

Direct observation of Young's double-slit interferences in vibrationally resolved photoionization of diatomic molecules

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Vibrationally resolved valence-shell photoionization spectra of H₂, N₂ and CO have been measured in the photon energy range 20–300 eV using third-generation synchrotron radiation. Young's double-slit interferences lead to oscillations in the corresponding vibrational ratios, showing that the molecules behave as two-center electron-wave emitters and that the associated interferences leave their trace in the angle-integrated photoionization cross section. In contrast to previous work, the oscillations are directly observable in the experiment, thereby removing any possible ambiguity related to the introduction of external parameters or fitting functions. A straightforward extension of an original idea proposed by Cohen and Fano [Cohen HD, Fano U (1966) *Phys Rev* 150:30] confirms this interpretation and shows that it is also valid for diatomic heteronuclear molecules. Results of accurate theoretical calculations are in excellent agreement with the experimental findings.

photoelectron spectroscopy | molecular spectroscopy | molecular ionization | density functional theory | quantum chemistry

The recognition of wave-particle duality, resolving centuries of scientific debate, is nowadays considered as a milestone in the development of Quantum Mechanics. This revolutionary concept has been repeatedly demonstrated in variations of Young's double-slit experiment, where a beam of massive particles, from electrons (1) to fullerenes (2), with momentum p_e , passing through two slits separated by a distance comparable to their associated de Broglie wavelength ($\lambda_e = h/p_e$) displays temporal and spatial coherence evidenced through interferogram fringes (3). In the 1960's, Cohen and Fano (4) conjectured the possibility to realize the double-slit experiment on the microscopic length scale by photoionizing a diatomic molecule, where the source of free electrons is delocalized over two atomic centers. A sketch of the interference expected from the coherent emission of the two centers is shown in Fig. 1.

Coherence is observable when the electron-wave length λ_e is of the order of R_e , or equivalently, when the photon energy $h\nu$ is of the order of $I_p + h^2/(2m_e R_e^2)$, where R_e is the internuclear distance at equilibrium, m_e is the electron mass, and I_p is the vertical ionization potential. These energies correspond to incoming photons of a few hundred eV, i.e., to vacuum or extreme ultraviolet radiation. Fingerprints of this coherent emission can be found in the total photoionization cross section, which in the case of a homonuclear diatomic molecule is approximately given by the formula

$$\sigma = \sigma_0 \left[1 + \frac{\sin(k_e R_e)}{k_e R_e} \right], \quad [1]$$

where σ_0 is an atomic photoionization cross section (for an effective charge Z_{eff}) and $k_e = 2\pi/\lambda_e$ is the electron-wave vector. The

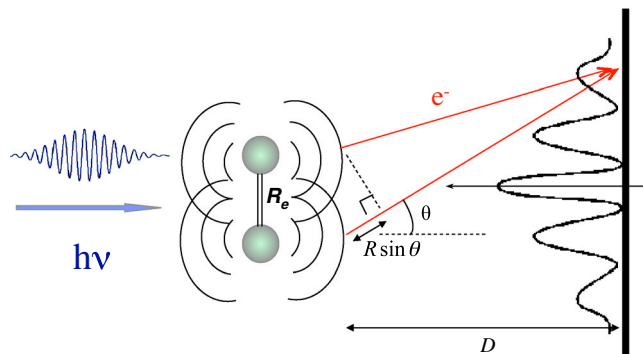


Fig. 1. Sketch of the two-center interference effect resulting from the photoionization of a diatomic molecule with a bond length R_e on a detector placed at a distance D . The difference in length, $R_e \sin \theta$, between the paths followed by the electron waves on their way to the detector in the θ direction leads to interferences similar to those observed in Young's double-slit experiment. Maxima appear for $\theta = \arcsin(n\lambda_e/R_e)$ and minima for $\theta = \arcsin(n\lambda_e/2R_e)$.

oscillatory term within brackets quantifies the interference effect (hereafter called Cohen-Fano, CF, interference). The beauty of such a simple expression is that it is proportional to the very general intensity pattern produced by two dipole antennas separated by a distance R_e that radiate coherently (5).

Eq. 1 is obtained by assuming that the ionized molecular orbital ψ can be expressed by a linear combination of atomic orbitals (LCAO):

$$\psi = \frac{1}{\sqrt{2}}(1s_A + 1s_B), \quad [2]$$

where $1s_A$ and $1s_B$ are identical $1s$ atomic orbitals centered on atoms A and B of the molecule. Generalization to the heteronuclear case is straightforward (see, e.g., ref. 6 and *Results and Discussion* below). Another approximation introduced in deriving Eq. 1 is that the internuclear separation is fixed. However, the nuclei actually move under the influence of the Born-Oppenheimer electronic potential and, consequently, the excess photon energy $\Delta E = h\nu - I_p$ can be partitioned between electrons and nuclei. Although the extent of this effect is partially alleviated

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by the Franck-Condon principle, which restricts the effective ionization transitions to a limited range of electron energies, small changes in k_e can induce large changes in the cross section, especially towards the low energy region where it varies rapidly. Furthermore, as a consequence of vibration, the internuclear distance, R , evolves from the inner to the outer classical turning point of that vibration, so that it is not unambiguously defined and some intrinsic uncertainty exists as to which value must be used in (1).

