

Supplementary information

EXAFS Self-Interference and the occurrence of shape resonances

For emission out of the molecule along the molecular axis, the direct wave interferes with an electron wave that is scattered an odd number of times and dominated by single-scattering (66% back-scattering), whereas for emission into the molecule, the direct wave interferes with an electron wave scattered an even number of times. This process is dominated by double scattering (34% forward scattering), as depicted in the inset of Fig. 2. The frequency of the resulting oscillation depends on the observation angle and, for observation along the molecular axis, is proportional to twice the internuclear distance (bond length R) in both cases, because the path length differences between the emitter reference atom are the same, as shown in the inset of Fig. 2. However, the apparent difference in path length is only approximately equal to the actual path-length difference of twice the bond length due to the potential-dependent scattering-induced phase shift¹ in the expression for Extended X-Ray Absorption Fine Structure (EXAFS) oscillations (see methods). In our case the Fourier transform yields an apparent path length of $1.73 R$ instead of $2 R$ for the dominant backward channel, corresponding to an energy-dependent phase shift kr_s with $r_s = 0.28 \text{ \AA}$ and an energy independent one of $\varphi = 1.3 \pi$. These values are in good agreement with predictions of potential scattering of the different partial waves. In the following, the term “double” bond length always refers to this effective double bond length. The scattering problem we are dealing with here is the one-dimensional equivalent of the EXAFS situation observed in X-ray absorption spectra². The unequal oscillation amplitude in the backward and forward channels reflects the intrinsic asymmetry of a one-dimensional system such as a heteronuclear diatomic molecule for emission into and out of the system. Interchanging the emitter sites just reverses

the meaning of forward and backward. This feature gives rise to the mirror symmetric molecular frame angular distributions at the two K-edges.

Note that at first glance the well-known shape resonance in K-shell photoionization of CO^3 is seen in the forward channel only. Its main contribution is four-fold scattering of the photoelectron oscillating with twice the frequency of the characteristic double-scattering oscillation in this channel. In addition, a double- and single-scattering contribution to an energetically-shifted shape resonance appears in both the forward and backward channels, but is masked by the close-lying stronger EXAFS scattering oscillation amplitude at higher energy. There is a transition region between the two regimes of interferometric EXAFS coherence for λ smaller than R on the one hand, and the standing waves supporting Near-Edge X-Ray Absorption Fine Structure coherence (NEXAFS) for λ larger than R on the other hand⁴⁻⁶. The different contributions of the two shape resonances at energies corresponding approximately to de Broglie wavelengths of two and four times the apparent bond length in the forward and backward channel are marked by bars in Fig. 2. These features are mostly unexplored at present and will not be further discussed here.

The sum of the contributions for the two channels exhibits an oscillation dominated by the backward channel with its stronger oscillation amplitude due to the larger probability for single scattering compared to double scattering. To make this effect more evident, the diffraction intensities have been normalized to the partial cross sections to eliminate its exponential decay behaviour and to display the oscillatory structure of the diffraction intensity more clearly. The agreement between this superposition and *ab initio* curves from threshold to the high energy limit shows that this simple one-centre inter-

ference model is not only capable of describing the EXAFS region properly, but the more subtle NEXAFS regime⁷, as well.

In addition to the self-interference structure, the unmodulated asymptotic limit of CO corresponds to a macroscopic double-slit experiment with one slit open while the other one is closed. This is in contrast to the homonuclear case where the spatial coherence between the two emitter sites and its associated interference pattern is expected to dominate the corresponding asymptotic behaviour. The different scattering contributions were separated out by a fitting procedure based on the generalized Cohen-Fano (GCF) model augmented by a standing-wave description of the shape resonances.

Experimentally, for two data points at low energy, the combined photon energy and electron spectrometer resolution was sufficiently high to allow separation of the g and u states by a parametric fit of the line structure. The diffraction intensities at higher energies had to be derived by fixing all parameters except the line intensities. For energies with markedly different g and u intensities, the results of this procedure could be independently confirmed by analysis of the corresponding symmetry-sensitive fragment ion angular distributions.

