Monitoring the Birth of an Electronic Wavepacket in a Neutral Molecule with Attosecond Time-Resolved Photoelectron Spectroscopy

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Abstract

Numerical simulations are presented to validate the possible use of cutting-edge attosecond time-resolved photoelectron spectroscopy to observe in real time the creation of an electronic wavepacket and subsequent electronic motion in a neutral molecule photoexcited by a UV pump pulse within a few femtoseconds.
CONTEXT AND OBJECTIVES

The recent emergence of attosecond extreme-ultraviolet (XUV) pulses [1, 2] has given access to observing and controlling ultrafast electronic motions in real time [3–9]. Goulielmakis and coworkers provided the first images of electronic motion in atoms using an attosecond probe pulse [7]. Such techniques have thus opened the door to studying molecular processes such as ultrafast charge migration after sudden ionisation [10, 11] and ultrafast exciton migration after creating a coherent superposition of electronic states [12–15]. Experimentally, laser control on the subfemtosecond time scale has already been evidenced on diatomic molecules: in the dissociative ionisation of the D₂ and CO molecules using the carrier envelope phase of a few-cycle pulse [16, 17] to induce charge localisation in the molecular cation; with the direct manipulation of charge oscillations in K₂ [18, 19] using selective population of dressed states within the framework of strong-field temporal control.

Attochemistry, i.e., laser control based on electronic coherence in a neutral molecule, should soon become a realistic technique, whereby the electronic motion is steered before the nuclear motion can occur and thus before intramolecular vibrational relaxation can play a role. In other words, one should now expect to possess the experimental tools for observing how chemical bonds really move in a molecular system over the course of a reaction and further control bond breaking and formation in real time. Ultrashort sources of coherent light are now approaching the few-femtosecond regime for UV laser pulses, whereas attosecond
pulses are already available in the XUV domain. One can also expect the emergence of few-cycle UV subfemtosecond pulses in a near future. However, deciphering experimental results in this context may prove challenging unless they are supported by an interpretation based on relevant numerical simulations and adequate theoretical representations.

Ozone is a well-studied small triatomic molecule which can be handled theoretically with high precision, and many theoretical and experimental data such as, e.g., photoelectron spectra or absorption cross sections are available for it. This molecule, of critical relevance for atmospheric physics and chemistry, exhibits a high absorption cross section between 200 and 300 nm followed by dissociation. This process explains the protective role of the ozone layer in the Earth atmosphere with respect to UV light from the Sun. From the experimental point of view, this also implies that ozone can be efficiently excited electronically by means of few-cycle 3rd harmonic pulses of Ti:Sa-lasers. In this UV region (called the Hartley band), the absorption is mostly due to a single electronic excited state (denoted B), such that an ultrashort UV pulse is expected to create a superposition of the electronic ground state (X) and the B state almost exclusively, thus making ozone a good candidate for observing a well-defined electronic wavepacket made of two states.

In previous works, we analysed with accurate quantum dynamics simulations the coupled electronic and nuclear motion in ozone over 25 fs after photo-excitation by a 3-fs UV pump pulse [20–22]. The time evolution of the electronic wavepacket showed a periodic transfer of electron density between the two bonds, which could be interpreted in chemical terms as an ultrafast oscillation between both mesomers of ozone (the two equivalent Lewis structures with localised charges and single or double bonds on either one or the other side of the molecule).

In the present work, we now concentrate on something different: namely, the ultrashort time scales, i.e., the very first few femtoseconds during which the electronic wavepacket is created. Our objective is to provide some critical information for the novel experiments that will observe this phenomenon in a neutral molecule for the first time [23]. In this, the pump pulse should be in the UV domain and no longer than a few femtoseconds (not to trigger the nuclear motion), while the probe pulse should be even shorter in order to observe the electronic motion with high-enough time resolution. The method of choice would thus be time-resolved photoelectron spectroscopy [24–30] using an attosecond XUV probe pulse.

