

Supplementary Information for

Recoil-induced ultrafast molecular rotation probed by dynamical rotational Doppler effect

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Supporting Information Text

1. Semiclassical theory of the dynamical rotational Doppler effect

Here we outline the theory of the Auger decay using a classical picture of molecular rotation. The studied Auger process consists of two steps. In the first step the incoming X-ray photon is absorbed by the CO molecule at the instant $t = 0$, and the C 1s electron is ejected with the momentum \mathbf{k} . This is described with the continuum state $\psi_{\mathbf{k}}(\mathbf{r})$ and the molecular core-ionized state $|c\rangle$. Due to the recoil momentum $\mathbf{k}' = -\mathbf{k}$ transferred to the molecule, it starts to rotate with the permanent angular velocity

$$\mathbf{w}_k = \frac{\alpha}{I}[\mathbf{R}(0) \times \mathbf{k}'] = \frac{\alpha}{I}[\mathbf{k} \times \mathbf{R}(0)] = \text{const.} \quad [1]$$

Here $I = \mu R^2$ is the moment of inertia and $\mu = m_C m_O / M$ the reduced mass. The radius vector of the carbon atom with respect to the center of gravity at $t = 0$ is $\mathbf{R}_C(0) = \alpha \mathbf{R}(0)$ with $\alpha = m_O / M$. Due to this recoil-induced rotation, the internuclear radius vector changes orientation and evolves into $\mathbf{R}(t)$ at the instant t of the second step, namely the Auger decay. The wave function of the final state $|\Psi_f\rangle$ can be written as the product of the wave function of the dication, $|f\rangle$, and of the Auger electron with momentum \mathbf{p} , $\psi_{\mathbf{p}}(\mathbf{r})$, namely as

$$|\Psi_f\rangle = |f\rangle \psi_{\mathbf{p}}(\mathbf{r}) \approx |f\rangle \psi_{\mathbf{p}}(\mathbf{r}_C) e^{i\alpha \mathbf{p} \cdot \mathbf{R}(t)}. \quad [2]$$

To obtain the right part of eq. 2 we used the fact that the main contribution to the Auger transition element A_p defined in eq. 4 originates from the region close to the carbon nucleus so that $\psi_{\mathbf{p}}(\mathbf{r}) \approx \psi_{\mathbf{p}}(\mathbf{r}_C) \exp[i\alpha \mathbf{p} \cdot \mathbf{R}(t)]$ with $\mathbf{r}_C = \mathbf{r} - \mathbf{R}_C$, see Ref. (1).

The amplitude of the Auger process is given by the product of the amplitudes of core-ionization $(\mathbf{e} \cdot \hat{\mathbf{k}})F$ and Auger decay A_p (1)

$$(\mathbf{e} \cdot \hat{\mathbf{k}})F A_p, \quad F = -i \int_0^{\infty} e^{i\alpha \mathbf{p} \cdot \mathbf{R}(t)} e^{i(\Delta E + D_{tr} + i\Gamma)t} dt \quad [3]$$

with $\Delta E = E_A - E_{res}$ being the difference between the Auger energy E_A and the resonance energy E_{res} of the C $1s^{-1} \rightarrow d^1 \Sigma^+$ Auger transition, $D_{tr} = \mathbf{k} \cdot \mathbf{p} / M$ being the translational Doppler effect, Γ the core-hole lifetime, \mathbf{e} is the polarization direction of the synchrotron light and $\hat{\mathbf{k}}(t) = \mathbf{k} / k$ the unit vector of the momentum of the photoelectron; note that throughout this work the hat indicates unit vectors. The amplitude of the Auger transition $|c\rangle \rightarrow |f\rangle \psi_{\mathbf{p}}$ is a function of the angle between the momentum \mathbf{p} and the molecular axis which has the following general expansion (2, 3):

$$\begin{aligned} A_p &= \langle f \psi_{\mathbf{p}} | \frac{1}{r_{12}} | c \rangle = \sum_l a_l P_l(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(t)) \\ &= a_0 + a_1(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(t)) + a_2 P_2(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(t)) + a_3 P_3(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(t)) + \dots \end{aligned} \quad [4]$$

The main physics of the studied effect is accounted by the first two terms in this expansion:

$$A_p \approx a_0 \left(1 + \frac{a_1}{a_0} (\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(t)) \right) = 1 + \frac{\eta}{2} (\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(t)) \quad [5]$$

with $a_1/a_0 = \eta/2$ (below we skip the constant prefactor assuming $a_0 = 1$). This equation models in average (see eq. 9 of the main text) the role of the polar anisotropy of A_p in the dynamical rotational Doppler effect studied here. The parameter η describes the polar asymmetry of the Auger angular distribution. We have found this parameter from the fitting of the theoretical spectral profile to the experimental one shown in Fig. 2 of the main text. The use of the approximation (eq. 5) instead of the strict expression (eq. 4) (see Ref. 27 and 28 in the main text) is the main reason of some disagreement between the theory and the experiment. In spite of this, the new physics we report is sufficiently described by this relatively simple model. Obviously the amplitude has to be integrated over all time delays t between the instant of the photoionization process and the Auger decay. To eliminate $\mathbf{R}(t)$ in F we first need to solve the equation of the rotational motion

$$\begin{aligned} \dot{\mathbf{R}}(t) &= \mathbf{w}_k \times \mathbf{R}(t), \\ \mathbf{R}(t) &= \mathbf{R}(0) + \int_0^t [\mathbf{w}_k \times \mathbf{R}(t_1)] dt_1. \end{aligned} \quad [6]$$

