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Michel Peters, Tung Nguyen-Dang, Christian Cornaggia, Sébastien Saugout, Eric Charron, et al..
Ultrafast Molecular Imaging by Laser Induced Electron Diffraction. 2010. hal-00521533v1

HAL Id: hal-00521533

<https://hal.science/hal-00521533v1>

Preprint submitted on 27 Sep 2010 (v1), last revised 8 Jun 2011 (v2)

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Ultrafast Molecular Imaging by Laser Induced Electron Diffraction

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(Dated: September 27, 2010)

We address the feasibility of imaging geometric and orbital structure of a polyatomic molecule on an attosecond time-scale using the Laser Induced Electron Diffraction, LIED, technique [T. Zuo *et al.*, Chem. Phys. Lett. **259**, 313 (1996)]. We present numerical results obtained for the CO₂ molecule using a single active electron model. The molecular geometry (bond-lengths) is determined within 3 % of accuracy from a diffraction pattern which also reflects the nodal properties of the initial molecular orbital. Robustness of the structure determination is discussed with respect to vibrational and rotational motions with a complete interpretation of the laser-induced mechanisms.

PACS numbers: 33.80.-b, 42.50.Hz, 34.80.Bm

With the development of attosecond laser sources [1], ultrafast molecular imaging has become a major research topic in modern physics. On one hand, attosecond laser pulses are directly used to image dynamical processes in schemes such as the attosecond pump-probe spectroscopic mapping of molecular motions [2] or the interferometric real-time observation of electronic motions [3]. On the other hand, a number of schemes have been proposed to image molecular structure which are all based on the rescattering mechanism [4–6]. As recalled schematically in the middle panels of Fig. 1, this consists of the tunnel ionization of an electron followed by its acceleration and its return by the field, to end with its recollision with the molecular ionic core. The possible outcomes of this mechanism are all relevant to molecular imaging. The elastic scattering of the returning electron with the ion core defines the LIED [7–13], which is to be opposed to ultrafast electron diffraction using an external electron source [14, 15]. Inelastic scattering of the returning electron may be accompanied by electronic excitation of the parent ion, its further ionization or the emission of high-energy radiation. This last process, High-Harmonic Generation (HHG), has been used directly as a probe or indirectly to unveil orbital and molecular structure, and even to image rotational and vibrational motions [16–22].

We wish to assess the feasibility of imaging polyatomic molecular structure (*i.e.* measuring its geometrical parameters, such as bond-lengths and/or bond-angles), on an attosecond time-scale using the LIED technique. We show how a diffraction pattern constructed from measurable photoelectron momentum distribution encodes informations on the electronic orbital nodal properties but also on the geometry of the nuclei. We assess the robustness of this two-fold structure determination procedure with respect to inevitable uncertainties about the alignment of the molecule relative to the field polarization direction, its bond lengths and angles. We consider a relatively simple model of the CO₂ molecule, the choice of

which being motivated by different considerations: Being linear in its symmetric equilibrium geometry, it is simple enough, in particular with respect to its alignment properties, yet with three nuclei, it has enough internal degrees of freedom to make its molecular structure determination challenging.

To concentrate on the problem of reading geometrical informations out of the photoelectron diffraction pattern in momentum space, we restrict our theoretical model to an effective single active electron (SAE) Hamiltonian, neglecting thus electron correlation effects. Nuclear dynamics and its coupling to the electron ionized out of a definite orbital (initial state) can be ignored at the time scale of a few-cycle pulse. Nuclear degrees of freedom are thus taken into account only through statistical distributions of bond-lengths R_{CO} and polar angles θ with respect to the laboratory y-axis along which CO₂ is supposed aligned (by a first laser pulse for instance). The intense single-cycle laser pulse, which monitors the electron dynamics, is polarized along laboratory x-axis and the essential of the electron diffraction process takes place in the (x,y)-plane, as illustrated in the upper inset of Fig. 1.