The coherence transition seen in the *ungerade* channel is also present in the *gerade* channel, except that a prominent multiple scattering shape resonance appears in the two-centre coherence regime. Careful analysis of the structural appearance of this resonance shows that its origin is triple- and four-fold scattering corresponding to a path length difference of four bond lengths. Therefore, the resonance at the de Broglie wavelength with this difference in path length gives rise to a particularly pronounced NEXAFS-like superposition because, for $\lambda/4 = \mathbf{R}$, a standing wave accompanied by electron trapping that is sensitive to the bond length⁶⁻⁸ can be supported. The odd and even components of

the reflected wave are transferred into the forward/backward channels of the localized heteronuclear diffraction intensities and give rise to pronounced oscillations at low kinetic energies. The corresponding results for CO suggest that the fourfold-scattering shape resonance appears roughly as a single-period oscillation of the scattering intensity with a frequency proportional to four times the bond length. Except for the occurrence of multiple scattering in the *gerade* channel, the coherence transition is completely analogous to that of the *ungerade* channel.

One consequence of the equivalence of the sum of the amplitudes in both the *g/u* and *f/b* systems is that beyond the effective EXAFS threshold, i.e., for a matter wavelength λ smaller than R , the scattering behaviour in the symmetric *g/u* system must have EXAFS-like character because this is the exclusive superposition mode on the non-oscillating background in the asymmetric *f/b* system of CO. Coexistence between the two modes of one- and two-centre coherence of scattering behaviour occurs in the predominantly standing-wave or shape resonance regime above the de Broglie wavelength $\lambda = R$ only. This argument for the observed effect on the basis of completeness of the two-dimensional Hilbert space of a one-dimensional system is complementary to that based on the more familiar uncertainty principle. The parity eigenstates g and u and their counter-parts, the momentum eigenstates f and b constitute two two-dimensional Hilbert spaces analogous to the CP eigenstates K_s and K_l and their counterparts K and \bar{K} of the neutral Kaon system. The latter one are eigenstates of the discrete flavour quantum number strangeness ± 1 in the standard model. They show a time-dependent oscillation as fingerprint of their entanglement⁹.

Supplemental References

1. Woodruff, D. P. *et al.* Direct methods in photoelectron diffraction; experiences and lessons learnt based on the use of the projection method. *J. Phys. Condens. Matter* **13**, 10625–10645 (2001).
2. Sayers, D. E. & Stern, E. A. New Technique for Investigating Nanocrystalline Structures: Fourier Analysis of the Extended X-Ray-Absorption Fine Structure. *Phys. Rev. Lett.* **27**, 1204-1207 (1971).
3. Dehmer, J. L. & Dill, D. Shape Resonances in K-Shell Photoionization of Diatomic Molecules. *Phys. Rev. Lett.* **35**, 213–215 (1975).
4. Rescigno, T. N. & Langhoff, P. W. K-Shell Photoionization in Molecular Nitrogen. *Chem. Phys. Lett.* **51**, 65-70 (1977).
5. Bianconi, A., Peterson, H., Brown, F. C. & Bachrach, R. Z. K-shell photoabsorption spectra of N₂ and N₂O using synchrotron radiation. *Phys. Rev. A* **17**, 1907-1911 (1978).
6. Stöhr, J. *et al.* Bonding and Bond Lengths of Chemisorbed Molecules from Near-Edge X-Ray-Absorption Fine-Structure Studies. *Phys. Rev. Lett.* **51**, 2414-2417 (1983).
7. Stöhr, J. *NEXAFS Spectroscopy*. Springer Series in Surface Sciences, ed. by Ertl, G., Gomer, R. & Mills, D.L. (Springer-Verlag Berlin Heidelberg New York, 1992).
8. Thomas, T. D. *et al.* Photon Energy Dependence of the $1\sigma_u/1\sigma_g$ Intensity Ratio in Carbon 1s Photoelectron Spectroscopy of Ethyne. *Phys. Rev. Lett.* **82**, 1120-1123 (1999).
9. Afriat, A. Kaons and Bell's Inequality, in *The Foundations of Quantum Mechanics*, edited by Garola C. & Rossi A. p. 19- 30 (World Scientific, Singapore, 2000).