With the identity $\mathbf{a} \cdot [\mathbf{b} \times \mathbf{c}] = \mathbf{b} \cdot [\mathbf{c} \times \mathbf{a}]$ we obtain $\alpha \mathbf{p} \cdot [\mathbf{w}_k \times \mathbf{R}(t)] = \mathbf{w}_k \cdot \mathbf{j}_p(t)$ where

$$\mathbf{j}_p(t) = \alpha [\mathbf{R}(t) \times \mathbf{p}] \quad [7]$$

is the recoil angular momentum due to the ejection of the Auger electron. Using eqs. 6 and 7 we can write

$$\begin{aligned} \alpha \mathbf{p} \cdot \mathbf{R}(t) &= \alpha \mathbf{p} \cdot \mathbf{R}(0) + \int_0^t \alpha \mathbf{p} \cdot [\mathbf{w}_k \times \mathbf{R}(t_1)] dt_1 \\ &= \alpha \mathbf{p} \cdot \mathbf{R}(0) + \int_0^t D_{\text{rot}}(t_1) dt_1 \end{aligned} \quad [8]$$

where

$$D_{\text{rot}}(t) = \mathbf{w}_k \cdot \mathbf{j}_p(t) \quad [9]$$

is the rotational Doppler shift (1, 4–6) at the instant of ejection of the Auger electron. With eq. 8 we can finally rewrite F as

$$F = -i e^{i\alpha\mathbf{p}\cdot\mathbf{R}(0)} \int_0^\infty e^{i \int_0^t D_{\text{rot}}(t_1) dt_1} e^{i(\Delta E + D_{\text{tr}} + i\Gamma)t} dt. \quad [10]$$

For simplicity this equation is used in the following as well as in the main text without the constant prefactor $i e^{i\alpha\mathbf{p}\cdot\mathbf{R}(0)}$.

To proceed further, we shall solve eq. 6 and obtain

$$\hat{\mathbf{R}}(t) = \mathbf{R}(t)/R = \hat{\mathbf{R}}(0) \cos(w_k t) + \hat{\mathbf{R}}_\perp \sin(w_k t) \approx \hat{\mathbf{R}}(0) + \hat{\mathbf{R}}_\perp w_k t, \quad [11]$$

where the unit vector $\hat{\mathbf{R}}_\perp = (\hat{\mathbf{w}}_k \times \hat{\mathbf{R}}(0))$ is orthogonal to $\hat{\mathbf{R}}(0)$, i.e. the molecular axis rotates in full agreement with the expectations with the constant angular velocity given in eq. 1. Throughout this work we use the linear over time approximation for $\hat{\mathbf{R}}(t)$, because the molecule has no time to perform a full rotation during the effective time of the process. This can be seen by the fact that even for the highest photon energy used in this work ($\omega = 12$ keV) we obtain

$$w_k \tau \leq 0.2 \ll 1, \quad [12]$$

where $\tau = 7.5$ fs is the lifetime of the C 1s core-ionized state so that it represents the typical timescale for the instant t of the Auger decay. The solution given by eq. 11 results in the following expression for the rotational Doppler shift:

$$D_{\text{rot}}(t) = \mathbf{w}_k \cdot \mathbf{j}_p(t) \approx D_{\text{rot},0} - \rho (\hat{\mathbf{R}}(0) \times \hat{\mathbf{k}})^2 (\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0))t, \quad [13]$$

$$\rho = \frac{\alpha^3 R^3 k^2 p}{I^2}.$$

Here $D_{\text{rot},0}$ describes the rotational Doppler shift at the instant $t = 0$. The parameter ρ is proportional to k^2 and, therefore, to the kinetic energy of the photoelectron and it defines the magnitude of the asymmetric contribution $\sigma_{\text{int}}(E)$ to the total cross section $\sigma(E)$, see eq. 16 below. Now we are at the position of finding the cross section and the Auger amplitude in the limit of our interests which are defined by eq. 12

$$\sigma(\Delta E) = \langle |(\mathbf{e} \cdot \hat{\mathbf{k}}) F A_p|^2 \rangle = \left\langle \left(1 + \zeta P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{p}}) \right) |F|^2 \left(1 + \eta(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0)) \right) \right\rangle,$$

$$F \approx -i \int_0^\infty dt e^{i[\Delta E + D_{\text{tr}} + D_{\text{rot},0} + i\Gamma]t} \left(1 - i \frac{\rho}{2} (\hat{\mathbf{R}}(0) \times \hat{\mathbf{k}})^2 (\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0))t^2 \right)$$