Electronic wavepackets are generated by solving the time-dependent Schrödinger equation in 2D using a third-order split operator algorithm (atomic units are used):

$$\Phi(\vec{r}, t) = U(t, t_0)\Phi(\vec{r}, t_0) \quad (1)$$

U being the unitary time evolution operator satisfying

$$i\frac{\partial}{\partial t}U(t, t_0) = H(\vec{r}, t)U(t, t_0) \quad (2)$$

with a SAE Hamiltonian of the form:

$$H(\vec{r}, t) = \frac{\vec{p}^2}{2} + V_{mol}(\vec{r}) + H_F(\vec{r}, t) \quad (3)$$

\vec{p} being the electron momentum and $V_{mol}(\vec{r})$ a soft-

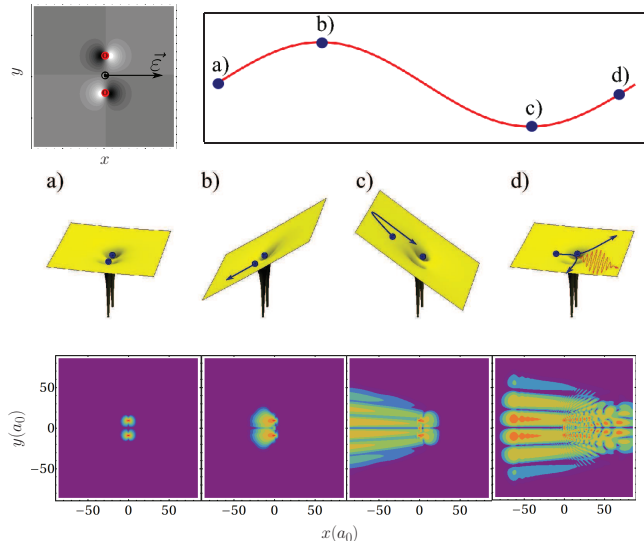


FIG. 1. Schematic view of the three-step mechanism for the electron motion in a double-well Coulomb potential as inspired from Ref. [23]. The upper part displays the HOMO of CO₂, on the left, and the time variation of the field amplitude, on the right. Panels (a) to (d) correspond to different times within the optical cycle ($\omega = 0.06$ a.u., $E = 0.15$ a.u.), as indicated by the dots on the field evolution and as discussed in the text. Corresponding approximately to the above schematic diagrams, numerical results for the time evolution of the electron wavepacket are shown on the bottom part.

Coulomb potential:

$$V_{mol}(\vec{r}) = \sum_{\alpha=1}^3 \frac{-Z_{\alpha}(\vec{r}_{\alpha})}{\sqrt{|\vec{r}_{\alpha}|^2 + a_{\alpha}^2}}, \quad \vec{r}_{\alpha} = \vec{r} - \vec{R}_{\alpha}, \quad (4)$$

with (position-dependent) effective charges Z_{α} , and softening parameters a_{α} ($\alpha = 1$ to 3, labeling the three nuclei, located at fixed position vectors \vec{R}_{α}). H_F is the electron-laser dipole coupling Hamiltonian in the length gauge:

$$H_F(\vec{r}, t) = \vec{r} \cdot \vec{\mathcal{E}}(t) \quad (5)$$

and the laser field $\vec{\mathcal{E}}(t)$ is taken as the one-cycle laser pulse:

$$\vec{\mathcal{E}}(t) = \begin{cases} \vec{\varepsilon}E \sin \omega t, & \forall t \leq T = 2\pi/\omega \\ 0, & \forall t > T = 2\pi/\omega \end{cases} \quad (6)$$

$\vec{\varepsilon}$ being the polarization vector along the x-axis. The functions $Z_{\alpha}(\vec{r}_{\alpha})$ are constructed so as to give a field-free eigenstate of the SAE Hamiltonian identifiable with one of the highest occupied molecular orbitals, HOMO- n ($n=0,1,\dots$), in the sense of giving the same ionization energy and the same nodal properties as the actual molecular orbital of the 22-electron molecule. Imaginary time

propagation of a trial function enforcing relevant symmetry properties yields the SAE wavefunction to be used as initial state.

