Doppler Splitting of In-Flight Auger Decay of Dissociating Oxygen Molecules: The Localization of Delocalized Core Holes

O. Björneholm, M. Bässler, A. Ausmees, I. Hjelte, R. Feifel, H. Wang, C. Miron, M. N. Piancastelli,* and S. Svensson
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

S. L. Sorensen
Department of Synchrotron Radiation Research, Institute of Physics, Lund University, Box 118, S-221 00 Lund, Sweden

F. Gel'mukhanov and H. Ågren
IFM, Institute of Physics and Measurement Technology, University of Linköping, S-581 83 Linköping, Sweden

(Received 17 May 1999)

By exploiting the core-excitation-induced dissociation of O_2, we find that the Auger emission exhibits a Doppler-like energy shift. We show this to be a manifestation of localization of the core hole and propose that the problem of core-hole localization versus delocalization in core-hole spectroscopies may be resolved by considering the nature of the measurement.

PACS numbers: 33.70.–w, 03.65.Bz, 33.20.Rm

In polyatomic systems, it is customary to group electronic levels as core or valence. Overlapping valence orbitals are delocalized, as is evident for both molecular orbitals and metal conduction bands. The situation is less clear-cut in the case of core levels. At the infancy of core level studies, the core orbitals were considered to be delocalized just as valence orbitals, while early quantum computations indicated that approximate wave functions are unstable towards localization [1]. Polyatomic and diatomic homonuclear species were soon recognized to behave differently, with a physical localization of the core holes being possible through antisymmetric vibronic coupling in the case of polyatomics [2], while this mechanism is absent for homonuclear diatomics, such as O_2. Using third-generation synchrotron radiation facilities for x-ray Raman experiments, the localization problem has been readdressed, and several studies hint at delocalization effects in core holes [3–7]. In particular, resonant x-ray emission or scattering experiments provide evidence that the inversion symmetry selection rule is maintained for x-ray scattering of O_2 and N_2 [3,4]. Although it was shown that the x-ray scattering tensor is invariant with respect to localized and delocalized representations (or to any unitary transformation between these representations), arguments regarding localization were still put forward on the grounds of the role of the measurement itself [8,9]. Thus the x-ray emission experiments on O_2 and N_2 conducted in Refs. [3,4] favored a delocalized representation of the core-hole states. This means that this core-hole state of O_2 cannot be described with only one localized core hole in a nonentangled state; O^*O (* indicates a core excitation), but must be treated as a coherent superposition of the O^*O and OO^* states, an entangled state. The increasing O-O distance upon dissociation does not change this; the pair of fragment atoms must still be described by an entangled state.

X-ray emission is not the dominant decay channel of the core-hole states in low-Z atoms; the majority of the decays take place by an Auger mechanism, in which an electron is emitted. It was recently predicted [10] that large Doppler effects may be apparent for Auger electrons associated with atomiclike peaks [11–17]. Such peaks are attributed to resonant x-ray Raman scattering (RXS) for which ultrafast dissociation along the core-excited state potential leads to Auger decay in one of the dissociation products, as schematically shown in Fig. 1. Such an electronic Doppler shift, $\mathbf{p} \cdot \mathbf{v}$, can exceed the core-hole lifetime width Γ by several times due to a large speed $\mathbf{v}$ of

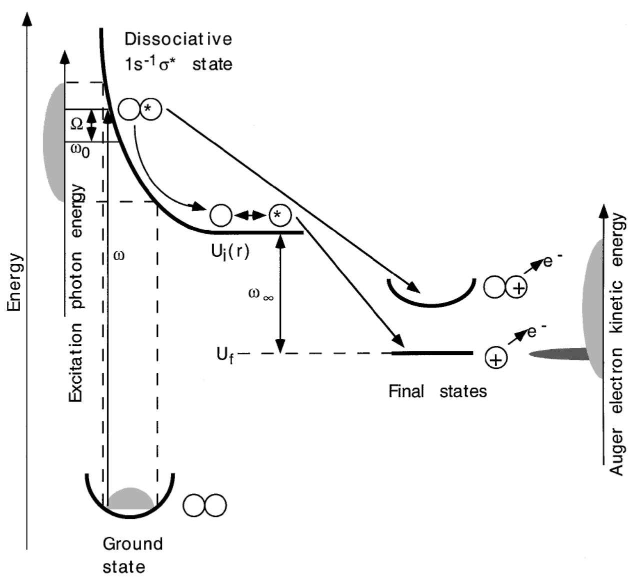

FIG. 1. A schematic representation of the formation of "molecular" and "atomic" contributions to the Auger spectrum by the combined resonant Auger decay and molecular dissociation processes. Some selected quantities used in Eq. (1) are also indicated.