$$= F_0 + F_d, \quad [14]$$

where $\langle \dots \rangle \equiv \int \dots d\hat{\mathbf{k}} d\hat{\mathbf{R}}(0)$. Note that for $\sigma(\Delta E)$ the following approximations are made: First we replaced $(\mathbf{e} \cdot \hat{\mathbf{k}})^2$ by $1 + \zeta P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{p}})$ according to eq. 22, but neglect the constant factor $\frac{1}{3}(1 - \cos \chi)$ given in that equation. Second, in A_p the vector $\hat{\mathbf{R}}(t)$ is replaced by $\hat{\mathbf{R}}(0)$ since in the course of our experiments the molecule does not rotate more than 11° , see eq. 11 and 12. Third, in $|A_p|^2$ the term proportional to η^2 is neglected. The first and the second terms in the integrand of F give the "instantaneous" (F_0) and the "time-delayed" or "dynamical" (F_d) contribution, respectively, which can be expressed in the time-independent picture as

$$F_0 = \frac{1}{\Delta E + D_{\text{tr}} + D_{\text{rot},0} + i\Gamma}, \quad [15]$$

$$F_d = \frac{i\rho (\hat{\mathbf{R}}(0) \times \hat{\mathbf{k}})^2 (\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0))}{[\Delta E + D_{\text{tr}} + D_{\text{rot},0} + i\Gamma]^3}.$$

Taking into account that $|F|^2 \approx |F_0|^2 + 2\text{Re}(F_0 F_d^*)$ within the used approximation (12) one can see that the cross section $\sigma(\Delta E)$ consist of two parts:

$$\sigma(\Delta E) = \sigma_0(\Delta E) + \eta \sigma_{\text{int}}(\Delta E),$$

$$\sigma_0(\Delta E) = \left\langle \frac{1 + \zeta P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{p}})}{(\Delta E + D_{\text{tr}} + D_{\text{rot},0})^2 + \Gamma^2} \right\rangle, \quad [16]$$

$$\sigma_{\text{int}}(\Delta E) = 4\rho\Gamma \left\langle \frac{(\Delta E + D_{\text{tr}} + D_{\text{rot},0})f}{[(\Delta E + D_{\text{tr}} + D_{\text{rot},0})^2 + \Gamma^2]^3} \right\rangle,$$

where $f = [1 + \zeta P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{p}})](\hat{\mathbf{R}}(0) \times \hat{\mathbf{k}})^2 (\hat{\mathbf{R}}(0) \cdot \hat{\mathbf{p}})^2$ is the product of $(\mathbf{e} \cdot \hat{\mathbf{k}})^2$, $|A_p|^2$ and the squares of the denominator of $\text{Re}(F_0 F_d^*)$.

Note that the integrands of $\sigma_0(\Delta E)$ and $\sigma_{\text{int}}(\Delta E)$ depend implicitly on $\hat{\mathbf{k}}$ and $\hat{\mathbf{R}}(0)$ because of D_{tr} and $D_{\text{rot},0}$. Taking into account that the integrand in $\sigma_0(\Delta E)$ does not change under transformation $\Delta E, \hat{\mathbf{k}} \rightarrow -\Delta E, -\hat{\mathbf{k}}$, while the integrand in $\sigma_{\text{int}}(\Delta E)$ changes sign, we get the following symmetry properties

$$\sigma_0(\Delta E) = \sigma_0(-\Delta E), \quad \sigma_{\text{int}}(\Delta E) = -\sigma_{\text{int}}(-\Delta E). \quad [17]$$

As can be seen in eqs. 16 and 17 the dynamics of the rotational Doppler shift results in an additional contribution $\sigma_{\text{int}}(\Delta E)$ which is an antisymmetric function of ΔE . Thus the interference between the "instantaneous" and "time-delayed" Auger channels is responsible for the observed asymmetry of the Auger spectral profile.

2. Anisotropy parameter

The Auger process depends on the angle between \mathbf{e} and \mathbf{p} . Therefore one can average the ionization probability $P_{\mathbf{k}} = (\mathbf{e} \cdot \hat{\mathbf{k}})^2$ over orientations of \mathbf{e} around the momentum of the Auger electron \mathbf{p} with fixed angle $\chi = \angle(\mathbf{e}, \mathbf{p})$. Using equation

$$\overline{e_i^* e_j} = \frac{1}{2} (\delta_{ij}(1 - \cos^2 \chi) + (3 \cos^2 \chi - 1)\hat{p}_i \hat{p}_j), \quad [18]$$

we obtain

$$P_{\mathbf{k}} = \overline{(\mathbf{e} \cdot \hat{\mathbf{k}})^2} = \frac{1}{2} (1 - \cos^2 \chi + (3 \cos^2 \chi - 1)(\hat{\mathbf{p}} \cdot \hat{\mathbf{k}})^2). \quad [19]$$

