

MEASUREMENTS OF CORE HOLE LOCALIZATION IN X-RAY RAMAN SCATTERING

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The problem of core hole localization in symmetrical systems is a fundamental problem of x-ray spectroscopy and concerns some basic aspects of quantum theory. Recent theoretical as well as experimental investigations of resonant x-ray Raman scattering indicate that the solution to this problem depends on the measurement. In the present work we propose an experimental scheme which allows a direct measurement of the atom to which the core hole is localized. The idea behind the proposal is based on the electron Doppler effect and the photoelectron-photoion coincidence technique.

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Despite the success of recent studies of the resonant x-ray Raman scattering (RXS) process [1–3], one of its fundamental problems remains elusive when related to the world of our experience, namely the problem of the core hole localization (CHL) of x-ray excited symmetrical systems. Theory and recent synchrotron radiation experiments have demonstrated a close link between the CHL problem and the problem of quantum measurements. One can argue that a simple answer to the question; *is the core hole localized or not*, is absent by virtue of the fact that it strongly depends on the scheme of measurement. For example, RXS in the soft x-ray region demonstrates strict parity selection rules which has motivated a conclusion of delocalized core holes [4–6]. Due to the strong orientational dephasing these parity selection rules break down in the hard x-ray region [4, 7]. A dephasing takes the quantum superposition into a statistical mixture of the localized core excited states, which is classically meaningful and interpretable. In this case a more adequate physical picture is based on the representation of localized core holes [8, 4]. The results of these two experiments give an example, not uncommon in quantum physics, that the measurements select the appropriate physical representation [9].

The aim of this letter is to suggest alternative experiments that allow a direct measurement of localization of the core hole to one of the core excited state atoms in a diatomic molecule. The idea is based on the Doppler effect; while the ordinary photon Doppler effect in the x-ray region is negligibly small in comparison with the lifetime broadening Γ of the core excited state, the Doppler shift of an Auger electron $k\nu$ is important if the molecule is core excited above the dissociation threshold [10]. Here k and ν are the momentum of the Auger electron and speed of a core excited atom in the dissociative region of the molecular system of reference, respectively. This Doppler shift can exceed Γ by several times when a molecule is core excited above the dissociation threshold.

It is, by now, well established [10–13] that when core excitation takes place above the dissociation threshold the RXS spectral profile consists of a narrow atomic-like resonance and red and blue "molecular" wings, see Fig.1. We consider the atomic-like resonance

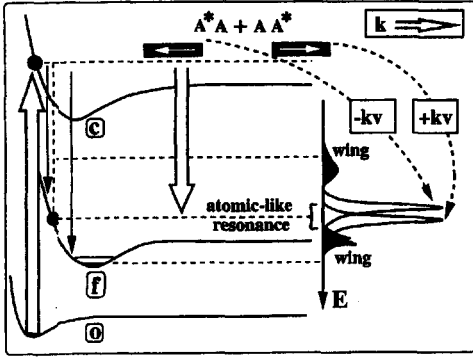


Fig.1. Scheme of the formation of the RXS profile

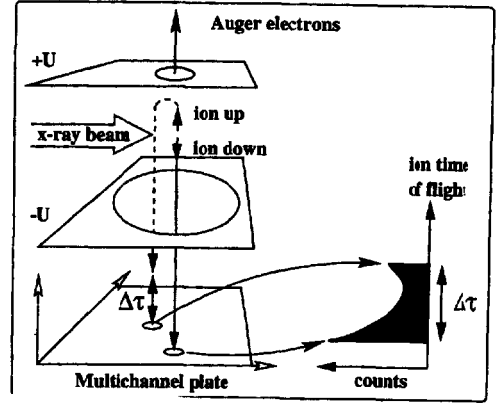


Fig.2. Scheme of PEPICO experiment. The difference of the times of flight of up and down ions is denoted as $\Delta\tau$

which is caused by the decay transitions in the dissociative region where the potentials of the core excited and final states ($U_c(R)$ and $U_f(R)$) are constant. The molecule is core excited by a soft x-ray photon from a gerade ground state to an ungerade core excited state. The wave function of the core excited state in the dissociative region is given by a superposition

$$\Psi_u = \frac{1}{\sqrt{2}}(\Psi(A^*A) - \mathcal{P}\Psi(AA^*)) \quad (1)$$

of the configurations $\Psi(A^*A)$ and $\Psi(AA^*)$ with the core hole on the left and right atoms, respectively. The sign of the factor $\mathcal{P} = \pm 1$ depends on the parities of the atomic orbitals involved in the photoabsorption transition. For more transparency we consider the realistic case when the electron Doppler shift is larger than Γ . In this case the interference of the scattering channels A^*A and AA^* is suppressed and the cross section of an inelastic RXS event with emission of an Auger electron is simply the sum of the two contributions (Fig.1) [10]

$$\sigma_{\mathbf{k}}(\omega, E) = \sigma_{\mathbf{k}}^L(\omega, E) + \sigma_{\mathbf{k}}^R(\omega, E), \quad \sigma_{\mathbf{k}}^{L,R}(\omega, E) \propto \frac{1}{(\Delta E \pm k v)^2 + \Gamma^2}, \quad (2)$$

where $\Delta E = E - \omega_o$, E is the energy of an Auger electron, $k = \sqrt{2E}$, $v \simeq ([U(R_o) - U_c(\infty)]/2m)^{1/2}$, $\omega_o = U_c(\infty) - U_f(\infty)$ is the resonant frequency of the atomic-like resonance caused by decay transitions in the dissociative region. The partial cross sections $\sigma_{\mathbf{k}}^L(\omega, E)$ and $\sigma_{\mathbf{k}}^R(\omega, E)$ (2) correspond to the configurations $\Psi(A^*A)$ and $\Psi(AA^*)$, respectively (Atomic units are used throughout the paper). Due to the Doppler shift $k v$ the directions of propagation of the Auger electron and the ions are strongly correlated when $k v \gg \Gamma$. This means that if the direction of the Auger electron propagation is fixed, the ions propagate in the vicinity of the dissociation cone, $\theta = \pm \arccos(\Delta E/kv)$, where θ is the angle between \mathbf{k} and \mathbf{v} .

