Cite this: DOI: 10.1039/xxxxxxxxxx

Role of tunnel ionization in high harmonic generation from substituted benzenes

Dane R. Austin,^a Felicity McGrath,^a Lukas Miseikis,^a David Wood,^a Peter Hawkins,^b Allan S. Johnson,^a Morgane Vacher,^c Zdeněk Mašín,^d Alex Harvey,^d Misha Ivanov,^d Olga Smirnova,^d and Jon P. Marangos^a

Received Date
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

We theoretically study high-harmonic generation in toluene, ortho-xylene and fluorobenzene driven by a 1.8 μm ultrashort pulse. We find that the chemical substitutions have a strong influence on the amplitude and phase of the emission from the highest occupied molecular orbital, despite having a small influence on the orbital itself. We show that this influence is due to the tunnel ionization step, which depends critically on the sign and amplitude of the asymptotic part of the wave function. We discuss how these effects would manifest in phase-sensitive high-harmonic generation spectroscopy experiments.

1 Introduction

In high-harmonic generation (HHG) spectroscopy, strong-field ionization (SFI) creates a free electron that subsequently recombines with the cation. The emitted radiation encodes information about the cation and its evolution in the interval between ionization and recombination which is typically a fraction of a laser cycle. It has been used to probe static structure¹, nuclear motion^{2,3}, charge migration^{4,5} and molecular vibrations⁶. Most HHG spectroscopy has used atoms or small molecules (typically di- or tri-atomic) driven by near-IR laser pulses with a corresponding cation evolution duration of ≈ 3 fs. Extended to larger systems, and driven by mid-infrared laser fields, HHG spectroscopy seems promising for studying fundamental processes in photochemistry such as the coupling of electronic and nuclear dynamics^{7,8}. However, HHG involves an interplay of ionization, cation evolution and recombination in the presence of a strong laser field, and all three steps must be fully described to interpret experiments.

In molecules, SFI can create several cation eigenstates which contribute coherently to the high-harmonic emission. The initial eigenstate populations are determined by tunnel ionization rates, which are affected by the ionization potentials and the molecular geometry and orientation relative to the laser polarization. The various theories of tunnel ionization in molecules, such as MO-ADK⁹ and MO-SFA^{10–12}, all feature the same strong dependence on field strength and IP found in atomic tunnel ionization, as well as predicting that ionization will be suppressed along nodal planes of the molecular orbitals. The relative phases of the cation eigenstates have been studied in less detail. These phases may depend on electron correlations during ionization¹³ and possible tunneling delays^{14,15}, and determine the position of the hole left behind in the cation, necessary for predicting its subsequent evolution. In HHG spectroscopy, the relative phases of the cation states after ionization shape the spectrum through interference, but this must be disentangled from the propagation and recombination steps. Experiments⁴ in CO_2 found that the relative phase was consistent with a quasi-static picture of the bound-state orbital wavefunctions tunnelling through a barrier. However this view may be complicated by laser coupling of the cation states¹⁶. In this case a dressed state picture is helpful; studies in iodoacetylene⁵ found that the tunnel ionization launches the single lowest eigenstate of the cation dressed by a static electric field. Furthermore, by orienting the molecules, the effects of ionizing along the iodine or hydrogen end of molecule could be compared and found

^a Blackett Laboratory, Imperial College London, London, United Kingdom. Fax: 020 7594 7714; Tel: 020 7594 7520; E-mail: d.austin@imperial.ac.uk

^b Department of Physics, Philipps-Universität Marburg, Renthof 5, D-35032 Marburg, Germany.

^c Department of Chemistry, Imperial College London, London, United Kingdom.

^d Max-Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Berlin, Germany.

to significantly affect the subsequent population evolution driven by the laser field. The ability to selectively ionize along a given axis raises interesting possibilities for larger organic molecules, in which hydrogen atoms may be substituted by a wide range of atoms or groups.