In our experiment the momentum of the Auger electron \mathbf{p} is parallel to \mathbf{e} only approximately. Namely, the Auger electrons are collected in a cone around the polarization vector \mathbf{e} with the opening angle $2\chi = 45^\circ$. Therefore the probability $P_{\mathbf{k}}$ should be integrated in this range

$$\frac{1}{2} \int_0^\chi d\chi' \sin \chi' (1 - \cos^2 \chi' + (3 \cos^2 \chi' - 1)(\hat{\mathbf{p}} \cdot \hat{\mathbf{k}})^2) = \frac{1}{3} (1 - \cos \chi) (1 + \zeta P_2(\hat{\mathbf{p}} \cdot \hat{\mathbf{k}})), \quad [20]$$

where $P_2(\hat{\mathbf{p}} \cdot \hat{\mathbf{k}})$ is the Legendre polynomial and

$$\zeta = \cos \chi (1 + \cos \chi) \approx 1.78 \quad [21]$$

is the anisotropy parameter. In our simulations the unimportant prefactor $(1 - \cos \chi)/3$ is dropped and we use the following equation for the ionization probability

$$P_{\mathbf{k}} = 1 + \zeta P_2(\hat{\mathbf{p}} \cdot \hat{\mathbf{k}}). \quad [22]$$

3. Role of the anisotropy of photoionization

In the previous sections, we described the photoionization process using the plane-wave approximation for the fast photoelectron. In this case, the transition dipole moment \mathbf{d} for the ionization of a C 1s electron is parallel to the momentum of the photoelectron, i.e. $\mathbf{d} \propto \mathbf{k}$. The ionization probability $P_{\mathbf{k}}$ depends quadratically on $(\hat{\mathbf{p}} \cdot \hat{\mathbf{k}})$ (see eqs. 19 and 22). In principle, a term linear in $(\hat{\mathbf{p}} \cdot \hat{\mathbf{k}})$ can also contribute to $P_{\mathbf{k}}$, due to scattering of the fast electron by the oxygen atom. To describe the latter effect, we have to go beyond the plane wave approximation. Since the momentum of the photoelectron is large

$$kR \sim 50 \gg 1, \quad [23]$$

it is sufficient to take only the single scattering correction to the plane wave (7) into account. Within this approximation, the wavefunction near the core-ionized n -th atom

$$\begin{aligned} \psi_{\mathbf{k}} &= \sum_{lm} B_{lm}^{(n)} R_l(r_n) Y_{lm}(\hat{\mathbf{r}}_n), \\ B_{lm}^{(n)} &\approx 4\pi i^l \left[e^{i\mathbf{k} \cdot \mathbf{R}_n} Y_{lm}(\hat{\mathbf{k}}) + \sum_{n'(\neq n)} \frac{e^{ikR_{nn'}}}{R_{nn'}} Y_{lm}(\hat{\mathbf{R}}_{nn'}) e^{i\mathbf{k} \cdot \mathbf{R}_{n'}} f_{n'}(\hat{\mathbf{R}}_{nn'} \cdot \hat{\mathbf{k}}) \right] \end{aligned} \quad [24]$$

consists of the plane-wave contribution as well as the scattering contributions from the surrounding atoms ($n' \neq n$). Here, \mathbf{r}_n is the radius vector of the electron with respect to the center n , \mathbf{R}_n the radius vector of the n -th atom, and $R_l(r_n)$ the solution of the radial Schrödinger equation near the n -th atom. The amplitude $f_{n'}(\hat{\mathbf{R}}_{nn'} \cdot \hat{\mathbf{k}})$ for the scattering of the electron by the n' -th atom depends on the angle between the momentum \mathbf{k} and the radius vector between the n -th and n' -th atoms, $\mathbf{R}_{nn'} = \mathbf{R}_n - \mathbf{R}_{n'}$.

For the present case of C 1s ionization of the CO molecule, only the p-wave ($l = 1$) contributes to the transition dipole moment \mathbf{d} and the amplitude of the photoionization process ($\mathbf{e} \cdot \mathbf{d}$)

$$\begin{aligned} \mathbf{d} &\propto \hat{\mathbf{k}} + \hat{\mathbf{R}}(0) \frac{e^{i(kR - \mathbf{k} \cdot \mathbf{R}(0))}}{R} f_o(\hat{\mathbf{k}} \cdot \hat{\mathbf{R}}(0)), \\ (\mathbf{e} \cdot \mathbf{d}) &\propto (\mathbf{e} \cdot \hat{\mathbf{k}}) + (\mathbf{e} \cdot \hat{\mathbf{R}}(0)) \frac{e^{i(kR - \mathbf{k} \cdot \mathbf{R}(0))}}{R} f_o(\hat{\mathbf{k}} \cdot \hat{\mathbf{R}}(0)), \end{aligned} \quad [25]$$

where $\mathbf{R}(0) = \mathbf{R}_C(0) - \mathbf{R}_O(0)$ is the internuclear axis at the time of the photoionization, see above, and $f_o(\hat{\mathbf{k}} \cdot \hat{\mathbf{R}}(0))$ the amplitude for the scattering process of electron by oxygen atom. Using eq. 18 we obtain