Over the last few years, a substantial experimental effort has been devoted to investigate these two-center interferences in the simplest diatomic molecules, mainly in the context of photoionization [see, e.g., (7–17)], but also in ionizing collisions with fast ions (18–21) and electrons (22–24). However, due to the rapid decrease of σ_0 with photoelectron energy, i.e., with k_e , the oscillations are usually hidden and must be uncovered through dividing the total cross section by an independent but arbitrary estimate of σ_0 , leading to equivocal interpretations (18, 19). This difficulty has been so far circumvented by considering the ratio of two rapidly decreasing cross sections associated with different molecular ionization channels [e.g., the g/u ratio resulting from K-shell photoionization of N_2 (11, 25)].

As seen from Fig. 1, it is clear that CF interferences should also appear in electron angular distributions from fixed-in-space diatomic molecules, because the variation of the photoionization cross section with emission angle, θ , should reflect the sequence of alternate intensity maxima and minima. However, measuring such differential cross sections is not an easy task because the relevant events have low statistics. Furthermore, the visibility of two-center interferences critically depends on the orientation of the molecule with respect to the polarization axis (5, 26).

As a consequence of the limitations mentioned above, there is still no direct experimental report of CF interferences in the photoionization cross section of the simplest molecule H_2 , which is the benchmark used to derive Eq. 1 and for which most of the theoretical calculations have been performed (5, 26–28). A similar lack of evidence exists for photoionization of heteronuclear diatomic molecules. In the latter case, coherent emission of the electron wave from the two centers is possible provided that the ionized molecular orbital is sufficiently delocalized over the two nuclei. However, because the two centers are not identical, the interferences should be different from those expected in homonuclear molecules (e.g., as in a Young's experiment performed with two different slits).

With the advent of high-brilliance third-generation light sources and the significant progress in electron detection techniques, it has become possible to obtain vibrationally resolved spectra deep in the continuum. In this work, we report vibrationally resolved valence-shell photoionization spectra of H_2 , N_2 , and CO , and show that, in all cases, CF interferences are readily observable in the corresponding vibrational ratios (hereafter called ν -ratios). Thus, no external parameter or “atomic” cross section σ_0 is needed to uncover the CF interferences, and, in contrast to previous investigations, the information is retrieved from a single ionization channel, which largely simplifies the analysis. The interpretation is confirmed by results of state-of-the-art theoretical calculations. Some general implications of these findings are discussed in the conclusion.

Results and Discussion

Figs. 2, 3, and 4 present the measured and calculated ν -ratios as functions of photon energy for the valence-shell ionization processes in H_2 , N_2 , and CO , respectively, $H_2 \rightarrow H_2^+(1\sigma_g^{-1}, \nu')$ (Fig. 2), $N_2 \rightarrow N_2^+(3\sigma_g^{-1}, \nu')$ and $N_2 \rightarrow N_2^+(1\pi_u^{-1}, \nu')$ (Fig. 3), and $CO \rightarrow CO^+(5\sigma^{-1}, \nu')$ and $CO \rightarrow CO^+(1\pi^{-1}, \nu')$ (Fig. 4). For each molecule, the ν -ratios have been extracted by normalizing the vibrationally resolved cross sections to that of the dominant ν -channel. It should be noted that the reported ratios vary from

