psi_0 \right\rangle + \left\langle \Psi_f^{2+} \psi_{k_a}^- | V | \Psi_{\sigma_u}^+ \right\rangle \left\langle \Psi_{\sigma_u}^+ \psi_{k_p}^- | d | \Psi_0 \right\rangle^2 \quad (1)$$

It is only the interference term between the  $1\sigma_g$  and  $1\sigma_u$  amplitudes in Eq. 1 (the product of the terms being added in the coherent sum) that can break the symmetry of the system, as the individual cross sections are symmetric under inversion.

To simulate the photoionization process and the photoelectron wave function  $\psi_{k_p}^-$ , we applied the random phase approximation (RPA) with relaxation effects included (18, 19). The equations derived by Zähringer *et al.* (20) were used for the calculation of the Auger decay amplitudes (21) into three final  $N_2^{2+}$  states,  $1\Sigma_g^+(1\pi_u^{-2})$ ,  $1\Delta_g(1\pi_u^{-2})$ , and  $3\Pi_g(1\pi_u^{-1}, 2\sigma_u^{-1})$ , which correspond to the experimental KER values. For every final state, the Auger electron wave function  $\psi_{k_a}^-$  was calculated using the Hartree-Fock (HF) approximation in the frozen field of the corresponding doubly charged ion. We note that the contribution from the  $3\Pi_g(1\pi_u^{-1}, 2\sigma_u^{-1})$  state is very small.

The results shown in Fig. 1, C and D, for an assumed delocalized core hole were calculated from the square of the  $1\sigma_g$  amplitudes in Eq. 1. The case of the localized core hole was calculated by a coherent sum of the gerade and ungerade amplitudes with equal weight for the *g* and *u* states. In general, although the calculations provide two different types of distributions (localized and delocalized) for the Auger electron and the photoelectron, the experiment shows that the emission pattern depends on the observation angle of either the Auger electron or the photoelectron.

The experiment was performed at the Advanced Light Source of Lawrence Berkeley

National Laboratory via the cold target recoil ion momentum spectroscopy (COLTRIMS) technique (22, 23). Circularly polarized photons (419 eV) from beamline 11 were intersected with a precooled supersonic beam of  $N_2$  in the vibrational ground state. The photoelectron was guided by parallel electric (12 V/cm) and magnetic (6.5 G) fields toward a multichannel plate detector (diameter 80 mm) with delay-line position readout (24). Those  $N_2^{2+}$  ions that fragmented within  $15^\circ$  parallel to the electric field axis of our spectrometer were guided toward a second position-sensitive detector, 72 cm from the interaction point. From the position of impact and the

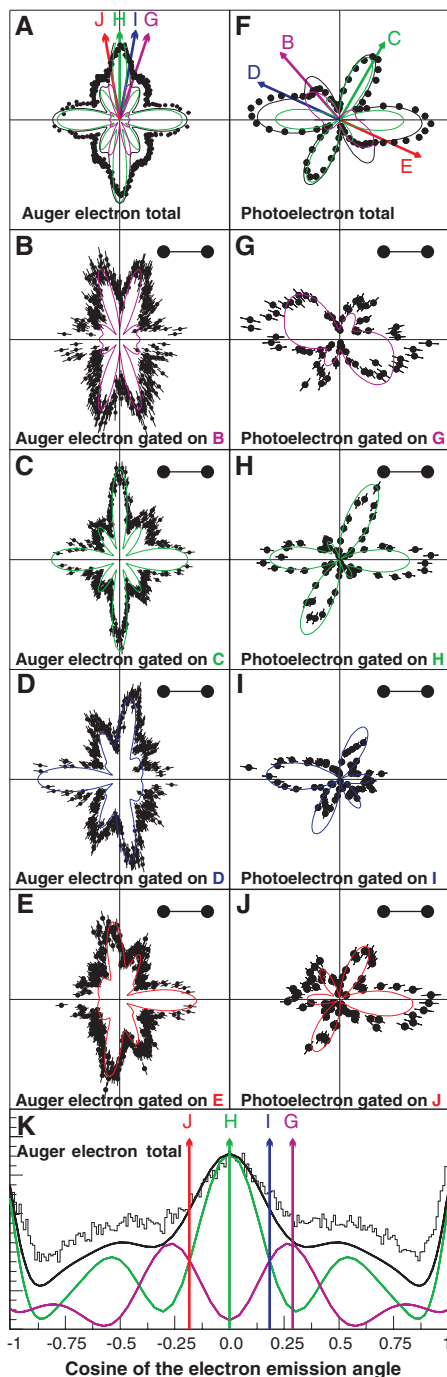
time of flight of the photoelectron and ions, we could determine their vector momenta. To improve the ion momentum resolution, we used a three-dimensional time and space-focusing ion optics setup [see figure 12 in (22)]. Momentum vectors of the photoelectron and the two ions from the four-body final state ( $e_{\text{photo}}$ ,  $e_{\text{Auger}}$ ,  $N^+$ , and  $N^+$ ) were measured directly, whereas the momentum of the fourth particle, the Auger electron, was obtained through momentum conservation.