The lower panels of Fig. 1 gather the results for the time-propagation of an initial state $\Phi(\vec{r}, t_0)$ taken as the HOMO, of B_{1g} symmetry in the D_{2h} point group, characterized by a nodal plane which is preserved through time-evolution, when the laser polarization is orthogonal to the molecular axis. Each panel depicts the wavepacket at times of the trajectory-style schematic representation given in the middle part of the figure: (a), for $t = 0$, is the field-free HOMO; (b), for $t \simeq T/4$, is the first peak intensity giving rise to ionization; (c), for $t \simeq 3T/4$, is the approximate classical turning point of the first electron wavepacket; and (d), for $(t \simeq T)$, illustrates the recollision process. The most important observations from these spatial wavefunctions are the fringes obtained during the forward ($x < 0$) motion as a signature of the two O atoms acting as electron ejection sources, on one hand, and a rich pattern of interference fringes in the backward ($x > 0$) motion resulting from the electron diffraction analogous to Young's slit experiments with photons, on the other hand.

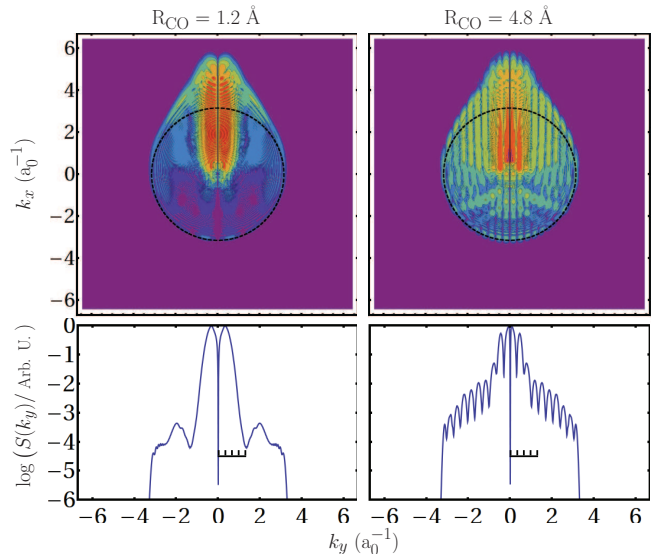


FIG. 2. Electron diffraction patterns in the momentum space (k_x, k_y) representation (upper panel) for two different interatomic distances R_{CO} under the same excitation conditions as Fig. 1. Dashed circles indicate points with final energy equal to the maximum classical recollision energy. On the lower panel, the averaged diffraction patterns are shown on a logarithmic scale normalized to the maximal value.

More relevant for structure determination is the diffraction pattern in reciprocal momentum space, accessible experimentally through time-of-flight electron velocity mapping, and defined by the Fourier transform $\Phi_A(k_x, k_y)$ of the asymptotic electron wavepacket (*i.e.*

at large $|x|$ and $|y|$, at a time also taken sufficiently large to achieve convergence). This information is shown on Fig. 2, for two different internuclear distances R_{CO} : (a) for the molecule in its equilibrium geometry and (b) for a symmetrically stretched molecule. The upper panels of Fig. 2 display the square modulus of $\Phi_A(k_x, k_y)$. The features of the momentum distribution are in agreement with the interpretation found in [10] based on classical trajectories. The lower panels show the k_x -averaged diffraction pattern:

$$S(k_y) = \int |\Phi_A(k_x, k_y)|^2 dk_x. \quad (7)$$

One notes the increase in the number of fringes counted on the $S(k_y)$ curves when stretching the molecule from $R_{\text{CO}} = 1.2 \text{ \AA}$ to 4.8 \AA : Within a typical interval of $0 < k_y < 3 \text{ a}_0^{-1}$, there are four times more fringes for $R_{\text{CO}} = 4.8 \text{ \AA}$ than for $R_{\text{CO}} = 1.2 \text{ \AA}$, as seen in Fig. 2 using the four tick marks ruler displayed therein.