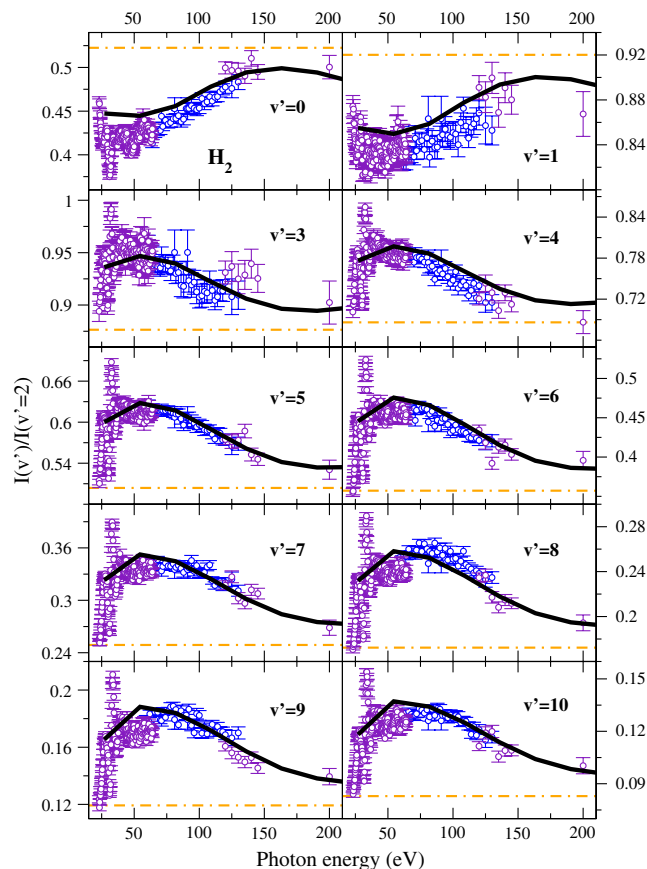


Fig. 2. Ratios of the vibrationally resolved photoionization spectra to the $\nu' = 2$ cross section as a function of photon energy for the H_2 molecule. Circles with error bars: experimental results; the different colors indicate different runs. Full black curve: theoretical results. Dashed-dotted line: Franck-Condon value.

~ 1 down to $\sim 10^{-3}$ for the three molecules and that the measurements obtained from different runs lead to very similar results. For H_2 , the agreement between theory and experiment is excellent, except at very low photon energies where narrow features associated with the H_2 autoionizing states cannot be described by the present implementation of the theory (see *Materials and Methods*). Good agreement, although not as perfect as for H_2 , is also obtained for N_2 and CO , apart from deviations for the largest ν -values and photon energies, for which the vibrationally resolved cross sections are very small.

The sharp structures observed in the ν -ratios of CO and N_2 at low photon energies are not so well reproduced by theory, particularly for $N_2(1\pi_u^{-1})$, because they result from shape resonances in the ionization continua (25, 29). Nevertheless the strong feature in the $N_2(3\sigma_g^{-1})$ channel is correctly located. As expected, oscillations are less visible for CO than for N_2 , due to the fact that CO has two different centers (see below). In this respect, it is worth stressing that two-center interferences have been predicted even for the very asymmetric molecule HeH^+ in ionizing collisions with highly charged atomic projectiles (6, 30), but have never been actually observed for any heteronuclear molecule.

A feature common to all the ν -ratios of the three diatomic molecules investigated is the presence of pronounced oscillations around the value predicted by the Franck-Condon (FC) approximation, commonly defined as the squared overlap between the initial and final vibrational wave functions and, consequently, independent of photon energy. The departures from the FC value are as large as 20% or even more in the case of H_2 . In pioneering work on $N_2 2\sigma_u^{-1}$ photoionization (29), a breakdown of the FC approximation was reported in the observed ν -ratios and was

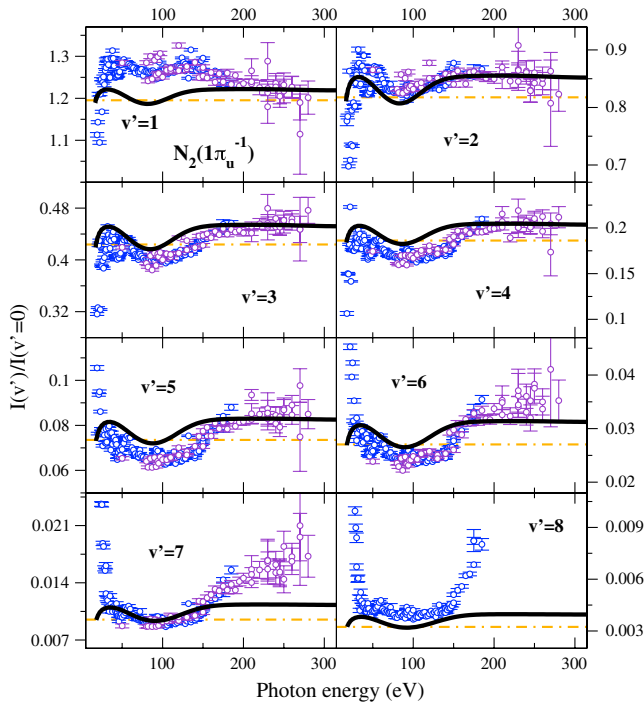
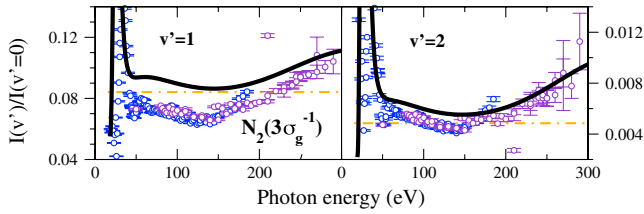