We recently conducted an HHG spectroscopic comparison of benzene, its methyl-substituted forms toluene and the three isomers of xylene, and the singly halo-substituted fluorobenzene, bromobenzene and chlorobenzene. Benzene is particularly attractive for such a systematic scan of the available chemical substitutes because of the two highest occupied molecular orbitals (HOMOs) — which participate most strongly in HHG — only the HOMO is significantly altered by the substitution. The emission from the HOMO-1 is therefore expected to act as a reasonably stable reference. Practically speaking, benzene and its fluoro- and methyl-substituted forms have similar ionization potentials (8.45–9.25 eV), meaning that the appropriate laser intensities (those which cause sufficient ionization to observe harmonics, but do not fully deplete the ground state) are similar between the molecules, enabling comparison of harmonics measured under identical laser conditions. The boiling points of the molecules vary (from 80° to 156°) and hence achieving similar target densities requires control of the temperature as the vapour is delivered to the vacuum. Our setup¹⁷ enables rapid switching between molecules and delivery of the vapour into the vacuum through a 200 μm diameter heated nozzle. We did not attempt to align or orient the sample; instead our aim was to explore what may be learned from HHG spectroscopy in unaligned samples. Although alignment and orientation of some benzene substitutes has been demonstrated¹⁸, for many large molecules, achieving alignment/orientation in a sample of sufficient density for HHG is likely to be infeasible. One possible workaround would be to use the comparison of HHG spectra from molecules with different chemical substitutions to extract similar information to that obtained from aligned or oriented samples. A full interpretation of our unaligned experimental spectra is currently underway.

To interpret the experimental spectra, we developed a theoretical model incorporating various extensions to the strong-field approximation (SFA) appropriate for the molecules under study. Here, we exploit the ability of the SFA to unpick the steps of HHG to study the role of the substitution as a function of the relative orientation of the electric field and molecular axis. We focus on emission from the HOMO only, since it is more strongly affected by the substitution than the HOMO-1. This work is a necessary step in understanding the differences between the spectra from unaligned samples. We find that, in addition to the well known role of the photorecombination cross section¹⁹, the tunnelling step can be profoundly altered when tunnelling occurs along a substitution. This is because the substitution introduces additional outer lobes in the orbital which have opposite sign and

greater spatial extent than those of benzene. This can lead to a large phase and amplitude asymmetry between the emission caused by positive and negative half-cycles of the laser.

We discuss how the asymmetry would manifest in a phase-sensitive HHG spectroscopy experiment with oriented molecules.

This paper is structured as follows: section 2 presents the theoretical model, section 3.1 studies the asymmetries in the HHG from toluene at specific orientations which select emission from the HOMO, and section 3.2 looks at how these asymmetries manifest once all orientations are considered. Sections 3.3 and 3.4 look at ortho-xylene and fluorobenzene respectively, which provide contrasting examples of how the shape of the HOMO around the substitute group affects HHG. Section 4 gives a summary and conclusion.

2 Numerical model

We use a form of the SFA²⁰ extended to high-harmonic generation in molecules by summing coherently over multiple cation states^{4,16,21–23}. For completeness, our model also includes laser induced dynamics in the cation between ionization and recombination²⁴.

In the following, boldface symbols represent spatial vectors, and an overbar over a quantity indicates it is a vector or matrix running over the cation states. For a particular molecular orientation, the high-frequency part of the dipole response at recombination time t_r is

$$\mathbf{D}(t_r) = \int_{-\infty}^{t_r} \tau^{-3/2} e^{iS(t_r, t_i)} \bar{\mathbf{d}}_r^\dagger(\mathbf{v}(t_r)) \bar{\mathbf{U}}(t_r, t_i) \mathbf{E}(t_i) \cdot \bar{\mathbf{d}}_i(\mathbf{v}(t_i)) dt_i. \quad (1)$$