$$\begin{aligned} (\mathbf{e} \cdot \hat{\mathbf{d}})^2 &\approx \frac{1}{2} \left[1 - \cos^2 \chi + (3 \cos^2 \chi - 1)(\hat{\mathbf{k}} \cdot \hat{\mathbf{p}})^2 \right. \\ &\left. + \left((1 - \cos^2 \chi)(\hat{\mathbf{k}} \cdot \hat{\mathbf{R}}(0)) + (3 \cos^2 \chi - 1)(\hat{\mathbf{k}} \cdot \hat{\mathbf{p}})(\hat{\mathbf{R}}(0) \cdot \hat{\mathbf{p}}) \right) 2\text{Re} \left(\frac{e^{i(kR - \mathbf{k} \cdot \mathbf{R}(0))}}{R} f_o(\hat{\mathbf{k}} \cdot \hat{\mathbf{R}}(0)) \right) \right], \end{aligned} \quad [26]$$

In the next step we shall average the cross section over all molecular orientations $\hat{\mathbf{R}}(0)$. It is important to notice that the scattering contribution $\propto \exp(-i\mathbf{k} \cdot \mathbf{R}(0))$ experiences fast oscillations due to the large values for kR (see eq. 23). The fact that $kR \sim 50 \gg 1$ allows performing the integration over $\hat{\mathbf{R}}(0)$ of the scattering term $\propto f_o(\hat{\mathbf{k}} \cdot \hat{\mathbf{R}}(0))$ using the following asymptotic formula

$$\frac{1}{4\pi} \int e^{-i\mathbf{k} \cdot \mathbf{R}(0)} \Phi(\hat{\mathbf{R}}(0)) d\hat{\mathbf{R}}(0) \approx \frac{1}{2ikR} (e^{i kR} \Phi(-\hat{\mathbf{k}}) - e^{-i kR} \Phi(\hat{\mathbf{k}})). \quad [27]$$

According to this equation, both the forward scattering ($\mathbf{R}(0) \uparrow \uparrow \mathbf{k}$) and the backward scattering ($\mathbf{R}(0) \uparrow \downarrow \mathbf{k}$) contribute to the cross section. In the following we will only take the forward scattering into account since in the high-energy region $|f_o[\pi]| \ll |f_o[0]|$, where $f_o[\theta]$ is the scattering amplitude for the angle θ . With this approximation and the factorization of the cross section $\sigma(\hat{\mathbf{R}}(0))$ of a fixed-in-space molecule, see the integrand in eq. 3 of the main article, namely with

$$\begin{aligned} \sigma(\hat{\mathbf{R}}(0)) &= \overline{(\mathbf{e} \cdot \hat{\mathbf{d}})^2} \sigma_{\text{Auger}}(\hat{\mathbf{R}}(0)), \\ \sigma_{\text{Auger}}(\hat{\mathbf{R}}(0)) &= |F|^2 Q_{\mathbf{p}} = |F|^2 (1 + \eta(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0))) \end{aligned} \quad [28]$$

we obtain

$$\begin{aligned} \sigma &= \frac{1}{4\pi} \int \sigma(\hat{\mathbf{R}}(0)) d\hat{\mathbf{R}}(0) = \frac{1}{4\pi} \int \overline{(\mathbf{e} \cdot \hat{\mathbf{d}})^2} \sigma_{\text{Auger}}(\hat{\mathbf{R}}(0)) d\hat{\mathbf{R}}(0) \\ &\approx P_{\mathbf{k}} \left\{ \frac{1}{4\pi} \int \sigma_{\text{Auger}}(\hat{\mathbf{R}}(0)) d\hat{\mathbf{R}}(0) - \frac{\text{Im}(f_o[0])}{kR^2} \sigma_{\text{Auger}}(\hat{\mathbf{k}}) \right\}. \\ &= P_{\mathbf{k}} \left\{ \frac{1}{4\pi} \int \sigma_{\text{Auger}}(\hat{\mathbf{R}}(0)) d\hat{\mathbf{R}}(0) - \frac{\sigma_{\text{tot}}}{4\pi R^2} \sigma_{\text{Auger}}(\hat{\mathbf{k}}) \right\}. \end{aligned} \quad [29]$$

Here σ_{tot} is the total cross section of scattering of an electron by the oxygen atom. The quantity $P_{\mathbf{k}}$ is defined in eqs. 19 and 22 and $f_o[0]$ is the forward scattering amplitude. From this equation, we can readily see that the photoionization does not cause any extra angular contribution to the total cross section such as a term linear in $(\hat{\mathbf{k}} \cdot \hat{\mathbf{p}})$. Indeed, $P_{\mathbf{k}}$ depends quadratically on $(\hat{\mathbf{k}} \cdot \hat{\mathbf{p}})$ and the rotational Doppler shift is absent in the scattering term because $D_{\text{rot}} \propto [\mathbf{k} \times \mathbf{R}(0)] \equiv 0$ for $\mathbf{k} \parallel \mathbf{R}(0)$.