Fig. 3. Same as Fig. 2 but for N_2 photoionization from the $1\pi_u$ (top) and $3\sigma_g$ (bottom) valence orbitals and referred to $v' = 0$.

attributed to the existence of Cooper minima, originating from a change in sign of the dipole matrix element due to radial nodes in the initial orbital (as in the $2\sigma_u$ one). In the present work, the initial orbitals $1s\sigma_g$ of H_2 , $1\pi_u$ of N_2 , and 1π of CO do not have radial nodes, so this effect can be ruled out. In order to prove that the observed and calculated oscillations can be ascribed to CF interferences, Eq. 1 was used to evaluate approximate vibrationally resolved cross sections according to the simple formula:

$$\sigma(v') = \sigma_0 \left| \int_0^\infty \chi_{v_0}(R) \left[1 + \frac{\sin(k_{e,v'}R)}{k_{e,v'}R} \right]^{1/2} \chi_{v'}(R) dR \right|^2, \quad [3]$$

where $k_{e,v'}$ is the electron-wave vector when the remaining molecular ion is in the v' vibrational state, R is the internuclear distance, $\chi_{v'}$ is the corresponding vibrational wave function, and χ_{v_0} is the vibrational wave function of the initial state. The corresponding v -ratios have been calculated by further assuming that the “atomic” cross sections σ_0 are identical for the two vibrational channels involved in a particular ratio so that they cancel out. In the case of a heteronuclear molecule, Eq. 1 has to be modified in order to account for the different nature of the two centers. Following the work of refs. 6, 30, the vibrationally resolved cross sections can be given by:

$$\sigma_{AB}(v') = \sigma_0 \left| \int_0^\infty \chi_{v_0}(R) \left[1 + 2c_A c_B \frac{\sin(k_{e,v'}R)}{k_{e,v'}R} \right]^{1/2} \chi_{v'}(R) dR \right|^2, \quad [4]$$

where c_A and c_B are the mixing coefficients in the LCAO expansion of the molecular orbital ψ

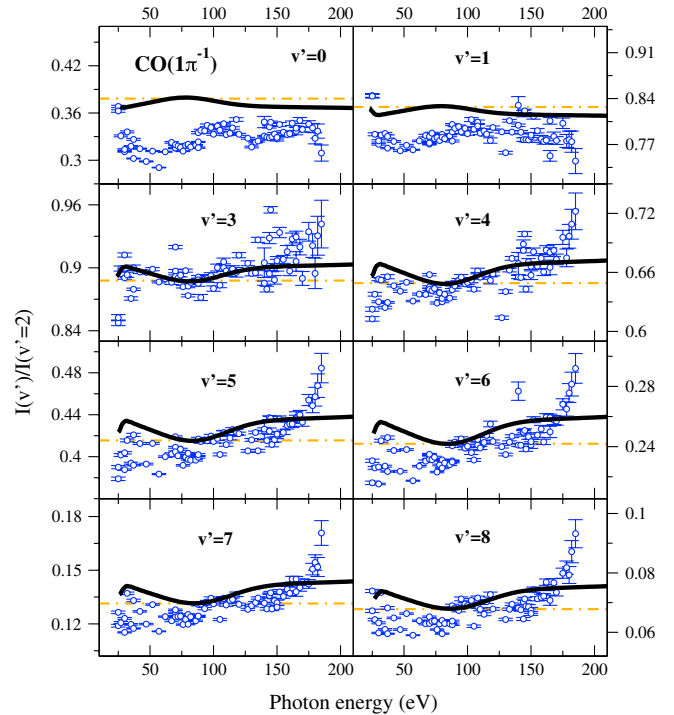
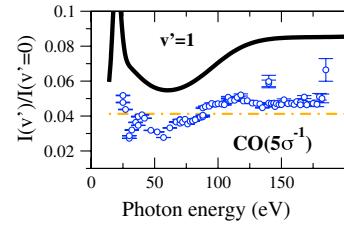


Fig. 4. Same as Fig. 2 but for CO photoionization from the 1π and 5σ valence orbitals.

$$\psi = c_A 1s_A + c_B 1s_B \quad [5]$$

and $c_A^2 + c_B^2 = 1$. For the CO molecule, the values $c_A^2 = 0.32$ and $c_B^2 = 0.68$ were chosen, because they correspond to the normalized electron occupancy of the C and O valence orbitals, respectively, resulting from a simple Hartree-Fock calculation performed with a minimal basis of atomic orbitals. Although, for this molecule, valence molecular orbitals result from the mixing of more than two atomic orbitals, including the $2s$ and $2p$ ones, the present simplified model retains the assumption that photoionization originates from the coherent emission of two centers with spherical electron distributions as those used in Eq. 5).