The experiment yielded the full  $4\pi$  solid angle distribution for the Auger electron and photoelectron and  $\sim 1\%$  solid angle for the ion momentum. We obtained an overall resolution of better than 50 meV for the KER and 0.5 atomic unit momentum resolution on the center of mass motion (the calculated Auger electron). The breakup is known to be much faster than the rotation, so the direction of the  $N^+$  fragments coincides with the direction of the molecule upon photoabsorption (25) [axial recoil approximation (26)]. By coincident measurement of electron and fragmentation direction, we determined the electron angular distributions in the body-fixed frame of the molecule without aligning the gas-phase molecule in advance (27). The data were recorded in list mode, so any combination of angles and energies of the particles could be sorted in the off-line analysis without repeating the experiment. All spectra reported were taken simultaneously with the same apparatus to reduce possible systematic errors.

The coincident detection measurements directly show the localized character of the emission site for certain emission angles of the Auger electron. Figure 2A displays the photoelectron angular distribution for a 9-eV photoelectron ejected by circularly polarized light in the molecular frame. No specific Auger electron direction is selected in this spectrum (noncoincident detection). The data agree very well with similarly measured published data (28). The distribution has inversion symmetry because the  $N^+$  fragments are indistinguishable. However, if we examine a subset of these data in which the Auger electron is emitted at an angle of  $80^\circ$  with respect to the molecular axis, the inversion symmetry of the photoelectron angular distribution is strongly broken (Fig. 2B). These coincident data closely resemble the pattern found for carbon K-shell ionization in CO, shown in Fig. 2C for comparison. CO is isoelectronic with  $N_2$ , and the carbon K shell is selected by the energy. The comparison suggests that in Fig. 2B the K hole in  $N_2$  is localized to the right.

We now show that the results presented in Fig. 2 strongly depend on the choice of direction of the Auger electron. The angular distributions of the Auger electron and photoelectron are shown in Fig. 3, A and F, respectively. In both cases, the corresponding other electron is not detected (integrated over all angles in our case): The experiment thus measures the incoherent sum of the theoretical amplitudes for the gerade and ungerade contributions. Although theoret-

**Fig. 3.** Auger electron and photoelectron angular distributions in the molecular frame for circularly polarized light with an incident energy of  $E_\gamma = 419$  eV. Dots are experimental data; lines represent theory according to Eq. 1. The molecular axis ( $N_2$ ) is shown by the barbell, and the photon propagation direction is into the plane of the figure. (A to E) Auger electron angular distribution; (F to J) photoelectron angular distribution. (A) and (F), non-coincident detection (integrated over the second electron); (B) to (E), Auger electron distributions when photoelectrons are emitted at selected angles as indicated in (F); (G) to (J), photoelectron distributions when Auger electrons are emitted at selected angles as indicated in (A). (K) The same data as in (A), but not in polar form. The pink and green lines represent the *g* and *u* contributions; the black line is the sum.



ically we can perform the full calculation with either localized or delocalized hole states, only the experiment tells unambiguously which description is appropriate. The experimental data allow selection of the theoretical model that adequately describes the observed phenomena. From such noncoincident angular distributions, no information about the character of the core hole can be obtained. The calculated Auger electron angular distribution shows very narrow structures.

The photoelectron angular distributions for four different fixed directions of the Auger electron are shown in Fig. 3, G to J. We find a striking change in these distributions upon small changes in the angle of the coincident Auger electron. If the Auger electron is detected in a direction where, according to the calculations, only the components associated with filling a  $1\sigma_u$  vacancy contribute ( $72.5^\circ$ , Fig. 3A), then the photoelectron shows an angular distribution that coincides with that calculated for the gerade photoelectron. Correspondingly, if the Auger electron is detected around  $90^\circ$  to the molecular axis, where the  $1\sigma_u$  contribution has a node, the photoelectron angular distribution appears dominated by ungerade symmetry. Note that for this particular geometry at  $90^\circ$  to the molecule, our analysis of the symmetry of the Auger electron does not even require a calculation. If we ignore the small contribution from the  $^3\Pi_g(1\pi_u^{-1}, 2\sigma_u^{-1})$  final state, then the node at  $90^\circ$  follows from the properties of an ungerade Auger electron wave of  $\sigma$  or  $\delta$  symmetry. Two waves emerging from a double slit with  $\pi$  phase shift destructively interfere at the center between the slits.

