

# From double-slit interference to structural information in simple hydrocarbons

Rajesh Kumar Kushawaha<sup>a,b</sup>, Minna Patanen<sup>c</sup>, Renaud Guillemin<sup>a,b</sup>, Loic Journal<sup>a,b</sup>, Catalin Miron<sup>c</sup>, Marc Simon<sup>a,b</sup>, Maria Novella Piancastelli<sup>a,b,d,1</sup>, C. Skates<sup>e</sup>, and Piero Decleva<sup>e,f,g</sup>

<sup>a</sup>Laboratoire de Chimie Physique-Matière et Rayonnement, Université Pierre et Marie Curie, 75231 Paris Cedex 05, France; <sup>b</sup>Laboratoire de Chimie Physique-Matière et Rayonnement (Unité Mixte de Recherche 7614), Centre National de la Recherche Scientifique, 75231 Paris Cedex 05, France; <sup>c</sup>Synchrotron SOLEIL, l'Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette Cedex, France; <sup>d</sup>Department of Physics and Astronomy, Uppsala University, 75120 Uppsala, Sweden, <sup>e</sup>Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy; <sup>f</sup>Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali Unità di Trieste, 34127 Trieste, Italy; and <sup>g</sup>Democritos Modeling Center for Research in Atomistic Simulation, Consiglio Nazionale delle Ricerche-Istituto Officina dei Materiali, 34149 Trieste, Italy

Edited by R. Stephen Berry, The University of Chicago, Chicago, IL, and approved August 8, 2013 (received for review April 9, 2013)

**Interferences in coherent emission of photoelectrons from two equivalent atomic centers in a molecule are the microscopic analogies of the celebrated Young's double-slit experiment. By considering inner-valence shell ionization in the series of simple hydrocarbons C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, we show that double-slit interference is widespread and has built-in quantitative information on geometry, orbital composition, and many-body effects. A theoretical and experimental study is presented over the photon energy range of 70–700 eV. A strong dependence of the oscillation period on the C–C distance is observed, which can be used to determine bond lengths between selected pairs of equivalent atoms with an accuracy of at least 0.01 Å. Furthermore, we show that the observed oscillations are directly informative of the nature and atomic composition of the inner-valence molecular orbitals and that observed ratios are quantitative measures of elusive many-body effects. The technique and analysis can be immediately extended to a large class of compounds.**

coherent state and molecular photoemission | interference phenomena

**W**ave-particle duality, nowadays considered as a milestone in the development of quantum mechanics, is the revolutionary concept that was experimentally demonstrated by Young's double-slit experiment in 1801. In Feynman's words, wave-particle duality is "a phenomenon which is impossible. . . to explain in any classical way, and which has in it the heart of quantum mechanics" (1). Once the wave nature of light was revealed in such an experiment, similar experiments were carried out with several particles, including electrons (2, 3) and even heavy species such as C<sub>60</sub> (4), in which a beam passed through two slits separated by a distance comparable to their associated de Broglie wavelength.

In 1966, Cohen and Fano (5) interpreted the oscillatory behavior of the photoabsorption spectra of N<sub>2</sub> and O<sub>2</sub> molecules (6) by theorizing the possibility of realizing the double-slit experiment in the photoionization of homonuclear, diatomic molecules, where the electrons are emitted by two equivalent atomic centers. Due to coherence in the initial molecular state, the absorption of a single photon by the homonuclear molecule gives rise to two coherent electron waves, which naturally lead to interference oscillations.

Further theoretical studies were carried out on the coherent emission of electrons from the H<sub>2</sub> molecule and the H<sub>2</sub><sup>+</sup> ion by photoionization (7) and by fast electron impact (8, 9). The interference in the D<sub>2</sub> molecule was also studied using electron impact (10). Projectiles such as heavy ions have also been used to study similar phenomena in diatomic molecules (11, 12). Interference phenomena were also found and studied extensively in the K-shell ionization of diatomic molecules, such as N<sub>2</sub> (13, 14). Recently, the cold target recoil ion momentum spectroscopy (COLTRIMS) technique has been used to study the double-slit interference effect in the double ionization of H<sub>2</sub> induced by synchrotron radiation (15, 16).