Note that the scattering anisotropy of the photoionization, see eq. 14, does not affect the dynamical contribution $(\nu_{\rho}(\hat{\mathbf{R}}(0) \times \hat{\mathbf{k}})^2 (\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0)) t^2)$ because it equals zero due to $\mathbf{R}(0) \parallel \mathbf{k}$. To conclude, the anisotropy of photoionization does not create an asymmetry of the Auger profile.

4. Quantum theory

The numerical simulations were performed using strict quantum theory of rotational motion characterized by the rotational energies $E_J = J(J+1)/2I$ of the rotational states $|JM\rangle$. The amplitude of the Auger process subsequent to the core ionization

$$\mathcal{F} = \sum_{JM} \frac{\langle J_0 M_0 | (\mathbf{e} \cdot \hat{\mathbf{k}}) e^{i\alpha \mathbf{k} \cdot \mathbf{R}} | JM \rangle \langle JM | A_p e^{i\alpha \mathbf{p} \cdot \mathbf{R}} | J_f M_f \rangle}{\Delta E + D_{\text{tr}} - (E_J - E_{J_f}) + i\Gamma} \quad [30]$$

is defined by the matrix element of transition from the initial rotational state $|J_0 M_0\rangle$ to the rotational state $|JM\rangle$ of the core-excited state and by the matrix element of the transition from the rotational state $|JM\rangle$ to the final rotational state $|J_f M_f\rangle$. It is important to notice that the sum over the intermediate rotational states $|JM\rangle$ results in the interference contributions similar to that of the lifetime vibrational interference (8, 9). This interference in the energy domain is equivalent to the dynamics and interference in the time domain (8, 9) as we will see also below. Since the ejection of the fast photoelectron heats the CO molecule up to an effective rotational temperature of 4000 K we can neglect the initial room temperature and assume $J_0 = M_0 = 0$.

To find the Auger amplitude, we need the equation, see Ref. (10),

$$e^{i\alpha \mathbf{k} \cdot \mathbf{R}} = 4\pi \sum_{lm} i^l j_l(\alpha k R) Y_{lm}^*(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{R}}). \quad [31]$$

Using the quantum theory of angular momentum (10) and the sum rule

$$\begin{aligned} &\sum_{M_f} C_{j_1 0 J_f M_f}^{J M_f} C_{j'_1 0 J_f M_f}^{J' M_f} Y_{J' M_f}^*(\hat{\mathbf{k}}) Y_{J M_f}(\hat{\mathbf{k}}) \\ &= (-1)^{J_f} \frac{1}{4\pi} (2J' + 1)(2J + 1) \sum_l C_{J' 0 J_0}^{l 0} C_{j_1 0 j'_1 0}^{l 0} \left\{ \begin{matrix} J_f & J & j_1 \\ l & j'_1 & J' \end{matrix} \right\} P_l(\cos \theta) \end{aligned} \quad [32]$$

one can obtain the following expression for the cross section of the studied Auger process:

$$\begin{aligned}\sigma &= \sum_{J_f M_f} |\mathcal{F}|^2 d\hat{\mathbf{k}} = \sigma_0 + \eta\sigma_{\text{int}}, \\ \sigma_0 &= \sigma^{(0)} + \zeta\sigma^{(2)}, \quad \sigma_{\text{int}} = \sigma_{\text{int}}^{(0)} + \zeta\sigma_{\text{int}}^{(2)},\end{aligned}\tag{33}$$

where

$$\begin{aligned}\sigma^{(n)} &= \sum_{j_1, j_1'} \sum_{J, J'=0} \sum_{J_f, \ell} (-1)^{J_f} \cos\left(\frac{\pi}{2}[J + j_1 - (j_1' + J')]\right) j_J(\alpha k R) j_{J'}(\alpha k R) j_{j_1}(\alpha p R) j_{j_1'}(\alpha p R) \\ &\times (2j_1 + 1)(2j_1' + 1)(2J_f + 1) \sqrt{(2J + 1)(2J' + 1)} C_{j_1 0 J_f 0}^{J 0} C_{j_1' 0 J_f 0}^{J' 0} \\ &\times C_{J' 0 J 0}^{\ell 0} C_{j_1 0 j_1' 0}^{\ell 0} \left\{ \begin{matrix} J_f J j_1 \\ \ell j_1' J' \end{matrix} \right\} \int_0^\pi d\theta \sin\theta P_\ell(\cos\theta) P_n(\cos\theta) \text{Re}(z_{J, J_f} z_{J', J_f}^*), \\ \sigma_{\text{int}}^{(n)} &= - \sum_{j_1, j_1'} \sum_{J, J'=0} \sum_{L, J_f, \ell} (-1)^{J_f} j_J(\alpha k R) j_{J'}(\alpha k R) j_{j_1}(\alpha p R) j_{j_1'}(\alpha p R) \\ &\times (2j_1 + 1)(2j_1' + 1)(2J_f + 1) \sqrt{(2J + 1)(2J' + 1)} \\ &\times \cos\left(\frac{\pi}{2}[J + L - (j_1' + J')]\right) \sin\left(\frac{\pi}{2}(j_1 - L)\right) (C_{j_1 0 1 0}^{L 0})^2 C_{L 0 J_f 0}^{J 0} C_{j_1' 0 J_f 0}^{J' 0} \\ &\times C_{J' 0 J 0}^{\ell 0} C_{L 0 j_1' 0}^{\ell 0} \left\{ \begin{matrix} J_f J L \\ \ell j_1' J' \end{matrix} \right\} \int_0^\pi d\theta \sin\theta P_\ell(\cos\theta) P_n(\cos\theta) \text{Im}(z_{J, J_f} z_{J', J_f}^*).\end{aligned}\tag{34}$$