As can be seen in Fig. 5, the model reproduces almost perfectly the oscillations in H_2 and in $N_2(3\sigma_g^{-1})$, apart from a global scaling factor, which is likely due to the assumption of identical σ_0 for the two vibrational channels involved in the ratio and to the fact that such a simple model does not include any electron correlation or “molecular” distortion of the initial and final electronic wave functions. A similar good agreement has been obtained for the other v -ratios shown in Fig. 2. Comparison is slightly less satisfactory for $CO(5\sigma^{-1})$ due to the additional approximation introduced when expressing the 5σ orbital as a single combination of $1s$ atomic orbitals in Eq. 5. For $N_2(1\pi_u^{-1})$ and $CO(1\pi^{-1})$, the agreement with the model is only qualitative. Such an agreement is not surprising because Eq. 1 was derived with a superposition of $1s$ orbitals centered on each nuclei, i.e., $1\sigma_g \sim 1s_A + 1s_B$ as initial molecular orbital. However, the initial molecular orbitals in N_2

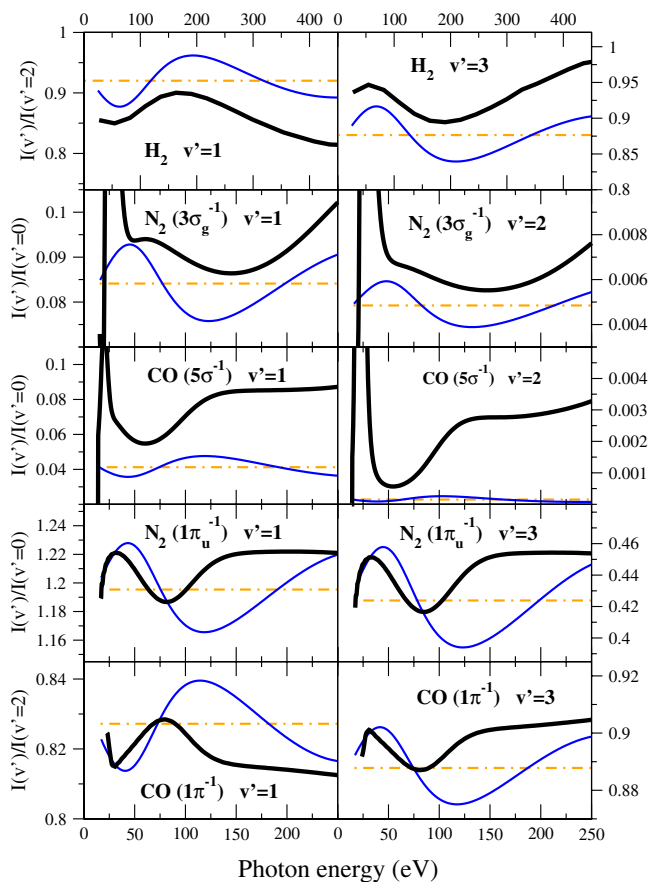


Fig. 5. Comparison of the calculated v -ratios with those obtained from the simple model described by (Eq. 3). Thick continuous curve: theoretical results (see Figs. 2–4). Thin continuous curve: results of the model. Dashed-dotted line: Franck-Condon value.

$1\pi_u^{-1}$ and CO $1\pi^{-1}$ ionization are, at least, a superposition of $2p_{+1}$ (or $2p_{-1}$) orbitals, i.e., $1\pi \sim 2p_{+1,A} + 2p_{+1,B}$ (in reality, they involve even more atomic orbitals). In the original paper by Cohen and Fano (4), it was suggested that photoionization from a π orbital should exhibit twice as many maxima as from σ orbitals [i.e., the dependence should be $\sin(2k_e R_e)$ as opposed to $\sin(k_e R_e)$ in Eq. 1]. Checking for this possibility leads to an even poorer agreement, so it can be concluded that the original model captures the essential features of the ratios. Interestingly, the period of the oscillations is shorter for N_2 and CO than for H_2 , which reflects the fact that N_2 and CO have an equilibrium internuclear distance significantly larger than H_2 ($2.07a_0$ and $2.13a_0$ compared to $1.4a_0$, respectively).