Direct observation of the interference pattern in photoionization is often difficult, being a small modulation superimposed

on a rapidly decreasing cross-section. The cleanest observation is expected by measuring the ratio of two cross sections, corresponding to symmetrical (g) and antisymmetrical (u) combinations of 1s orbitals, which are expected to give oscillations in antiphase, thus magnifying the interference pattern. For the same reason, no oscillation is present in the unresolved g/u cross-section. Unfortunately, the g/u splitting of core orbitals is generally too small to be observable, due to the dominating natural lifetime broadening. However, in N<sub>2</sub> (17) and C<sub>2</sub>H<sub>2</sub> (18, 19), it is of the order of 100 meV, owing to the very short interatomic distance associated with the triple bond, and beautiful interference patterns have been observed (13, 14). Another possibility that has been exploited recently is to observe the interferences from the ratios of individual vibrational components, and clear patterns have been observed in both the valence shell and core regions (20, 21). This method has some advantages but requires vibrational resolution, which is often not achievable in more complex systems.

Beyond the fundamental interest in observing quantum interference between electron waves coherently emitted, many important questions remain to be addressed by a broader study of these interference patterns:

A strong geometrical dependence of the interference patterns is expected, as also predicted by the Cohen–Fano formula (5). This dependence may provide a means of accurate determination of molecular geometries, especially when photoemission is the primary investigation tool.

## Significance

**Electrons emitted from equivalent centers in isolated molecules via the photoelectric effect interfere, providing an atomic-scale equivalent of the celebrated Young's double-slit experiment. We have developed a theoretical and experimental framework to characterize such interference phenomena accurately, and we have applied it to the simplest hydrocarbons with different bond lengths and bonding types. We demonstrate that such fundamental observations can be related to crucial structural information, such as chemical bond lengths, molecular orbital composition, and quantitative assessment of many-body effects, with a very high accuracy. The experimental and theoretical tools we use are relatively simple and easily accessible, and our method can readily be extended to larger systems, including molecules of biological interest.**

Author contributions: M.S., M.N.P., and P.D. designed research; R.K.K., M.P., R.G., L.J., C.M., M.S., M.N.P., and P.D. performed research; R.K.K., M.P., R.G., L.J., C.M., C.S., and P.D. analyzed data; and R.K.K., M.S., M.N.P., and P.D. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

<sup>1</sup>To whom correspondence should be addressed. E-mail: maria-novella.piancastelli@fyisik.uu.se.







**Table 1. Fitting parameters of the observed spectra of C<sub>2</sub>H<sub>2</sub> for accurate estimation of the bond length**

| $R_{CC}$ | $\alpha$ | $\beta$ | $\chi^2$ |
|----------|----------|---------|----------|
| 1.2027   | 0.7177   | 4.584   | 0.06973  |
| 1.2322   | 0.7500   | 9.462   | 0.10135  |
| 1.1732   | 0.6925   | -2.707  | 0.09236  |
| 1.2616   | 0.7771   | 12.500  | 0.19299  |
| 1.1438   | 0.6623   | -14.775 | 0.15578  |

The value of the fitted parameters, such as  $\chi^2$ ,  $\alpha$ , and  $\beta$ , for various bond lengths is shown in the table. The first line is the experimental carbon-carbon bond length ( $R_{CC}$ ) value ([cccbdb.nist.gov](http://cccbdb.nist.gov)) (36).

relationship could be valid only in selected cases, and did not have a general outcome, the method we propose here is founded on quantities directly related to bond distances and really can be considered as a way of deriving bond lengths with a ruler, with the “ruler” being the oscillation period. To carry on further with such a comparison, we stress that our method has significant advantages over absorption techniques because of the initial-state discrimination offered by photoelectron detection compared with total absorption, which gives the possibility of distinguishing among inequivalent sites that are summed in the absorption signal. Furthermore, our method can be applied to core, inner-valence, and outer-valence ionization processes, allowing one to choose the most suitable dataset from the standpoint of both experimental accessibility and ease of interpretation.