However, such cutting-edge experiments may not provide clear-cut evidence for different
reasons. Many ionic channels can be accessed upon photoionising from either X or B, and a number of transitions will overlap within the same energy window. In addition, the bandwidth of the attosecond probe will be large: a few eV for a few-hundred-as pulse. This may prevent any characteristic feature in the spectrum to be observed. Preliminary numerical simulations are thus essential for future experiments in order to prove first that contributions from X or B will indeed be discriminated over time and to identify which energy window is adequate to do so. To this end, using accurate quantum dynamics and quantum chemistry calculations, we generated the time-resolved photoelectron spectrum (TRPES) expected to be observed under such conditions, as further explained below. Our results clearly show that depletion of X and production of B will be observed in two distinct energy regions, despite a large bandwidth and overlapping channels.

RESULTS AND DISCUSSION

Let us start with the photoelectron spectra obtained by photoionising from either X or B. First, assuming an “atomic” picture (whereby the rovibrational dynamics and its influence on the structure of the spectrum are ignored), the corresponding intensities appear as stick spectra (see Fig. 1a),

\[ I_k(\varepsilon) = \sum_j I_{jk} \delta(\varepsilon - \varepsilon_{jk}), \]

where \( \varepsilon \) is the kinetic energy release (KER) of the electron, with peaks centered at \( \varepsilon_{jk} = E_k + E_{ph} - E_j \), \( E_{ph} \) being the probe photon energy, and \( E_k \) and \( E_j \), the energies of the neutral molecule in state \( k = X, B \) and of the cation in state \( j \), respectively (see table I).

Assuming one-photon XUV ionisation and using the sudden approximation [31], the ionisation intensities are near-proportional to the Dyson norms at the Franck-Condon (FC) point, 

\[ I_{jk} = \langle \Phi_{jk}^D | \Phi_{jk}^D \rangle, \]

where the Dyson orbitals are defined as

\[ \Phi_{jk}^D(\vec{r}) = \sqrt{N} \int d\vec{r}_1...d\vec{r}_{N-1} \psi_k^N(\vec{r}_1,...\vec{r}_{N} = \vec{r}) \psi_{j-1}^{N-1}(\vec{r}_1,...\vec{r}_{N-1}). \]

This approximation is valid when the continuum does not exhibit a rich structure [30].

The first three states of the cation correspond to intense and narrow peaks in the photoelectron spectrum when ionising from X [32] (ionisation potentials X-1, X-2, and X-3 around 12-13 eV), thus making them good candidates for characterising the time evolution of the population of X. If ionisation also occurs from B, and accounting for an energy shift between
both states of about 6 eV, means that these three peaks may overlap with peaks corresponding to ionisation from B to cation states around 18-19 eV above X (between B-12 and B-16; see Table I). We thus limited the KER window to a lower bound of 80.8 eV for a probe photon at 95.0 eV, thus restricting \( j \) to 1, ..., 4 when ionising from X and to 1, ..., 19 from B, up to about 20 eV above X, according to the energies given in Table I. As can be observed in Fig. 1a, both spectra from X and B appear together below 83 eV (but the peaks from X dominate), whereas only B contributes above 83 eV with peaks of significant magnitude.

![Graph](image)

FIG. 1: Panel a: Stick photoelectron spectra from X (blue) or B (red) as functions of the KER for a probe photon energy \( E_{ph} = 95 \text{ eV} \) [23]; Panel b: convoluted photoelectron spectra from X (blue) or B (red).

Now, such a clear discrimination between both types of spectra could be lost once accounting for the widths of the peaks. An intrinsic width will be due to the rovibrational structure for each photoionisation channel, while the bandwidth of the probe pulse may further enlarge them. We used a probe pulse of full duration at half-maximum (FDHM) of 500 as, corresponding to a standard deviation of the intensity \( \sigma = 1.5 \text{ eV} \) in the energy domain [23]. In this context, the broadening of the spectra due to the bandwidth is far larger than that due to the rovibrational structure, thus validating the “atomic” picture as a first approximation (fixing the geometry at the FC point for determining the relative intensities of the peaks). We thus convoluted the stick spectra with a Gaussian window function of standard deviation \( \sigma \), so as to mimic the bandwidth of the XUV photoionising probe pulse,

\[
I_k(\varepsilon) = \frac{1}{\sigma \sqrt{2\pi}} \sum_j e^{-\frac{(\varepsilon - \varepsilon_{jk})^2}{2\sigma^2}} I_{jk},
\]

(3)