The equation is an integral over ionization times t_i and the integrand, a matrix product, can be read from right to left. The factor describing the angular dependence of the ionization rate is a column vector over cation states

$$\bar{\mathbf{d}}_i(\mathbf{v}) = (\mathbf{d}_i^{(1)}(\mathbf{v}), \mathbf{d}_i^{(2)}(\mathbf{v}), \dots)^T \quad (2)$$

where $\mathbf{d}_i^{(n)}(\mathbf{v})$ is the ionization dipole of state n for momentum $\mathbf{v}$. The usual SFA definitions²⁰ apply; the kinetic momentum is $\mathbf{v}(t) = \mathbf{p} + \mathbf{A}(t)$ where $\mathbf{p}$ is the canonical momentum of stationary phase

$$\mathbf{p} = \frac{-\int_{t_i}^{t_r} \mathbf{A}(t) dt}{\tau}, \quad (3)$$

the trajectory duration $\tau = t_r - t_i$, and $\mathbf{E}(t)$ and $\mathbf{A}(t)$ are the laser electric field and vector potential respectively. The next term in the integrand of (1) is a matrix describing evolution of the cation states under the influence of the laser field. It is the solution of

the Schrödinger equation

$$\frac{d\bar{U}(t, t_i)}{dt} = -i [\bar{I}_p - \mathbf{E}(t) \cdot \Delta\bar{\boldsymbol{\mu}}] \bar{U}(t, t_i) \quad (4)$$

$$\bar{U}(t_i, t_i) = \bar{I} \quad (5)$$

where the diagonal matrix $\bar{I}_p$ contains the ionization potentials $I_p^{(1)}, I_p^{(2)}, \dots$ on its main diagonal, $\Delta\bar{\boldsymbol{\mu}}$ is a matrix of cation state dipole couplings (the dot product $\mathbf{E}(t) \cdot \Delta\bar{\boldsymbol{\mu}}$ runs over the spatial coordinates) and $\bar{I}$ is the identity matrix. The recombination step is described in (1) by $\bar{\mathbf{d}}_r(\mathbf{v})$, a column vector of recombination dipoles in the same format as $\bar{\mathbf{d}}_i(\mathbf{v})$, and $\dagger$ denotes the conjugate transpose. Finally the scalar exponential contains the standard SFA action

$$S(t_r, t_i) = - \int_{t_i}^{t_r} \frac{(\mathbf{p} + \mathbf{A}(t))^2}{2} dt \quad (6)$$

and the $\tau^{-3/2}$ factor describes spreading of the continuum electron wavepacket.

The ionization dipole amplitude is the length-gauge plane-wave approximation

$$\mathbf{d}_i^{(n)}(\mathbf{v}) = \langle \mathbf{v} | (I - |\psi_n\rangle \langle \psi_n|) \mathbf{x} | \psi_n \rangle \quad (7)$$

where $|\psi_n\rangle$ is the Dyson orbital corresponding to cation state n . The projection operator in (7) arises from our use of the dressed form of the SFA, as described by eq. (33) of Smirnova et al.²⁵. This is necessary for invariance with respect to translation of the molecule.

For the recombination dipole, we use field-free²⁶ photorecombination cross sections when these are available; this is consistent with quantitative rescattering theory^{19,27}. The cross sections and Dyson orbitals for fluorobenzene and toluene are calculated using the R-matrix method²⁸ with modifications²⁹ that enable description of the high energy region crucial for HHG in the long-wavelength regime. We have employed the Static Exchange (i.e. Hartree-Fock) model. The calculation included a diffuse basis of continuum orbitals with angular momentum up to $L = 6$. The inclusion of the diffuse continuum functions has proved important for an accurate description of the exponential tail of the Dyson orbitals. For ortho-xylene, the photorecombination cross sections were unavailable and so we use the plane wave approximation, and focus on the role played by the tunnel ionization step. For these molecules, we used as approximate Dyson orbitals the natural orbitals (those that diagonalise the 1-electron density matrix) calculated with the complete active space self-consistent field (CASSCF) electronic structure method state-averaging (equally) over the two lowest-energy cationic eigenstates. We used the 6 π orbitals as active with the 6-31G* basis set.