Here $n = 0, 2$, $u = k/M$ is the translational recoil velocity, the symbols with curly brackets are 6j-symbols, and

$$\begin{aligned}z_{J, J_f} &= \frac{1}{\Delta E + pu \cos\theta - (E_J - E_{J_f}) - i\Gamma}, \\ \text{Re}(z_{J, J_f} z_{J', J_f}^*) &= \frac{[E + pu \cos\theta - (E_J - E_{J_f})][E + pu \cos\theta - (E_{J'} - E_{J_f})] + \Gamma^2}{\{[E + pu \cos\theta - (E_J - E_{J_f})]^2 + \Gamma^2\} \{[E + pu \cos\theta - (E_{J'} - E_{J_f})]^2 + \Gamma^2\}}, \\ \text{Im}(z_{J, J_f} z_{J', J_f}^*) &= \frac{\Gamma(E_J - E_{J'})}{\{[E + pu \cos\theta - (E_J - E_{J_f})]^2 + \Gamma^2\} \{[E + pu \cos\theta - (E_{J'} - E_{J_f})]^2 + \Gamma^2\}}.\end{aligned}\tag{35}$$

The two terms $\sigma^{(0)}$ and $\zeta\sigma^{(2)}$ of eq. 33 are shown in Fig. S1. They possess a symmetric profile and describe the broadening of the Auger line due to the translational and rotational Doppler effects. The term $\zeta\sigma^{(2)}$ is caused by the anisotropy of the core ionization $\zeta P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{p}})$, see eq. 22. This term has a dip around $\Delta E = 0$ and is responsible for the Doppler splitting of the Auger profile (see Figure 2a and Figure 4a of the main article).

The term

$$\eta\sigma_{\text{int}} = \eta(\sigma_{\text{int}}^{(0)} + \zeta\sigma_{\text{int}}^{(2)})\tag{36}$$

of eq. 33 is caused by the interference between intermediate rotational levels of the core-ionized state. This can be seen by the fact that it is absent for the case of only one rotational level J in the core-ionized state. In this case holds $J = J'$ and $\text{Im}(z_{J, J_f} z_{J', J_f}^*) \equiv 0$ so that $\eta\sigma_{\text{int}}$ vanishes, see eq. 34. It is important to notice that this term is proportional to η and exists only because of the anisotropic contribution $(\eta/2)(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}})$ to the Auger transition matrix element A_p as given in eq. 5. The interference contribution described by eq. 36 has an antisymmetric dependence on ΔE , see Fig. S1b, since the interference of the rotational levels is equivalent to the dynamics in the time domain (dynamical rotational Doppler effect). This is in nice agreement with the semiclassical theory, see eqs. 16 and 17 above.

Finally we shall point out the strong correlation of the rotational and translational motions via rotational and translational Doppler effect. For this purpose we display in Fig. S1 the individual contributions to eq. 33 once by taking the translational Doppler effect fully into account (solid lines) and once by neglecting it (dashed lines), i.e. using in eq. 35 $pu \rightarrow 0$. As the most obvious difference we see that $\sigma_{\text{int}}^{(0)} = 0$ when the translational Doppler shift is absent. The reason for this correlation is that both the translational and rotational Doppler shifts depend on the momenta \mathbf{k} of photoelectron and of the Auger electron \mathbf{p} .

Role of recoil-induced vibrational excitation

The recoil effect affects the probability $P_{0\nu}$ of the vibrational excitation (11, 12)

$$\begin{aligned}P_{0\nu} &= \frac{1}{2} \int_0^\pi P_{0\nu}(\theta) \sin\theta d\theta, \\ P_{0\nu}(\theta) &= \left| \langle \psi_0(x) | e^{i\alpha k x \cos\theta} | \psi_\nu(x - x_0) \rangle \right|^2,\end{aligned}\tag{37}$$

where the factor $\exp(i\alpha k x \cos\theta)$ describes the momentum exchange between the photoelectron and molecule, $\psi_0(x)$ and $\psi_\nu(x - x_0)$ are initial and final vibrational wave functions, $x = R - R_0$ is the displacement from the ground state equilibrium,