0031-9007/00/84(13)/2826(4)$15.00

the dissociating fragments and a large momentum **p** of the Auger electron.

In the present paper we report new experimental data on the same core-excited state of O_2 as in Ref. [3]. We have observed a Doppler-like splitting of the Auger electron lines from dissociating oxygen molecules. This constitutes a strong argument for a localized description of the core-hole states, in apparent contradiction with the x-ray Raman experiment on O_2, which favored a description with two coherently superposed core holes [3].

The experiments were performed at the new I411 beam line at MAX-LAB in Lund, Sweden [18]. Consistent results have been obtained in two different sets of experiments.

In the experiment, electrons from the $\mathrm{O}1s$ core level of the oxygen molecules were excited to the $3\sigma_u$ (σ^*) level [19,20]. Such a neutral, core-excited intermediate state subsequently undergoes Auger decay, in which a valence electron fills the $\mathrm{O}1s$ hole, and another valence electron, the Auger electron, is expelled from the molecule. This process is very rapid, and the lifetime of the core-excited state is of the order of 3 fs. However, another competing process can take place, namely dissociation of the molecule. The $1s^{-1}3\sigma_u$ state is strongly antibonding, and causes dissociation on the same time scale as the core-hole lifetime [21,22]. As a result of these two parallel and competing processes, the experimentally observed resonant Auger spectrum will contain contributions from decays occurring both in the O_2 molecule and the O atom; see Fig. 1. The Auger decay is faster than the dissociation: the fraction of "atomic" decays has been estimated to be around 10% of all decays [21,22]. Using the core-hole clock model of Ref. [23], this indicates a characteristic dissociation time of 7 fs.

The resonant photoabsorption is orientationally selective [8,24,25]. The resulting partial alignment constitutes a key point for the present experiment. In this case we specifically consider a core excitation to an unoccupied σ molecular orbital by linearly polarized radiation. The transition dipole moment $\mathbf{d}_{io}$ is then parallel to the molecular axis $\mathbf{n}$. The absorption cross section is proportional to $\cos^2\theta$, where θ is the angle between the molecular axis and the polarization vector $\mathbf{e}$. Molecules aligned parallel to the polarization vector $\mathbf{e}$ will thus be preferentially excited [19,26]. This results in the creation of a partially aligned (parallel to $\mathbf{e}$) ensemble of core-excited molecules within the overall random collection of molecules [8,24]. The partial alignment persists sufficiently long, since the Auger decay and dissociation processes occur on a time scale approximately 100× shorter than the period of rotation around the molecular axis. In the excitation step the two oxygen atoms are completely equivalent. The core hole may be created on either of them with equal probability, and the core-excited state has to be treated as a coherent superposition of the $\mathrm{O}^*\mathrm{O}$ and OO^* states.

As discussed, the x-ray emission from the same core-excited state has been used to show that the delocalization persists during the lifetime of the core hole, at least for the "molecular" fraction [3]. What happens when the core-excited molecule dissociates? In Fig. 2 the resonant Auger spectrum recorded using a photon energy corresponding to the $\mathrm{O}1s$ to σ^* absorption maximum is shown, together with an enlargement of the energy interval containing the main Auger transition of O^* atomic fragments. (The other "atomic" Auger lines identified in Refs. [21] and [22] exhibit the same behavior. The present line was selected as it has high intensity and does not overlap with other spectral features.) This spectral feature has been measured with the electron-energy analyzer parallel (0°) and perpendicular (90°) to the polarization direction of the exciting radiation, coinciding with the direction of preferential alignment of the molecules. The 0° spectrum reveals two peaks, separated by 0.75 eV, whereas the 90° spectrum consists of a single peak, situated in between the two 0° peaks (the asymmetry of the 90° peak towards lower kinetic energies is most likely due to Auger decays occurring during the dissociation process; see, for instance, Ref. [27]). The observed behavior can be understood only by assuming localization of the core holes. In the 90° case, the two dissociation directions are symmetric with respect to the measurement direction, and the Doppler effect is not manifested as a splitting. In the 0° case, the two O atoms take off in the direction of the polarization vector. Such a dissociation gives the atom containing the core hole velocity either in the direction towards the analyzer, or away from it, see Fig. 2, resulting in a Doppler shift of the observed kinetic energy.