This observation directly gives informations on the nuclear geometry, more specifically on the internuclear distance R_{CO} , as can be seen by the following simple symmetry considerations: The CO_2 initial orbital (HOMO) is anti-symmetric with respect to the mirror plane containing the carbon atom, and so is the electronic wavefunction at all time, assuming perfect alignment of the molecule, orthogonal to the laser polarization. It can thus be approximately written as:

$$\Phi(\vec{r}, t) \simeq f(x, y - R_{\text{CO}}) - f(x, y + R_{\text{CO}}) \quad (8a)$$

which, through Fourier transformation, gives:

$$\tilde{\Phi}(\vec{k}, t) \simeq (e^{iR_{\text{CO}}k_y} - e^{-iR_{\text{CO}}k_y}) \tilde{f}(\vec{k}) \quad (8b)$$

The squared modulus of this function behaves as $\sin^2(R_{\text{CO}} k_y)$ and exhibits zeros for $k_y = n\pi/R_{\text{CO}}$. The positions of the dark fringes are thus directly related to the internuclear distance R_{CO} and are indicated by vertical lines in Fig. 3. The local minima in the calculated spectrum $S(k_y)$ are seen to agree fairly well with these predicted positions. The complete quantitative analysis based on the wavepacket evolution within the model assumptions finally gives $R_{\text{CO}} = 1.23 \text{ \AA}$ and 4.92 \AA with a deviation of less than $\pm 3\%$ from the initial input value.

The structural reading made above of the diffraction pattern refers to a perfectly aligned molecule in a fixed nuclear geometry configuration. In reality, molecules are subject to rotations and vibrations, and these geometrical parameters are usually distributed over some range dictated by the rotational and vibrational state in which the parent molecule is initially prepared. This distribution is assumed here to be of the form:

$$D(X; \sigma) = N(\sigma) \exp\left(-\frac{X^2}{2\sigma^2}\right) \quad (9)$$

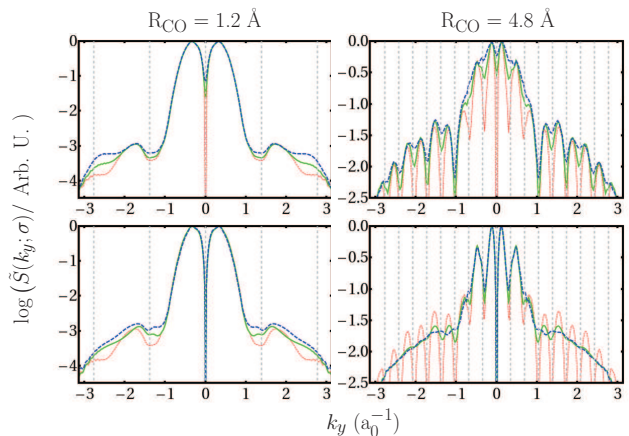


FIG. 3. Robustness study of averaged diffraction patterns under the same excitation conditions as Fig. 1. The first row shows the influence of molecular misalignment. The red (thin dotted) curve corresponds to a perfect alignment, green (thick and continuous) and blue (thick and dashed) to deviations (for 90 % of the ensemble) with $|\theta| \leq 5^\circ$ and $|\theta| \leq 10^\circ$, respectively. The second row displays the dependence on the width of R_{CO} distribution. Red (thin) curve represents the ideal case, green (thick and continuous) and blue (thick and dashed) curves are distributions with $R_{\text{CO}} \pm 0.5 \text{ \AA}$ and $R_{\text{CO}} \pm 1.0 \text{ \AA}$, respectively. Integer multiples of π/R_{CO} are shown by vertical dotted lines.