Our results show that if the Auger electron is selected in a direction where only gerade waves contribute, the corresponding photoelectron wave has ungerade parity, and vice versa. Because the photoelectron and the hole states must have opposite parities, knowledge of the photoelectron parity reveals the parity of the hole state, which must be delocalized in this case.

The other extreme is shown in Fig. 3, I and J. Here the Auger electron is selected in directions slightly to the left or the right of  $90^\circ$  to the molecular axis, where, according to the calculations, the g and u components contribute equally. In this case, the photoelectron angular distribution shows the strongly broken symmetry already discussed in connection with Fig. 2. The hole appears localized on the right or left atom, respectively. A change of the Auger angle from  $80^\circ$  to  $100^\circ$  is sufficient to apparently switch the site of the core hole from left to right (Fig. 3, I and J). On the other hand, these angular distributions are correctly reproduced by our calculation using a coherent superposition of the gerade and ungerade hole states in Eq. 1.

In our calculations, we used gerade and ungerade orbitals, but we would obtain equivalent results with left- and right-localized functions. Wave functions in one basis are easily expressed through the wave functions in the other basis. It is the coherent combination of amplitudes, ex-

pressed in either basis, that leads to the observed results. Photoelectron ejection and the subsequent decay create a fully entangled electron pair, which by our measurement we project onto either of these basis states. This is by analogy to an entangled two-photon state, for which measurement of one photon by a horizontal linear polarizer projects the other photon onto a state of vertical polarization; similarly, circular polarizers project onto left and right circular bases.

If we select from all Auger electrons depicted in Fig. 3A only those associated with a photoelectron in a certain direction (indicated by the arrows in Fig. 3F), then measuring the photoelectron in a direction where only gerade photoelectrons contribute projects the Auger electrons onto the ungerade continuum states (Fig. 3B). Correspondingly, selecting a photoelectron direction where only the u state contributes results in a g-type angular distribution of the Auger electron (Fig. 3C). Selecting photoelectron angles where g and u contribute equally projects the Auger electron onto a left (Fig. 3D) or right (Fig. 3E) state.

What conclusion can be drawn with respect to the question of core hole localization? To discuss this question in a quantum mechanically meaningful way, it is first necessary to include the decay, which is an inherent property of the excited molecule. Whether the core hole is better thought of as being localized or delocalized depends on the direction in which the photoelectron or Auger electron is emitted. Detecting the direction of the photoelectron in the experiment selects between cases in which the transient core hole is best described by a delocalized state of g or u symmetry, and other cases for which it is more appropriate to think of a localized hole. This situation can be described by a coherent superposition of gerade and ungerade states, or alternatively by a superposition of states corresponding to a hole on the left and one on the right.

In using a coherent superposition of g/u hole states to analyze our results, we have ignored any physical processes that might destroy this localization. The g/u hole states have a small energy splitting (9, 11), which can be expressed in the time domain as a hopping of a  $1s$  vacancy between the two atoms (3). The 100-meV splitting corresponds to a hopping time from one side to the other of  $\sim 20$  fs. This time is long relative to the  $\sim 7$ -fs lifetime of the hole states, so in most cases the Auger decay takes place before the hole changes sites. Cases where the hopping time and Auger lifetime are comparable would require a time-dependent treatment and invite time-resolved experiments. An example of a time-resolved experiment for a different process was recently reported (29). To date, only the coupling of vacancies to the nuclear degrees of freedom (such as vibrational modes) has been considered in the literature. Our experiment shows that this topic should be revisited while carefully addressing the electronic decay of the states (30).

More generally, we have shown that detecting the signals (electrons in our case) from the

creation and time-delayed decay of vacancies gives insight into the transient structure of extremely short-lived species. This methodology is not limited by the time resolution of the pump and probe pulses. Therefore, it allows us to exploit high-resolution radiation sources such as synchrotrons and future free-electron lasers. The ultrafast time correlation is provided by the short-lived transient species and its decay dynamics. Recent progress in coincidence techniques for electrons from surfaces (31–33) shows that application of this scheme in solid-state physics is within reach.

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