As a first approximation, it is possible to use a simple classical model, taking into account the angular

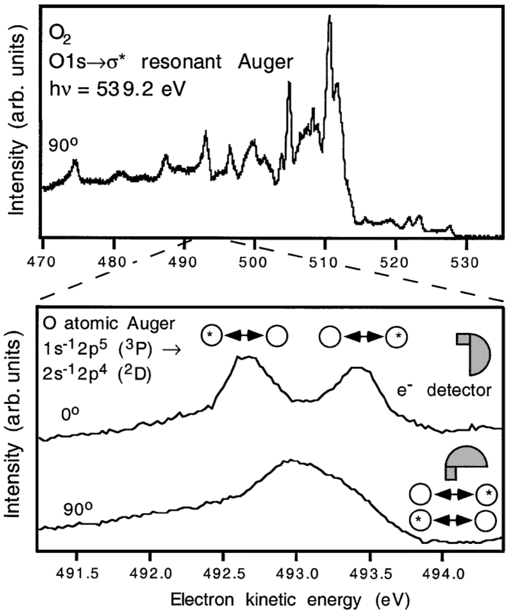

FIG. 2. The Auger lines resulting from the main Auger transition in oxygen atoms following the dissociation of O_2 measured parallel and perpendicular to the polarization direction of the exciting radiation.

dependencies of the excitation probability and the atomic velocity component in the measurement direction, to analyze the results. The experimentally obtained Doppler splitting of 0.75 eV then yields a value of 8 eV for the kinetic-energy release in the core-excitation-induced dissociation, a value which is in excellent agreement with what is expected from calculated potential energy curves [26]. This corresponds to a rate of increase of the O-O distance of 14 km/s or 0.14 Å/fs, which may be compared to the ground state equilibrium interatomic distance of 1.21 Å and the lifetime of the core-excited state, approximately 3 fs. The Doppler splitting may thus be used to obtain detailed information about atomic dynamics on the very low femtosecond time scale.

The description based on classical theory can be given a quantum mechanical treatment within the framework of resonant x-ray scattering, RXS, which also covers the nonradiative Auger decay. When the resonant x-ray scattering process takes place in an oriented homonuclear diatomic molecule, the scattering cross section profile of the atomiclike resonance contains two peaks corresponding to two counterpropagating atoms [10]

$$\sigma(\mathbf{n}) = \sigma_{\mathbf{n},\mathbf{p}} |\mathbf{e} \cdot \mathbf{d}_{io}|^2 \left[\frac{1}{(\Delta E - \mathbf{p} \cdot \mathbf{v})^2 + \Gamma^2} + \frac{1}{(\Delta E + \mathbf{p} \cdot \mathbf{v})^2 + \Gamma^2} \right]. \tag{1}$$

$\Delta E = E - \omega_\infty$ is the Auger electron kinetic energy relative to ω_∞, where $\omega_\infty = U_i(\infty) - U_f(\infty)$ represents the resonant energy of the Auger decay transition $i \rightarrow f$ in the dissociated "atomic" region between the core excited i and final f states. Using $\Delta U = U_i(R_0) - U_i(\infty)$, the kinetic energy release in the dissociation may be written as $\Omega + \Delta U - \Delta E$. Letting μ represent the reduced mass of the two oxygen atoms, the magnitude of the resulting velocity v of each atom in the dissociative region is given by $v = \sqrt{(\Omega + \Delta U - \Delta E)/2\mu}$ (directed along the molecular axis **n**). This speed v depends on the detuning $\Omega = \omega - \omega_0$ of the incident photon frequency ω relative to the resonant frequency of the photoabsorption transition $\omega_0 = U_i(R_0) - E_0$ [10]. Here E_0 is the total energy of the molecule in the ground state, and $U_j(R)$ is the interatomic potential. The anisotropy of RXS due to the Auger decay is included in the prefactor $\sigma_{\mathbf{n},\mathbf{p}}$. The interference of the scattering channels through the core-hole states localized on different atoms is neglected here. This approximation reproduces the gross spectral features of RXS [10].