Moreover, chemical information, which is an input in the calculation, as the composition of the relevant MOs, is contained in the spectrum, although it is not so directly derivable from the spectral structures. However, the differential admixture of H 1s contribution, which has a fast-decreasing cross section, in the two orbitals considered can be directly monitored from the high-energy limit of the one-cycle averaged ratio. Qualitatively, this is the largest in C<sub>2</sub>H<sub>2</sub>, and it decreases rapidly in C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. Population analysis shows that although the content of C 2s in the  $\sigma_u$  orbital is nearly constant, it is steadily decreasing from C<sub>2</sub>H<sub>2</sub> to C<sub>2</sub>H<sub>6</sub> in  $\sigma_g$  because of increasing bonding with the hydrogens, which is nicely observed in the experimental g/u ratio. It must be stressed that orbital composition is intimately related to the theoretical models chosen. In the most general formulation, this is tied to the so-called “Dyson orbital” as the initial state, which is defined perfectly well for any wave function. At the Hartree–Fock (HF) and static DFT levels, it reduces to the HF or Kohn–Sham orbital, respectively. The latter is used in the present modeling. The most obvious test of orbital composition stems from the comparison of the calculated profile with the experimental one, with different initial orbitals. This approach has been widely used, for example, in the context of MO analysis in electron momentum spectroscopy studies (e.g., refs. 40, 41). Therefore, precise orbital composition can be derived from comparison with the theoretical results using different initial orbitals. At a more qualitative level, behaviors can be directly obtained by profiles, as in the present case, for the amount of C 2s AO contribution in the initial orbitals, which is a piece of information especially valuable to obtain trends in, for example, chemically related systems, change of the bonding schemes, or amount of a specific AO in a given orbital. We speculate that it will be possible to develop simplified schemes, such as approximate multiple scattering models based on sums of atomic amplitudes, to invert experimental data in a semiquantitative way. Another very important output of our method is a precise determination of the ratio of spectroscopic factors, a number of great significance in many-body theory (the norm of the Dyson orbital), which is quite difficult to compute precisely [a look at the literature for the

present molecules shows ratios differing by a factor of 2 in different calculations (42, 43)].

## Conclusion

The present work clearly demonstrates the importance of the MO localization/delocalization for interference phenomena in photoionization. We have given a first example of a general phenomenon, namely, long-range structures in molecular photoionization. It occurs in all photoionization cross-sections: core, inner-valence, and outer-valence ones. These structures, which are easily experimentally accessible and are most evident in terms of cross-section ratios, are highly informative of geometrical structure, conformational equilibria, molecular electronic structure, and many-body effects that can often be qualitatively understood in simple structural terms and may be quantitatively reconstructed by least-squares fitting by means of accurate theoretical modeling with robust and established computational simulations.

The present results open the way to extensive investigations of such phenomena in a wide range of systems. Present DFT simulation of the spectra is very accurate and may provide an important tool for their quantitative analysis.

## Materials and Methods

**Sample Handling, Beamline, and Electron Spectrometer.** Experiments have been carried out at the soft X-ray PLEIADES beamline of the Synchrotron SOLEIL (31). An 80-mm period Apple II undulator was used, which covers the energy range of 35–1,000 eV, with variable polarization starting from 55 eV. The measurements were carried out using a wide-angle lens VG-Scienta R4000 electron spectrometer installed at a fixed position, with the electron detection axis perpendicular to the storage ring plane. X-ray light polarization was set at the magic angle of 54.7° with respect to the electron detection axis. The gas-phase samples C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> (99.95% purities; Air Liquide) were introduced in a gas cell with polarized electrodes, which were adjusted to minimize the effect of plasma potentials caused by the ion density gradient created along the synchrotron beam propagating through the gas cell. The gas pressure in the spectrometer vacuum chamber was kept constant at about  $6.5 \times 10^{-6}$  mbar for all measurements. The contribution of the R4000 electron analyzer to the instrumental broadening was 200 meV, defined by the pass energy of 100 eV and the curved entrance slit of 0.8 mm. A platinum-coated diffraction grating with 1,600 L/mm was used to produce monochromatic radiographs, and the monochromator exit slit was adjusted to maintain the photon energy resolution at about 200 meV in the photon energy range of 70–700 eV used in this study.

**Theoretical Methods.** Cross-section calculations have been performed at the static-exchange DFT level (i.e., using both bound and continuum orbitals obtained as eigenfunctions of the Kohn–Sham Hamiltonian defined by the ground-state density  $\rho$ ):

$$h_{KS} \varphi_{n\lambda\mu} = E_{n\lambda} \varphi_{n\lambda\mu}$$

$$h_{KS} = -\frac{1}{2}\Delta + V_N + V_C + V_{XC},$$

where  $V_N$  is the nuclear attraction potential,  $V_C(\rho)$  is the Coulomb potential, and  $V_{XC}(\rho)$  is the exchange correlation potential, defined by  $\rho$ . For  $V_{XC}$ , we have used the LB-94 potential (32). All orbitals are expanded in a multicenter basis obtained as products of radial B-spline functions (34) times spherical harmonics, fully adapted to the molecular symmetry. Asymptotic angular expansions up to a maximum L angular momentum value of 20 for C<sub>2</sub>H<sub>2</sub> and 24 for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, which ensure complete convergence of the calculated cross-sections up to 40 arbitrary units of electron kinetic energy, have been used. Full details of the method have been documented previously (34, 35).