Our calculations use the five lowest lying cation states. These are well approximated by a single hole in the neutral (the Koop-

man picture^{30,31}), and therefore throughout this work we equivalently refer to them by their corresponding molecular orbital. For the purposes of HHG, we checked this equivalence directly by comparing spectra in benzene, for which both the Dyson and natural orbitals were available.

The diagonal elements of the cation state dipole couplings $\Delta\bar{\boldsymbol{\mu}}$ lead to dynamic Stark shifts and equal the difference between the dipole moments of the cation states and the neutral^{32–34}. The off-diagonal elements lead to laser-driven transitions between the cation states. We calculate $\Delta\bar{\boldsymbol{\mu}}$ directly from the orbitals as

$$\Delta\bar{\boldsymbol{\mu}}_{m,n} = \langle \psi_m | \mathbf{x} | \psi_n \rangle. \quad (8)$$

The results are all within 0.04 au of transition dipoles calculated from cation state wavefunctions.

We have tested our model for invariance with respect to translation of the molecule²⁵; to this end inclusion of dynamic Stark shifts is essential. To facilitate comparison of the three steps in HHG between the molecules, we take the centroid of the benzene ring as a common origin in all calculations.

Macroscopic trajectory selection is modelled by integrating coherently across the plane of the laser focus, which is taken as spatially and temporally Gaussian. For the temporal integration we use the adiabatic approximation³⁵. The macroscopic harmonic amplitudes are taken as the amplitude of the emission on-axis ($k_\perp = 0$) and at the centre of each harmonic ($\omega = q\omega_1$), which strongly favours the short trajectories. In this approximation the spectra are independent of the laser waist size and pulse duration except for a scale factor.

3 Results and Discussion

All simulations in this work use a laser wavelength of 1.8 μm and a peak intensity of $0.3 \times 10^{14} \text{ W/cm}^2$, with coherent macroscopic averaging as described in the previous section.

We first introduce the properties of the molecular orbitals under consideration. Their ionization potentials and bonding character are given in Table 1. The HOMO and HOMO-1 of each molecule, denoted X and A , have π character. They are degenerate in benzene and split by 0.2–0.4 eV in the substituted molecules. The remaining three states have ionization potentials several electron volts higher. The HOMO and HOMO-1 dominate the HHG emission and are shown in Fig. 1 for all the molecules we consider. The figure also shows the coordinate system used throughout and the grids indicate the yz planes referenced in the discussion below. Note that the contour surfaces in Fig. 1 are drawn at the rather low value of $|\psi| = 0.02$ in order to make visible the additional lobes caused by the substitution. In fact the overall impact of the substitution on the HOMO is minor; this is shown in the left column by the projections of the electron density on to the plane of

Molecule	State/Orbital	Character	Ionization pot. (eV)
fluorobenzene	X	π	9.2
	A	π	9.8
	B	π	13.8
	C	σ	13.7
	D	σ	14.4
toluene	X	π	8.8
	A	π	9.0
	B	σ	11.2
	C	σ	11.5
	D	π	12.0
ortho-xylene	X	π	8.6
	A	π	9.0
	B	σ	11.0
	C	σ	11.2
	D	σ	11.8

Table 1 Ionization potentials and characters of the relevant cation states. These are taken from photoelectron spectra^{36–40}.

the benzene ring

$$\rho_X^{\text{proj}}(\mathbf{x}_{\parallel}) = \int |\psi_X(\mathbf{x}_{\perp}, \mathbf{x}_{\parallel})|^2 d\mathbf{x}_{\perp} \quad (9)$$

where $x_{\perp}$ and $x_{\parallel}$ are coordinates perpendicular and parallel to the benzene ring plane respectively. It can be seen that the electron density is concentrated on the benzene ring. A quantitative measure of the similarity of the HOMOs of benzene and its substituted forms is given by the cross-correlation (normalized overlap integral). This is 0.96, 0.95 and 0.98 for ortho-xylene, fluorobenzene, and toluene respectively.