The oscillatory structures observed in the $I(v'_b)/I(v'_a)$ ratios stem from the fact that Eqs. 3 and 4 probe regions of R that are different for each v' . Indeed, by replacing in, e.g., Eq. 4 the variable R by the characteristic value $R_{v'}$ associated with the v' vibrational state, then performing a first-order expansion of $I(v'_b)/I(v'_a)$ in terms of $\delta R_{v'} = R_{v'} - R_{v'_a}$, and finally taking the limit to large values of the electron momentum k_e , one obtains

$$\frac{I(v'_b)}{I(v'_a)} = \frac{|\langle \chi_{v_0} | \chi_{v'_b} \rangle|^2}{|\langle \chi_{v_0} | \chi_{v'_a} \rangle|^2} \left[1 + 2c_A c_B \frac{\delta R_{v'}}{R_{v'_a}} \cos(k_e R_{v'_a}) \right]. \quad [6]$$

The formula predicts that the $I(v'_b)/I(v'_a)$ ratio should approximately oscillate around the FC value $|\langle \chi_{v_0} | \chi_{v'_b} \rangle|^2 / |\langle \chi_{v_0} | \chi_{v'_a} \rangle|^2$ with a $\cos(k_e R_{v'_a})$ dependence and amplitude proportional to $\delta R_{v'}/R_{v'_a}$. A similar qualitative behavior is observed in all the ratios depicted in Figs. 2, 3, and 4 (notice that, when $R_{v'}$ is smaller than

$R_{v'_a}$, the ratio $\delta R_{v'}/R_{v'_a}$ is negative and, therefore, the oscillations have opposite phase).

Conclusion

The present results unambiguously demonstrate the existence of CF interferences in vibrationally resolved valence-shell photoionization of homo- and heteronuclear diatomic molecules. The CF interferences lead to marked oscillations in the ratios between vibrationally resolved cross sections. Unlike detection schemes relying on fixed-in-space molecules, the experimental method is fast, applicable to any complex molecules, and does not require the use of arbitrary parameters. The oscillations are well reproduced by a straightforward extension of the original Cohen-Fano formula and by state-of-the-art calculations. Based on these combined experimental and theoretical results, several aspects of the CF interferences have been uncovered and clarified for the first time.

During photoionization, two concurrent processes can lead to interferences. One is the simultaneous emergence of the electron-wave from the two centers of the molecule. The other, not discussed here, is the scattering of the electron by the other atomic center (31, 32). The present work provides a simple way to identify the latter in a heteronuclear molecule. For example, it can be seen that, in the absence of electron delocalization, i.e., when $c_A = 1$ and $c_B = 0$ (or the other way around), the interference term in Eq. 5 vanishes and, consequently, coherent emission from the two atomic centers is no longer possible. Thus, in K-shell photoionization of CO, two-center coherent emission is not possible because the inner 1σ and 2σ molecular orbitals are almost entirely localized on the O and C atoms, respectively, and resemble the corresponding $1s$ atomic orbitals. Hence, in K-shell photoionization of CO, the observed interferences can only arise from the scattering of the ejected electron by the other atomic center (31, 32).

The presence of CF interferences due to two-center electron emission implies that v -ratios do not tend to the FC value expected from a vertical transition at the largest photon energies considered in this work. However, deviations from the FC behavior have also been observed in core photoionization of CO (33) and more complicated molecules, like CH_4 (34). Such deviations might be due to the scattering mechanism mentioned above and/or to the recoil of the remaining molecular ion (34).

Understanding the detailed mechanisms leading to interferences in the continuum has become increasingly important because many of the contemporary techniques that probe the structure of matter on the atomic scale are based on the wave nature of the free electron. Electron diffraction as well as transmission and scanning electron microscopy rely on the fact that long-range crystalline order acts as a diffraction grating for the incoming electron wave. For spectroscopies utilizing energetic radiation, the ionized atom is the actual source of electrons that scatter coherently within the surrounding. The near edge X-ray absorption fine structure (XANES) and extended X-ray absorption fine structure (EXAFS) fingerprints extracted from the X-ray photoabsorption coefficients are extremely sensitive markers for local electronic structure and coordination geometries (35, 36). Furthermore, as the time resolution of structural methods is rapidly reaching the pico-, femto-, and even attosecond time scales (37, 38), the interplay between geometric and electronic degrees of freedom must be taken into account to understand the dynamical nature of these interferences. It has been established that measuring Young's double-slit interferences does deliver unique information. For example, the R dependence of the two-center interferences observed in the photoionization of a diatomic molecule can track the variations of the electronic structure as it vibrates (5, 16, 39). Just as the set of atomic positions is the starting point of any crystallographic refinement or modeling of the XANES and EXAFS fingerprints, accurate electronic state calculations will become an inherent part of the

emerging ultrafast techniques, such as electron interferometry and holography (40) or coherent control (41). In this respect, the present work provides a robust frame in which theoretical approximations, unavoidable for complex molecules, can be checked, while capturing the essential dynamical aspects of interferences in the continuum.