Equation (1) shows immediately that the RXS spectrum has a double-peak structure

$$\Delta E = \pm p v, \qquad \mathbf{p} \parallel \mathbf{e} \tag{2}$$

when the analyzer selects Auger electrons propagating parallel to **e**. It is easy to see that the Doppler shift is equal to zero, $\mathbf{p} \cdot \mathbf{v} = 0$, when $\mathbf{p} \perp \mathbf{e}$. In this case the RXS profile has a one-peak structure. The distinction between two detector orientations $\mathbf{p} \parallel \mathbf{e}$ and $\mathbf{p} \perp \mathbf{e}$ can thus be used for a direct experimental evidence of the Doppler effect.

The double-peak structure of the RXS profile is an experimental evidence of the core-hole localization on a particular atom. When $\mathbf{p} \parallel \mathbf{v}$, atoms moving in opposite directions $-\mathbf{v}$ and $\mathbf{v}$ will have different "Doppler labels" (Doppler shifts): $-\mathbf{p} \cdot \mathbf{v}$ and $\mathbf{p} \cdot \mathbf{v}$. In this case only the "towards" (or "away") atom is in resonance with the Auger electron, while the partial cross section for the other atom is close to zero [see Eq. (1)]. Thus the "Doppler labels" allow one to select contributions to the RXS cross section from the core-excited state with the core hole localized at a certain atom [10].

When the Auger electron is emitted perpendicular to the molecular axis the RXS profile collapses to a single peak (see Fig. 2), since $\mathbf{p} \cdot \mathbf{v} = 0$. Since the Doppler shift is equal to zero in this case, one cannot distinguish between equivalent atoms in the O_2 molecule. Unaffected by the asymmetric 90° measurement, the entangled molecular $O^*O + OO^*$ state develops into the dissociated but entangled $O^* \leftrightarrow O + O \leftrightarrow O^*$ state.

The asymmetric 0° measurement, on the other hand, violates the symmetry of the partially oriented $O^*O + OO^*$ system and selects only one configuration, O^*O or OO^*, depending on the Auger electron energy and the direction of **p**. The asymmetric measurement process can thus be said to disentangle the state. It is important to stress that the outcome of Eq. (1) does not depend on a choice of representation—localized or delocalized—for the core-excited state. Rather, the change from the entangled to disentangled state representations, with an accompanying destruction of the quantum correlation, must be associated to the special measurement technique employed [28].

Studies of x-ray emission following O1s to σ^* excitation in O_2 showed that selection rules, resulting from core-excited states of g and u symmetry, are maintained [3,9]. In the interpretation, the x-ray emission experiment selects a delocalized representation. This means that this core-hole state of O_2 cannot be described with only one localized core-hole in a nonentangled state; O^*O (* indicates a core excitation), but must be treated as a coherent superposition of the O^*O and OO^* states, an entangled state. Out of an infinite number of representations it is the only one which gives scattering through independent and noninterfering core-excited state channels. This implies a certain coherent superposition of the core holes, at variance with the present case.

The core-hole states can thus exhibit coherent or incoherent behavior, depending upon the type of measurement. How can these two, apparently mutually exclusive, behaviors be described in one model? In a time-independent description of the process, the core hole is delocalized between the atom atoms. This may be described as an entangled $O^*O + OO^*$ state. Even at large internuclear separations, corresponding to a dissociated molecule, the entanglement is maintained, and the state may be described as $O^* \leftrightarrow O + O \leftrightarrow O^*$. This is a consequence of the coherence of the dissociation process producing the atom pair. There is an equal probability of finding it on one atom or the other if the experiment is designed in such a way as to distinguish between the two counterpropagating atoms. This is exactly what the asymmetric 0° measurement does in our case, and the core hole is then localized by the observation of the Doppler-split electron kinetic energies, i.e., it becomes incoherent with the other core hole. The asymmetric measurement process can thus be said to disentangle the $O^* \leftrightarrow O + O \leftrightarrow O^*$ state. Since the two O atoms are indistinguishable in a normal photoemission experiment, there is no way to "label" them, as actually is possible by the observation of a Doppler effect: The opposite Doppler shifts destroy the coherence between the two scattering channels. We thus have an illustration of how the measurement operator can select entangled or disentangled states depending on the nature of the experiment, which makes the core holes appear as either localized or delocalized.