The dipole coupling matrices $\Delta\bar{\mu}$ are presented in Table 2. The X and A states are only weakly polar (with respect to the neutral) and thus linear Stark shifting plays only a small role, producing a maximum energy shift of 0.3 eV in the methyl substituted species. A lower lying π orbital (B in fluorobenzene and D in toluene) is dipole coupled to X and A. At peaks of the laser field, this causes a dynamic quadratic Stark shift of the energies of these states of magnitude ≈ 0.3 eV. Because the effect is symmetric about the xy plane, it does not lead to asymmetry between molecules oriented or anti-oriented along the z axis, and so does not play a significant role here.

3.1 Toluene HOMO

We start by studying the behaviour of the emission produced by a single laser half-cycle as the molecule is rotated about an axis running through its centre perpendicular to the carbon-methyl bond. In this way, any asymmetry introduced by the presence of the methyl group can be easily detected. In the molecular frame, the electric field rotates in the yz plane indicated in Fig. 1. This

fluorobenzene					
	X	A	B	C	D
X	+0.06 $\hat{z}$	+0.12 $\hat{x}$	+1.96 $\hat{z}$		
A		+0.07 $\hat{z}$	−1.84 $\hat{x}$		
B			+0.08 $\hat{z}$		
C				+0.17 $\hat{z}$	−0.07 $\hat{x}$
D					−1.33 $\hat{z}$

toluene					
	X	A	B	C	D
X	+0.28 $\hat{z}$	+0.11 $\hat{x}$		−0.31 $\hat{z}$	+2.10 $\hat{z}$
A				+0.27 $\hat{x}$	−1.76 $\hat{x}$
B			+0.58 $\hat{z}$	−0.06 $\hat{x}$	
C				+0.78 $\hat{z}$	−0.08 $\hat{z}$
D					+0.08 $\hat{y}$ + 0.38 $\hat{z}$

o-xylene					
	X	A	B	C	D
X	+0.32 $\hat{z}$	+0.19 $\hat{x}$			−1.89 $\hat{z}$
A					+1.89 $\hat{x}$
B			+1.87 $\hat{z}$	−0.42 $\hat{x}$	
C				+2.10 $\hat{z}$	
D					−0.29 $\hat{z}$

Table 2 Dipole transitions between cation states; only components greater than 0.05 au are shown. The coordinate system is defined in Fig. 1, with the origin at the centroid of the benzene ring.

Fig. 1 Contours of $|\psi| = 0.02$ of the highest occupied molecular orbitals (middle column) and next highest orbital (right column) of the molecules considered here (rows). The grids are referred to in the text and show the plane of the laser field for the angle-dependent studies. The left column gives the projection of the electron density onto the benzene ring plane. The coordinate system used throughout is also shown in the middle.

Fig. 2 Spectral amplitude (a) and phase (b) of the attosecond burst from a single laser half-cycle in toluene with the laser field in the HOMO symmetry plane (as shown in Fig. 1); the radial direction corresponds to photon energy and the angle θ is between the ring carbon-methyl carbon bond and the direction of electron motion at ionization. The phase is plotted relative to the average over all angles (removing the angle-independent attochirp), and its color is set to grey where the amplitude is less than 1% of its maximum value. (c) Amplitude (blue, left y-axis) and phase (red, right y-axis) at 20 eV. Both y-axes have the same scale as the respective color scales in (a) and (b).