**ACKNOWLEDGMENTS.** The authors thank the Synchrotron SOLEIL staff for smooth operation of the facility and the personnel of the PLEIADES beamline for assistance in setting up the experiment (Project 20110691). P.D. acknowledges the generous granting of computing time from the Cineca. R.K.K. and M.N.P. thank the French Agence Nationale de la Recherche (ANR) for financial support in the framework of a “Chaire d’Excellence” grant. P.D. acknowledges support from Italian Project Programma di ricerca di Rilevante Interesse Nazionale (PRIN) 2009.

1. Feynman RP, Leighton R, Sands M (1965) *The Feynman Lectures on Physics* (Addison-Wesley, Reading, MA), Vol III, pp 1-1-1-9.
2. Jönsson C (1961) Elektroneninterferenzen an mehreren künstlich hergestellten Feinspalten. *Z Phys* 161:454-474, German.
3. Jönsson C (1974) Electron diffraction at multiple slits. *Am J Phys* 42:4-11.
4. Arndt M, et al. (1999) Wave-particle duality of  $C_{60}$  molecules. *Nature* 401(6754):680-682.
5. Cohen HD, Fano U (1966) Interference in the photo-ionization of molecules. *Phys Rev* 150:30-33.
6. Samson JAR, Cairns RB (1965) Total absorption cross sections of  $H_2$ ,  $N_2$ , and  $O_2$  in the region 550-200 Å. *J Opt Soc Am* 55:1035.
7. Walter M, Briggs J (1999) Photo-double ionization of molecular hydrogen. *J Phys B At Mol Opt Phys* 32:2487-2587.
8. Joulakian B, Hanssen J, Rivarola R, Motassim A (1996) Dissociative ionization of  $H_2$ , by fast-electron impact: Use of a two-center continuum wave function. *Phys Rev A* 54(2):1473-1479.
9. Milne-Brownlie DS, Foster M, Gao J, Lohmann B, Madison DH (2006) Young-type interference in ( $e$ ,  $2e$ ) ionization of  $H_2$ . *Phys Rev Lett* 96(23):233201.
10. Kamalou O, et al. (2005) Evidence for interference effects in both slow and fast electron emission from  $D_2$  by energetic electron impact. *Phys Rev A* 71:010702.
11. Stolterfoht N, et al. (2001) Evidence for interference effects in electron emission from  $H_2$  colliding with 60 MeV/u  $Kr^{34+}$  ions. *Phys Rev Lett* 87:023201.
12. Misra D, et al. (2004) Interference effect in electron emission in heavy ion collisions with  $H_2$  detected by comparison with the measured electron spectrum from atomic hydrogen. *Phys Rev Lett* 92(15):153201.
13. Rolles D, et al. (2005) Isotope-induced partial localization of core electrons in the homonuclear molecule  $N_2$ . *Nature* 437(7059):711-715.
14. Liu XJ, et al. (2006) Young's double-slit experiment using core-level photoemission from  $N_2$ : Revisiting Cohen-Fano's two-centre interference phenomenon. *J Phys B At Mol Opt Phys* 39:4801-4817.
15. Akoury D, et al. (2007) The simplest double slit: Interference and entanglement in double photoionization of  $H_2$ . *Science* 318(5852):949-952.
16. Kreidi K, et al. (2008) Interference in the collective electron momentum in double photoionization of  $H_2$ . *Phys Rev Lett* 100(13):133005.
17. Hergenroth U, Kugeler O, Rüdell A, Rennie EE, Bradshaw AM (2001) Symmetry-selective observation of the N 1s shape resonance in  $N_2$ . *J Phys Chem A* 105:5704-5708.
18. Kempgens B, et al. (1997) Core level energy splitting in the C 1s photoelectron spectrum of  $C_2H_2$ . *Phys Rev Lett* 79:3617.
19. Thomas TD, et al. (1999) 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.
20. Canton SE, et al. (2011) Direct observation of Young's double-slit interferences in vibrationally resolved photoionization of diatomic molecules. *Proc Natl Acad Sci USA* 108:7302-7306.
21. Argenti L, et al. (2012) Double-slit experiment with a polyatomic molecule: Vibrationally resolved C 1s photoelectron spectra of acetylene. *New J Phys* 14:033012.