Materials and Methods

The experiments were performed at the high-resolution AMO beamline 10.0.1 of the Advanced Light Source (ALS). Effusive molecular beams were ionized by linearly polarized radiation. The photoelectron spectra were measured using a Scienta SES-200 hemispherical analyzer (42) at 54.7° with respect to the light polarization axis (eliminating angular effects), and were corrected afterwards for spectrometer transmission. Owing to the high performance of the analyzer, the vibrational lines ν were kept resolved throughout the photon energy range covered (20 to 300 eV). With negligible stray background, reliable areas proportional to the cross sections were extracted by summing the counts in a given kinetic energy window, avoiding systematic uncertainties attached to baselines coming from overlapping peaks and bypassing recourse to fitting with analytical line shapes. Such a procedure was particularly important for these experiments because of the underlying rotational structure, almost resolved for the low ν and responsible for asymmetric broadening for the high ν .

The theoretical method to obtain the electronic and vibrational wave functions of H_2 makes use of B-spline functions and has been successfully

applied to study a variety of ionization problems in H_2 , such as resonant dissociative photoionization (43, 44) and ion impact ionization (45) in the dipole approximation. We refer the reader to those works and, for more details, to the reviews of refs. 46, 47. Electron correlation and interferences between the different ionization and dissociative channels are accounted for. As in ref. 26, we have not included doubly excited states in the basis of states because we are only interested in the region of high photon energies. To obtain the electronic wave functions of N_2 and CO, we have used an extension of density functional theory, DFT, developed by Decleva and coworkers to treat the molecular ionization continuum at the equilibrium position of the molecule in a basis of B-splines (47). The method has been shown to provide accurate photoionization spectra for simple as well as for very complex molecules [see, e.g., (47)]. In the present work, the method has been employed to obtain the continuum electronic wave functions over a wide range of internuclear distances. The vibrational wave functions have been obtained by using the potential energy curves that result from accurate multireference configuration interaction calculations.