Fig. 3 Length-gauge dipole matrix element of the toluene HOMO in the orbital's symmetry plane (as shown in Fig. 1); the angle is between the direction of a departing electron and the ring carbon-methyl carbon bond.

is a nodal plane of the HOMO-1, and so emission from that orbital is forbidden. Figures 2(a) and (b) show the result in polar form; zero degrees is defined to mean the ionizing electric field is antiparallel to the carbon-to-methyl bond i.e. the electron leaves through the methyl group and passes by it upon recombination. (We adopt this convention for all monosubstituted forms. For doubly substituted ortho-xylene the reference angle is taken as the bisector of the two bonds.) The amplitude and phase is also shown at 20 eV in panel (c). We first consider the amplitude. The weak emission around the poles ($\theta = 0$ and $\theta = \pi$) is from the C orbital. Although tunnel ionization from this orbital is suppressed by its higher ionization potential, 11.3 eV, this is partially overcome by its extension along the methyl group. Since the overall contribution from this orbital is minor, we do not consider it further. The four strong lobes centred in each quadrant come from the HOMO. In the upper half-plane, corresponding to the ionization from the methyl side, the amplitude is asymmetric between positive and negative angles. This is due to one hydrogen atom of the methyl group lying in the yz plane on the right side, with the other two hydrogens of the methyl group lying above and below this plane on the left side (see Fig. 1). This asymmetry disappears after integrating over the azimuthal angle (i.e. around the ring-methyl bond axis).

Turning to the phase, shown in Fig. 2(b), there is a striking $\approx 0.6\pi$ phase difference between emission in the lower and upper half-planes. Apart from this the phase is fairly uniform in the regions of strong emission.

To dissect this result we consider the length gauge dipole matrix element, which along with the ionization potential determines the ionization step. This matrix element appears in the SFA in momentum space, but because it appears inside an oscillating integral over ionization times that approximates a Fourier transform, its characteristics in real space are just as relevant to

understanding tunnel ionization. In particular, Murray et al.⁴¹ showed that the total tunnel ionization rate with the laser electric field lying along an arbitrary direction $\hat{z}$ can be determined by semi-classical propagation starting from the (laboratory frame) molecular orbital $\psi(\mathbf{k}_\perp, z_0)$ at a plane $z = z_0$, where the point $z\hat{z}$ lies somewhere in the classically forbidden region. Here $\mathbf{k}_\perp$ is momentum in the plane perpendicular to the laser electric field. Tunnel ionization filters out components with high transverse momentum, the acceptance width of filter being proportional to $I_p^{1/2}/E$. In HHG with a linearly polarized field, the filter is even more severe because electrons emitted with non-zero transverse momentum do not recombine. Therefore, for the purposes of HHG, the angular dependence of the amplitude and phase of tunnel ionization should be well described by $\psi(\mathbf{k}_\perp = 0, z_0)$, which is simply the length gauge dipole matrix element divided by z_0 . It also represents a projection of the wavefunction onto the laser polarization axis, mapping out its spatial extent. The length gauge dipole matrix element is shown in Fig. 3 using the same geometry as in Fig. 2. It is real-valued; this follows from the definition (7) and the fact that the orbitals are real-valued. The π orbitals of the unsubstituted benzene ring appear at ≈ 2 –8 au in the lower half plane ($|\theta| > \pi/2$). In the upper half plane, the substitution causes these lobes to be concentrated at distances from ≈ 2 –5 au. Furthermore, from ≈ 6 –8 au, the lobes around the methyl group result in significant extra lobes in the dipole matrix element of opposite sign to the main central lobes. Although these lobes are weaker, they are approximately twice as distant from the centre, leading to a strong ionization enhancement. Furthermore, the electron wavepacket which tunnels from them inherits their π phase shift with respect to the main π orbitals of the ring. One therefore expects the sign of the harmonic emission to be correspondingly negated, producing an $\approx \pi$ phase shift when the electron tunnels from the methyl group side. This partially accounts for the observed phase asymmetry.