We can show how the scattering channel corresponding to the core excited state localized on a certain atom can be selected experimentally. This is possible by means of the PEPICO (photoelectron-photoion coincidence) technique, as used in a scheme [14] shown in Fig.2. A permanent electric field is applied for electron extraction. The detection of

an electron triggers an ion extraction pulse. The impact of an ion on a position-sensitive multichannel plate (MCP) starts a fast decoder system that reads the position. At the same time, the signal goes through a fast multiplexer enabling the detection of two ions in coincidence with an electron. The signals from up and down ions are measured separately due to the delay time of the up ions (Fig.2).

The atom must be light to have a large Doppler shift, so low-Z homonuclear diatomic molecules, like N_2 , O_2 , and F_2 , which can be core excited above dissociation threshold are good candidates. Estimations show that one can expect Doppler shifts of $kv \lesssim 0.5$ eV while $\Gamma \sim 0.1$ eV for these molecules. Such Doppler shifts would be of the same order of magnitude as the spectral resolution for current PEPICO measurements (~ 0.5 eV).

The position of the Auger electron detector at one side of the region of ionization violates the symmetry of the composite system; measurement apparatus + molecule. Such an asymmetric measurement projects the quantum state (1) with an uncertain position of the core hole (Schrödinger-cat-like state: $\Psi_{CAT} = \Psi_{ALIVE} + \Psi_{DEAD}$) into a measurement eigenstate $\Psi(AA^*)$ (or $\Psi(A^*A)$) with a well defined position of the core hole due to the different Doppler labels for the two atoms. To see this directly it is convenient to use PEPICO to measure the difference of the partial cross sections (2)

$$\Delta\sigma_{\mathbf{k}}(\omega, E) = \sigma_{\mathbf{k}}^R(\omega, E) - \sigma_{\mathbf{k}}^L(\omega, E). \quad (3)$$

This function depends antisymmetrically on both the Auger electron energy E and its momentum \mathbf{k} . Figs.1 and 3 show that core excited states with the core hole on the right atom (AA^*) give the main contribution to the signal (3) if the Auger electron energy is equal to $\Delta E = kv$ and vice versa if $\Delta E = -kv$. It is important to note that the averaging of $\Delta\sigma_{\mathbf{k}}(\omega, E)$ over E or over directions of the Auger electron propagation leads to zero, $\overline{\Delta\sigma_{\mathbf{k}}(\omega, E)} = 0$. The difference (3) is equal to zero also when the velocity selectivity is absent (small Doppler effect), $kv \ll \Gamma$. This means that only the PEPICO measurements in the systems with the large electron Doppler shift, $kv \gtrsim \Gamma$, allow to select contributions to the RXS cross section from the core excited state with the core hole localized at a certain atom.

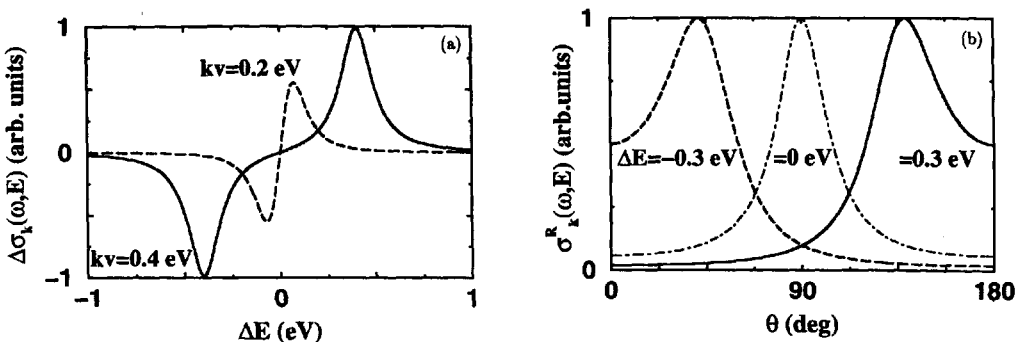


Fig.3. a - The asymmetry of the ion yield (3). The propagation of the Auger electron along the photodissociation axis: $\theta = 0^\circ$. $\Gamma = 0.1$ eV. b - The asymmetry of the Auger electron emission. $kv = 0.4$ eV, $\Gamma = 0.1$ eV

So one can conclude that asymmetric PEPICO measurements with the photoelectron detector at a certain side relative to the ionization region violate the symmetry of the

$A^*A + AA^*$ system and select only one configuration, A^*A or AA^* , depending on the Auger electron energy and the direction of \mathbf{k} . Such an appearance of classicality and of a change from the entangled (1) to disentangled states is caused by the asymmetrical macroscopic measuring apparatus and the electron Doppler effect, which thus destroys the quantum correlation between the localized states A^*A and AA^* .

Eq.(2) and Fig.3b show that the Auger electron preferentially is emitted in the same ($\theta < 90^\circ$) or opposite ($\theta > 90^\circ$) directions as the A^+ ion if $\Delta E > 0$ or $\Delta E < 0$, respectively. This asymmetry is another evidence of the core hole localization on a particular atom.

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