The resulting energy-resolved spectra are shown on [b]. Despite the strong enlargement, it is
TABLE I: Ab initio ionisation potentials and Dyson norms at the FC point with respect to either X or B (electronic structure calculations performed with the MOLPRO package at the MRCI/aug-cc-pVQZ level of theory). The energy difference between X and B is 5.78 eV. See [32] for a comparison with computed and experimental values.

| Cation states \((j)\) | \(E_j - E_X/eV\) | \(E_j - E_B/eV\) | \(I_{jX}\) | \(I_{jB}\) |
|------------------------|-----------------|-----------------|----------|----------|
| 1(\(^1^2A_1\))        | 12.38           | 6.59            | 0.60     | 0.05     |
| 2(\(^1^2B_2\))        | 12.51           | 6.72            | 0.45     | 0.07     |
| 3(\(^1^2A_2\))        | 13.20           | 7.42            | 0.63     | 0.03     |
| 4(\(^1^2B_1\))        | 14.15           | 8.36            | 0.00     | 0.00     |
| 5(\(^2^2A_2\))        | 14.45           | 8.66            | 0.00     | 0.00     |
| 6(\(^2^2B_2\))        | 15.18           | 9.40            | 0.01     | 0.07     |
| 7(\(^2^2A_1\))        | 15.58           | 9.80            | 0.00     | 0.05     |
| 8(\(^2^2B_1\))        | 16.35           | 10.56           | 0.19     | 0.36     |
| 9(\(^3^2A_2\))        | 16.50           | 10.72           | 0.00     | 0.00     |
| 10(\(^3^2B_1\))       | 17.10           | 11.32           | 0.08     | 0.07     |
| 11(\(^3^2A_1\))       | 17.32           | 11.54           | 0.20     | 0.25     |
| 12(\(^3^2B_2\))       | 17.65           | 11.87           | 0.04     | 0.23     |
| 13(\(^4^2B_2\))       | 18.19           | 12.41           | 0.01     | 0.03     |
| 14(\(^4^2A_2\))       | 18.63           | 12.85           | 0.00     | 0.00     |
| 15(\(^4^2B_1\))       | 18.61           | 12.83           | 0.00     | 0.00     |
| 16(\(^4^2A_1\))       | 19.07           | 13.29           | 0.00     | 0.01     |
| 17(\(^5^2B_2\))       | 19.61           | 13.83           | 0.03     | 0.08     |
| 18(\(^5^2A_1\))       | 19.49           | 13.70           | 0.22     | 0.08     |
| 19(\(^6^2B_2\))       | 19.94           | 14.16           | 0.19     | 0.02     |

To be expected that contributions from X and B can be discriminated below and above 83 eV, respectively.

Further, to simulate the creation of an electronic wavepacket in the neutral as a coherent superposition of X and B, we performed quantum dynamics simulations in the presence of a UV linearly-polarized Gaussian laser pump pulse with a carrier wavelength, intensity, and
FDHM at 260 nm, \(10^{13}\) W/cm\(^2\), and 3 fs, respectively [23]. In this, neither the electrons nor the nuclei were in a stationary state [20–22]. The multiconfiguration time-dependent Hartree (MCTDH) method [35, 36] was applied to solve the time-dependent nuclear Schrödinger equation within a two-electronic-state coupled representation. The potential energy surfaces and \(\vec{R}\)-dependent dipole moments occurring in the radiative coupling terms were taken from Refs. [37, 38]. The FC point \((R_1 = R_2 = 1.275 \text{ Å}; \theta = 116.9^\circ)\) has \(C_{2v}\) symmetry and, therefore, only the \(y\)-component \((B_2)\) of the transition dipole between X (\(1^1A_1\)) and B (\(1^1B_2\)) is nonzero. Thus, the only effective polarization of the electric field is \(y\).