In conclusion, the here-presented Doppler splitting of Auger electron lines not only yields detailed quantitative information about the dissociation dynamics on the very low femtosecond time scale, but also shows the issue of core-hole localization to be more complex, but even more interesting, than hitherto realized. In particular, we consider it another example of the observation, not uncommon in quantum physics, that the measurement itself selects the appropriate physical representation.

This work was supported by the Swedish National Research Council (NFR).

---

*Permanent address: Department of Chemical Sciences and Technologies, University "Tor Vergata," 00133 Rome, Italy.

[1] P. S. Bagus and F. Schaeffer, J. Chem. Phys. **56**, 224 (1972).

[2] W. Domcke and L. S. Cederbaum, Chem. Phys. **25**, 189 (1977).

[3] P. Glans *et al.*, Phys. Rev. Lett. **76**, 2448 (1996).

[4] P. Glans, P. Skytt, K. Gunnelin, J.-H. Guo, and J. Nordgren, J. Electron. Spectrosc. Relat. Phenom. **82**, 193 (1996).

[5] B. Kempgens *et al.*, Phys. Rev. Lett. **79**, 3617 (1997).

[6] T. D. Thomas, L. J. Sæthre, S. L. Sorensen, and S. Svensson, J. Chem. Phys. **109**, 1041 (1998).

[7] T. D. Thomas *et al.*, Phys. Rev. Lett. **82**, 1120 (1999).

[8] F. Gel'mukhanov and H. Ågren, Phys. Rev. A **49**, 4378 (1994).

[9] F. Gel'mukhanov and H. Ågren, J. Electron. Spectrosc. Relat. Phenom. **88**, 29 (1998).

[10] F. Gel'mukhanov, H. Ågren, and P. Sałek, Phys. Rev. A **57**, 2511 (1998).

[11] F. Gel'mukhanov and H. Ågren, Phys. Rev. A **54**, 379 (1996).

[12] E. Kukk *et al.*, Phys. Rev. Lett. **76**, 3100 (1996).

[13] O. Björneholm *et al.*, Phys. Rev. Lett. **79**, 3150 (1997).

[14] S. Tanaka, Y. Kayanuma, and K. Ueda, Phys. Rev. A **57**, 3437 (1998).

[15] Z. W. Gortel, R. Teshima, and D. Menzel, Phys. Rev. A **58**, 1225 (1998).

[16] Z. W. Gortel and D. Menzel, Phys. Rev. A **58**, 3699 (1998).

[17] P. Sałek, F. Gel'mukhanov, and H. Ågren, Phys. Rev. A **59**, 1147 (1999).

[18] M. Bässler *et al.*, J. Electron. Spectrosc. Relat. Phenom. (to be published).

[19] N. Kosugi, E. Shigemasa, and A. Yagishita, Chem. Phys. Lett. **190**, 481 (1992).

[20] M. Neeb, J.-E. Rubensson, M. Biermann, and W. Eberhardt, Phys. Rev. Lett. **71**, 3091 (1993).

[21] S. J. Schaphorst, C. D. Caldwell, M. O. Krause, and J. Jimenez-Mier, Chem. Phys. Lett. **213**, 315 (1993).

[22] C. D. Caldwell, S. J. Schaphorst, M. O. Krause, and J. Jimenez-Mier, J. Electron. Spectrosc. Relat. Phenom. **67**, 243 (1994).

[23] A. Naves de Brito *et al.*, J. Mol. Struct. **394**, 135 (1997).

[24] F. Gel'mukhanov and L. Mazalov, Opt. Spectrosk. **42**, 659 (1977) [Opt. Spectrosc. **42**, 371 (1977)].

[25] R. Mayer, D. W. Lindle, S. H. Southworth, and P. L. Cowan, Phys. Rev. A **43**, 235 (1991).

[26] A. Yagishita, E. Shigemasa, and N. Kosugi, Phys. Rev. Lett. **72**, 3961 (1994).

[27] E. Kukk *et al.*, J. Chem. Phys. **104**, 4475 (1996).

[28] F. Gel'mukhanov and H. Ågren, Pis'ma Zh. Eksp. Teor. Fiz. **67**, 1005 (1998) [JETP Lett. **67**, 1064 (1998)].