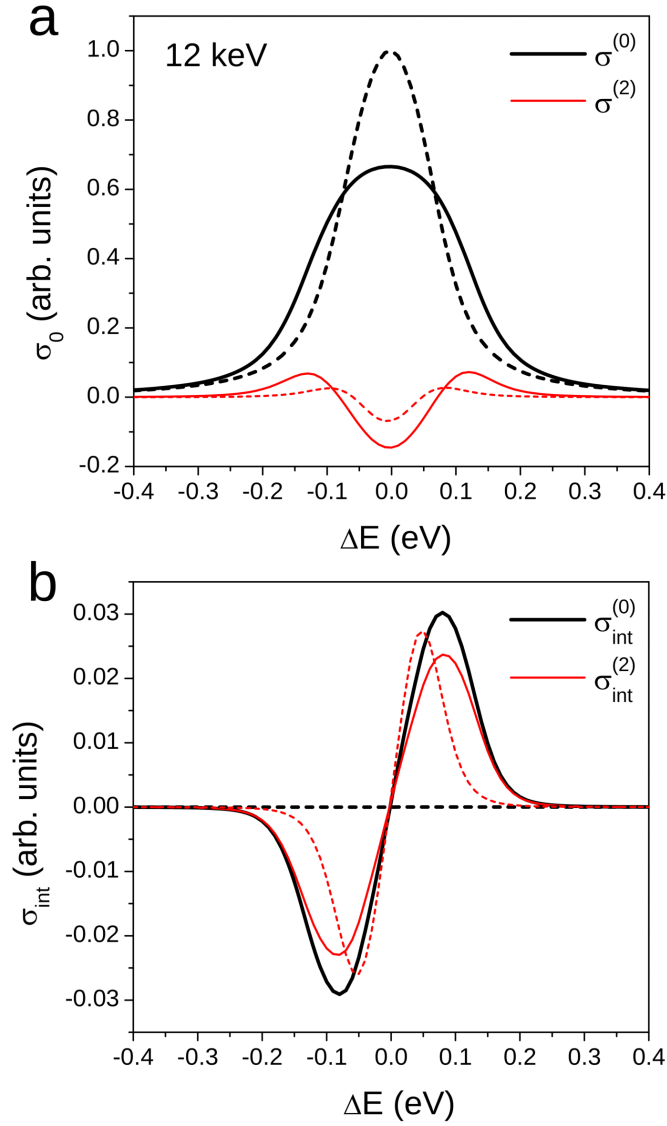


Fig. S1. Partial cross sections $\sigma^{(0)}$, $\sigma^{(2)}$, $\sigma_{\text{int}}^{(0)}$, and $\sigma_{\text{int}}^{(2)}$ of the Auger process given in eq. 33 which explain the Doppler broadening and asymmetry of the Auger profile. The calculations are performed using eq. 34 as well as a photon energy of $\omega = 12$ keV. **a**, The partial cross sections $\sigma^{(0)}$ and $\sigma^{(2)}$ form the symmetrical part of the total cross section. The dip around $\Delta E = 0$ seen in $\sigma^{(2)}$ is responsible for the formation of the Doppler splitting (see Figure 2a and Figure 4a of the main text). **b**, The contributions $\sigma_{\text{int}}^{(0)}$ and $\sigma_{\text{int}}^{(2)}$ have an antisymmetric spectral shape. These terms appear due to the quantum interference between different rotational levels of the core-excited state and because of the anisotropy of the Auger decay. The solid and dashed lines in **a** and **b** show the partial cross sections with and without ($p_u \rightarrow 0$) taking the translational Doppler effect into account, respectively.

$x_0 = R_0^{(i)} - R_0 = -0.0972$ a.u. (13) is the shift of the minimum of the potential of core-ionized state with respect to R_0 , $\theta = \angle(\mathbf{k}, \mathbf{R}_0)$, $k = \sqrt{2(\omega - I_{1sC})}$, $I_{1sC} = 296.24$ eV (3) is the ionization potential of the 1s electron of carbon. Results of calculations of $P_{0\nu}$ are collected in Table S1. One can see that mainly the vibrational levels $\nu = 0, 1, 2$ are populated when the photon energy is close to the ionization threshold (no recoil effect). The level $\nu = 3$ is very slightly populated when the photon energy approaches the highest energy in our experiment, $\omega = 12$ keV: its population grows from 2% ($\omega = I_{1sC}$) to 6% ($\omega = 12$ keV). Taking into account these results, as well as the same equilibrium distance of the core-ionized and the final $d^1\Sigma^+$ Auger states of CO (13), one can conclude that the role of the recoil-induced vibrational excitation is negligibly small for the effect studied here. Our calculations for low excitation energy agree with the experimental data (14).

Table S1. Recoil induced vibrational excitation of the CO molecule

ω (keV)	P_{00}	P_{01}	P_{02}	P_{03}	P_{04}
no recoil	0.5554	0.3266	0.0960	0.0188	0.0028
2.5	0.5139	0.3408	0.1143	0.0258	0.0044
8	0.4405	0.3507	0.1494	0.0455	0.0111
12	0.3990	0.3467	0.1685	0.0611	0.0184

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