22. Tachino CA, Galassi ME, Martín F, Rivarola RD (2009) Coherence in collisionally induced electron emission from diatomic heteronuclear molecules. *J Phys B At Mol Opt Phys* 42:075203.
23. Tachino CA, Galassi ME, Martín F, Rivarola RD (2010) Partial localization in coherent electron emission from asymmetric diatomic molecules. *J Phys B At Mol Opt Phys* 43:135203.
24. Benning PJ, et al. (1991) Electronic states of solid  $C_{60}$ : Symmetries and photoionization cross sections. *Phys Rev B Condens Matter* 44(4):1962-1965.
25. Liebsch T, et al. (1995) Angle-resolved photoelectron spectroscopy of  $C_{60}$ . *Phys Rev A* 52(1):457-464.
26. Söderström J, et al. (2012) Nonstoichiometric intensities in core photoelectron spectroscopy. *Phys Rev Lett* 108(19):193005.
27. Carroll TX, et al. (2013) Intensity oscillations in the carbon 1s ionization cross sections of 2-butyne. *J Chem Phys* 138(23):234310-234315.
28. Potts AW, Streets DG (1974) Photoelectron spectra of inner valence shells, Part 1. Unsaturated hydrocarbons. *J Chem Soc Faraday Trans 2* 70:875-884.
29. Streets DG, Potts AW (1974) Photoelectron spectra of inner valence shells Part 2.-unsaturated hydrocarbons. *J Chem Soc Faraday Trans 2* 70:1505-1515.
30. Pireaux JJ, et al. (1976) Core-electron relaxation energies and valence-band formation of linear alkanes studied in the gas phase by means of electron spectroscopy. *Phys Rev A* 14:2133-2146.
31. Miron C, et al. (2012) Imaging molecular potentials using ultrahigh-resolution resonant photoemission. *Nat Phys* 8:135-139.
32. van Leeuwen R, Baerends EJ (1994) Exchange-correlation potential with correct asymptotic behavior. *Phys Rev A* 49(4):2421-2431.
33. Bachau H, Cormier E, Decleva P, Hansen JE, Martín F (2001) Applications of B-splines in atomic and molecular physics. *Rep Prog Phys* 64:1815-1943.
34. Toffoli D, Stener M, Fronzoni G, Decleva P (2002) Convergence of the multicenter B-spline DFT approach for the continuum. *Chem Phys* 276:25-43.
35. Stener M, Fronzoni G, Decleva P (2005) Time-dependent density-functional theory for molecular photoionization with noniterative algorithm and multicenter B-spline basis set:  $CS_2$  and  $C_6H_6$  case studies. *J Chem Phys* 122(23):234301.
36. Strey G, Mills IM (1976) Anharmonic force field of acetylene. *J Mol Spectrosc* 59:103-115.
37. Zewail AH (2006) 4D ultrafast electron diffraction, crystallography, and microscopy. *Annu Rev Phys Chem* 57:65-103.
38. Blaga CI, et al. (2012) Imaging ultrafast molecular dynamics with laser-induced electron diffraction. *Nature* 483(7388):194-197.
39. Piancastelli MN (1999) The neverending story of shape resonances. *J Electron Spectrosc Relat Phenomena* 100:167-190.
40. Miao YR, Ning CG, Deng JK (2011) Calculation of Dyson orbitals using a symmetry-adapted-cluster configuration-interaction method for electron momentum spectroscopy:  $N_2$  and  $H_2O$ . *Phys Rev A* 83:062706-062707.
41. Tian Q, Yang J, Shi Y, Shan X, Chen X (2012) Outer- and inner-valence satellites of carbon dioxide: Electron momentum spectroscopy compared with symmetry-adapted-cluster configuration interaction general-R calculations. *J Chem Phys* 136(9):094306-094310.
42. Duffy P, et al. (1992) Electron momentum spectroscopy of the valence orbitals of acetylene: Quantitative comparisons using near Hartree-Fock limit and correlated wavefunctions. *Chem Phys* 165:183-199.
43. Hasegawa J, Ehara M, Nakatsuji H (1998) Theoretical study on the ionized states of ethylene by the SAC-CI (general-R) method. *Chem Phys* 230:23-30.