Again, using an “atomic” picture at the FC point, we define an effective electronic wavepacket as

\[
|\psi_{el}(t)\rangle = \sum_{k=X,B} c_k(t) \left| \psi_{el}^{(k)}; \vec{R}_{FC} \right>,
\]

where \(\left| \psi_{el}^{(k)}; \vec{R}_{FC} \right\rangle\) are the adiabatic electronic states of the neutral molecule at the FC point and \(c_k(t)\) are the renormalised nuclear wavepacket components,

\[
c_k(t) = \frac{\psi_{nuc}^{(k)}(\vec{R}_{FC}, t)}{\sqrt{\sum_{l=X,B} \left| \psi_{nuc}^{(l)}(\vec{R}_{FC}, t) \right|^2}}.
\]

The corresponding local populations \((k = k')\) and coherences \((k \neq k')\) at the FC point are \(\rho_{kk'}(t) = c_k(t)c_{k'}(t)\), while the global populations are \(P_k(t) = \int \left| \psi_{nuc}^{(k)}(\vec{R}, t) \right|^2 d\vec{R}\). They are plotted on Fig. 2, assuming that \(t = 0\) corresponds to the maximum of the pump pulse (the absolute time, \(t\), is thus mapped to the time delay, \(\tau\), between the maxima of the probe and the pump). As expected, the local populations are similar to the global ones up to about \(\tau = 2\) fs, which is the focus of the present work. They further decay while the nuclear wavepackets escape the FC region, whereas the global populations stay constant.

For a stick spectrum, the intensity as a function of the time delay can be approximated as (for each cation channel):

\[
I_j(\tau) = \sum_{k=X,B} \rho_{kk}(\tau)I_{jk}.
\]

Using the same convolution procedure as above leads to the following expression for the TRPES intensity (see Fig. 3),

\[
I(\varepsilon, \tau) = \sum_{k=X,B} \rho_{kk}(\tau)I_k(\varepsilon) = \frac{1}{\sigma \sqrt{2\pi}} \sum_{k=X,B} \rho_{kk}(\tau) \sum_j e^{-\frac{(\varepsilon - \varepsilon_{jk})^2}{2\sigma^2}} I_{jk}.
\]
Two significant effects can be noticed on Fig. 3: i) around 82 eV (panel b), between $\tau = -2$ and 2 fs – while the pump pulse is on – the intensity decreases from 0.40 to 0.33 before returning to its original value; ii) around 86 eV (panel c) the intensity increases from 0.01 to 0.04 and returns to 0.01 during the same delay time intervals. Better contrast is obtained by considering the differential TRPES obtained by removing the contribution from pure X at all times (see Fig. 4) in a similar fashion to differential optical densities in transient absorption spectroscopy. The depletion of X and the concommitent production of B are clearly characterised.

The photoionisation probabilities actually depend on the molecular geometry. This should be accounted for by integrating the Dyson norms over the nuclear coordinates when estimating the TRPES for longer times. The limiting case used here would keep its validity if the Dyson norms had significant magnitudes in the FC region only and decreased fast when dissociating the molecule. One would thus observe directly the escape of the wavepacket in the decay of the TRPES signal. On the other hand, the other limiting case with homogeneous Dyson norms would yield a constant signal beyond $\tau = 2$ fs. The experimental signal is likely to be somewhere in between.

In any case, monitoring the photoelectron spectrum of such a coherent superposition of X and B as a function of the time delay is expected to yield a time-dependent pattern that should reflect depletion of X below 83 eV and production of B above 83 eV on the ultrashort time scale. Again, results for $\tau = -2$ to 2 fs are expected to be similar to experiments,
FIG. 3: Panel a: TRPES (logarithmic scale) as a function of the time delay (horizontal axis) and kinetic energy release (vertical axis); panels b and c: cuts against time at fixed energy (linear scale).

FIG. 4: Differential TRPES as a function of the time delay (horizontal axis) and kinetic energy release (vertical axis).

whereas the behaviour beyond this time will depend on how the photoionisation probability depends on the molecular geometry. Our focus here is the ultrashort time scale in the context of attophysics and the emerging attochemistry field, whereby steering directly the electrons of a molecule is expected to provide control over reaction mechanisms in a near future.
SUMMARY AND CONCLUSIONS

The central objective of this theoretical work was to determine with numerical simulations if TRPES experiments will be able to monitor the generation of an electronic wavepacket in the ozone molecule on its real time scale. Observing the electronic motion in the neutral before any significant nuclear motion requires using a few-femtosecond UV pulse as a pump. Getting high-enough time resolution implies using an XUV attosecond pulse as a probe. The main limitation of such a measurement is the poor energy resolution due to the large bandwidth of the photoionising pulse. However, we have shown that two energy regions can be distinguished: one exhibiting depletion of X and one where production of B is specifically observed. Such conclusions await further confirmation from experimental investigations.

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