X being either θ or R_{CO} , corresponding to deviations from perfect alignment and elongations of the CO bond respectively, and σ is the associated standard deviation. The resulting (incoherently) averaged diffraction patterns:

$$\tilde{S}(k_y; \sigma) = \int dX D(X; \sigma) \int dk_x |\Phi_A(k_x, k_y; X)|^2 \quad (10)$$

are displayed in Fig. 3 for typical values of σ .

For the case of the angular deviation, we are referring to molecular post-pulse alignment efficiencies [24] by considering three values of σ . A perfect alignment scenario corresponds to $\sigma = 0^\circ$ and the zeros of its diffraction pattern are, as already mentioned, closely positioned on the expected locations (thin dashed red line in Fig. 3). We are considering two additional cases where the default to alignment is such that the molecular axis is within a cone of aperture either 10 or 20 degrees for 90 % of the molecules. This requires severe but, at least for the 20 degree aperture, still experimentally achievable alignment efficiencies. One observes a progressive contrast loss in the first row of Fig. 3, showing a high sensitivity to the alignment defect. The oscillations, although less contrasted, are still at their original ($\sigma = 0$) positions, for $|k_y|$ larger than 1 a_0^{-1} . The extraction of geometrical informations thus remains achievable in case of imperfect initial alignment of the molecular target.

To study the effect of the variation of the bond lengths R_{CO} , we considered distributions (for the two molecular geometries discussed above) with 90 % of molecules having a (symmetric) vibrational elongation within $R_{CO} \pm 0.5$ Å or $R_{CO} \pm 1.0$ Å. This corresponds to widths σ of an order of magnitude larger than that of the ground state of an harmonic oscillator describing the symmetric stretching mode. The results are gathered in the second row of Fig. 3.

The observations made above in the analysis of misalignment effect concerning the progressive loss of contrast are still valid: The zeroes remaining basically unshifted and workable for geometrical information and imaging purposes. But contrary to the case illustrated in the upper panel for which fringes within a region $|k_y| < 1$ a₀⁻¹ are rapidly washed out by the angular distribution, the sensitivity to deviations of R_{CO} from its input value is much less pronounced in this region of the scattered electron's momentum space.

This difference in sensitivity of the diffraction pattern in the small range of k_y can be easily rationalized by examining how the $\sin^2(k \cdot R_{CO})$ factor (which governs the diffraction amplitude in the present case) behaves under a small variation of θ from 0, or of R_{CO} from its input value, keeping the D_{2h} symmetry of the molecule. The same analysis as used for a misalignment situation also applies to a non symmetric variation of the two CO bond lengths, corresponding to a small amplitude vibrational motion in the antisymmetric stretch mode. Likewise, a bending motion should give the same effect as the symmetric variations of the CO bond lengths considered above. We thus expect diffraction patterns that are no less analyzable than shown in Fig. 3, and from which the CO equilibrium bond length, can be extracted unambiguously.

To conclude, we have suggested a simple and robust method to extract the molecular structure from the photoelectron spectra of a laser-driven linear, symmetric molecule. It is applicable to any sufficiently symmetric molecular system for which the HOMO, or any molecular orbital contributing dominantly to the ionization signal, has specific nodal properties that would allow for a simple interpretation of diffraction patterns. The detailed structure of the diffraction image depends on the MO from which the recolliding electron emanates, so that, in laser irradiation conditions that justify the SAE assumption, the reading gives information on orbital nodal structure as well as on the equilibrium geometry of the molecule. Also, as the acquisition process, relying on the rescattering mechanism, is faster than nuclear motions,

it can be used to produce a sequence of stroboscopic pictures, making up, for example, a movie of normal modes dynamics. The possible simultaneous contributions of other orbitals and the effect they have on the overall diffraction patterns are being explored, beyond the SAE approximation, in ongoing work at a multi-configuration level.

M.P. and T.T.N.D. acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial supports. The authors also acknowledge support from Agence Nationale de la Recherche (Project No. ANR-07-BLAN-0162-02).

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