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- Davisson C (1965) The discovery of electron waves. *Nobel lectures, Physics* 1922–1941:387–394.
- Arndt M, et al. (1999) Wave-particle duality of C_{60} molecules. *Nature* 401:680–682.
- Crease RP (2002) The most beautiful experiment. *Phys World*, 15 pp:19–20.
- Cohen HD, Fano U (1966) Interference in the photo-ionization of molecules. *Phys Rev* 150:30–33.
- Fernández J, Fojón O, Palacios A, Martín F (2007) Interferences from fast electron emission in molecular photoionization. *Phys Rev Lett* 98:043005.
- Tachino CA, Galassi ME, Martín F, Rivarola RD (2009) Coherence in collisionally induced electron emission from heteronuclear molecules. *J Phys B: at Mol Opt Phys* 42:075203.
- Itatani J, et al. (2004) Tomographic imaging of molecular orbitals. *Nature* 432:867–871.
- Meckel M, et al. (2008) Laser-induced electron tunneling and diffraction. *Science* 320:1478–1482.
- Yurchenko SN, Patchkovskii S, Litvinyuk IV, Corkum PB, Yudin GL (2004) Laser-induced interference, focusing, and diffraction of rescattering molecular photoelectrons. *Phys Rev Lett* 93:223003-1–223003-4.
- Rolles D, et al. (2005) Isotope-induced partial localization of core electrons in the homonuclear molecule N_2 . *Nature* 437:711–715.
- Liu XJ, et al. (2006) Young's double-slit experiment using core-level photoemission from N_2 : revisiting Cohen-Fano's two-center interference phenomenon. *J Phys B: at Mol Opt Phys* 39:4801–4817.
- Ueda K, et al. (2006) Role of the recoil effect in two-center interference in X-ray photoionization. *Chem Phys* 329:329–337.
- Akoury D, et al. (2007) The simplest double slit: interference and entanglement in double photoionization of H_2 . *Science* 318:949–952.
- Kreidi K, et al. (2008) Interference in the collective electron momentum in double photoionization of H_2 . *Phys Rev Lett* 100:133005.
- Zimmermann B, et al. (2008) Localization and loss of coherence in molecular double-slit experiments. *Nat Phys* 4:649–655.
- Schöffler MS, et al. (2008) Photo-double-ionization of H_2 : two-center interference and its dependence on the internuclear distance. *Phys Rev A* 78:013414.
- Okunishi M, et al. (2009) Two-source double-slit interference in angle-resolved high-energy above-threshold ionization spectra of diatoms. *Phys Rev Lett* 103:043001.
- 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.
- 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* 92:153201.
- Landers AL, et al. (2004) Interference effects in double ionization of spatially aligned hydrogen molecules by fast highly charged ions. *Phys Rev A* 70:042702.
- Chesnel JY, Hajaji A, Barrachina RO, Frémont F (2007) Young-type experiment using a single-electron source and an independent atomic-size two-center interferometer. *Phys Rev Lett* 98:100403.
- Chatterjee S, et al. (2009) Fast-electron impact ionization of molecular hydrogen: energy and angular distribution of double and single differential cross sections and Young-type interference. *J Phys B: at Mol Opt Phys* 42:075203.
- Chatterjee S, et al. (2008) Young-type interference effect on angular distribution of secondary electrons emitted from H_2 in collisions with fast electrons. *Phys Rev A* 78:052701.
- Hargreaves LR, et al. (2009) (e,2e) study of two-center interference effects in the ionization of N_2 . *Phys Rev A* 80:062704.
- Semenov SK, et al. (2006) Interference modulation in the vibrationally resolved photoionization of the $1\sigma_g$ and $1\sigma_u$ core levels of the N_2 molecule. *J Phys B: at Mol Opt Phys* 39:L261–L267.
- Fernández J, Fojón O, Martín F (2009) Double-slit, confinement and non Franck-Condon effects in photoionization of H_2 at high photon energy. *Phys Rev A* 79:023420.
- Semenov SK, Cherepkov NA (2003) Photoionization of the H_2 molecule in the random phase approximation. *J Phys B: at Mol Opt Phys* 36:1409–1422.
- Fojón OA, Fernández J, Palacios A, Rivarola RD, Mart F (2004) Interference effects in H_2 photoionization at high energies. *J Phys B: at Mol Opt Phys* 37:3035–3042.
- Rao RM, Poliakoff ED, Wang H, McKoy V (1996) Global franck-condon breakdown resulting from cooper minima. *Phys Rev Lett* 76:2666–2669.
- 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* 43:135203-1–135203-7.
- Adachi J, et al. (2003) Shape-resonance-enhanced vibrational effects in the angular distributions of C 1s photoelectrons from fixed-in-space CO molecules. *Phys Rev Lett* 91:163001.
- Jahnke T, et al. (2004) Vibrationally resolved K-shell photoionization of CO with circularly polarized light. *Phys Rev Lett* 93:083002.
- Matsumoto M, et al. (2006) Vibrationally resolved C and O 1s photoelectron spectra of carbon monoxides. *Chem Phys Lett* 417:89–93.
- Kukk E, et al. (2005) Violation of the Franck-Condon principle due to recoil effects in high energy molecular core-level photoionization. *Phys Rev Lett* 95:133001.
- Haumann M, Grundmeier A, Zaharieva I, Dau H (2008) Photosynthetic water oxidation at elevated dioxygen partial pressure monitored by time-resolved X-ray absorption measurements. *Proc Natl Acad Sci USA* 105:17384–17389.
- Arcovito A, et al. (2007) X-ray structure analysis of a metalloprotein with enhanced active-site resolution using in situ X-ray absorption near edge structure spectroscopy. *Proc Natl Acad Sci USA* 104:6211–6216.
- Ruan C-Y, Vignolotti F, Lobastov VA, Chen S, and Zewail AH (2004) Ultrafast electron crystallography: transient structures of molecules, surfaces, and phase transitions. *Proc Natl. Acad. Sci. USA* 101:1123–1128.
- Baum P, Zewail AH (2007) Attosecond electron pulses for 4D diffraction and microscopy. *Proc Natl Acad Sci USA* 104:18409–18414.
- Fernández J, Yip FL, Rescigno TN, McCurdy CW, Martín F (2009) Two-center effects in one-photon single ionization of H_2^+ , H_2 , and Li_2^+ with circularly polarized light. *Phys Rev A* 79:043409.
- Corkum PB, Krausz F (2007) Attosecond physics. *Nat Phys* 3:381–387.
- de Groot M, Field RW, Buma WJ (2009) Interference in acetylene intersystem crossing acts as the molecular analog of Young's double-slit experiment. *Proc Natl Acad Sci USA* 106:2510–2514.
- Berrah N, et al. (1999) High-resolution angle-resolved measurements in atoms and molecules using advanced photoelectron spectroscopy at the ALS. *J Elec Spec Relat Phenom* 101:1–11.
- Sánchez I, Martín F (1999) Multichannel dissociation in resonant photoionization of H_2 . *Phys Rev Lett* 82:3775–3778.
- Martin F, et al. (2007) Single photon-induced symmetry breaking of H_2 dissociation. *Science* 315:629–633.
- Laurent G, et al. (2006) Kinematically complete study of dissociative ionization of D_2 by ion impact. *Phys Rev Lett* 96:173201.
- Martin F (1999) Ionization and dissociation using B-splines: photoionization of the hydrogen molecule. *J Phys B: at Mol Opt Phys* 32:R197–R231.
- Bachau H, Cormier E, Decleva P, Hansen JE, Martín F (2001) Applications of B-splines in atomic and molecular physics. *Rep Prog Phys* 64:1815–1942.