An additional source of asymmetry is caused by linear dynamic Stark shifting of the HOMO which arises due to its dipole moment of $\Delta\mu_{XX} = 0.28\hat{z}$ (Table 2). This decreases (increases) the ionization rate when the electron tunnels towards (away from) the methyl group. The resulting change in the amplitude of the HHG is $\approx 10\%$. Linear Stark shifting⁴² also causes a net phase difference between the lower and upper half cycles of

$$\Delta\phi_{\text{Stark}} = -2 \cos \theta \Delta\mu_{XX} [A(t_r) - A(t_i)]. \quad (10)$$

At 20 eV, this evaluates to $\approx -0.1\pi$, a very minor contribution.

Finally, we consider the photorecombination cross section, shown in Fig. 4. The geometry is the same as the previous plots and zero degrees is defined as the recombining electron approaching the molecule from the substitution side. Therefore Fig. 4 can be directly related to Fig. 2. The lower and upper half-planes are quite similar, with the amplitudes within $\approx 10\%$ and an $\approx -0.2\pi$

Fig. 4 (a) Amplitude and (b) phase of the photorecombination cross section of the toluene HOMO in orbital's symmetry plane (as shown in Fig. 1); the angle is between the direction from which an electron returns and the carbon-methyl bond. The phase is set to grey where the amplitude is less than 5% of its maximum value. (c) Amplitude (blue, left y-axis) and phase (red, right y-axis) at 20 eV. Both y-axes have the same scale as the respective color scales in (a) and (b).

Fig. 5 Spectral amplitude (a) and phase (b) of the attosecond burst from a single laser half-cycle in oriented toluene. The radial direction corresponds to the photon energy and the angle θ is between the ring-methyl bond axis and the direction of electron motion at ionization. Rotation of the molecule about this bond axis is averaged over. The phase is plotted relative to that of the emission from an isotropic distribution, and its color is set to grey where the amplitude is less than 1% of its maximum value. (c) Amplitude (blue, left y-axis) and phase (red, right y-axis) at 20 eV. The vertical scales match the corresponding color scales in (a) and (b).

phase difference. The methyl substitute also causes weak structures at $\theta = \pm\pi/5$, but these are not evident in the HHG emission because they do not coincide with angles of strong tunnel ionization.

We conclude that the dominant source of the phase and amplitude asymmetry seen in Fig. 2 comes from the tunnel ionization step, and that bound state propagation and photorecombination play only a minor role. We now consider how this asymmetry would manifest once all orientations of the molecule are included.

3.2 Toluene — all orbitals

We now introduce the contribution of the HOMO-1 by performing a similar calculation to that of Fig. 2 but integrating over all rotations of the molecule about the ring-methyl bond axis. In this way, all orbitals can participate, and the distribution of molecular angles is closer to what may be achieved using experimental orientation techniques that have been demonstrated with HHG^{43–45}. Figure 5 shows the spectral amplitude (a) and phase (b) of the attosecond burst as a function of the angle θ between the the ring-methyl bond and the direction of electron motion at ionization. Only $0 < \theta < \pi$ is shown; the data are symmetric about $\theta = 0$. The positive and negative half cycles of the laser therefore correspond to θ and $\pi - \theta$ respectively. The peak around

$\theta = \pi/2$ is from the HOMO-1, and those at $\theta = \pi/4, 3\pi/4$ are from the HOMO. The phase, plotted with respect to the emission from an isotropic distribution, is antisymmetric about the equator ($\theta = \pi/2$). The 0.6π phase difference between upper and lower half-planes seen in the HOMO emission (Fig. 2(b)) only appears closer to the poles ($\theta < \pi/4$) and ($\theta > 3\pi/4$). This is because near the equator, the HOMO-1 is dominant, and its emission is symmetric. Moving from the equator to the poles, there is a smooth transition from the HOMO-1 to the HOMO.

In principle, the information in Fig. 5 may be obtained experimentally. Orientation of asymmetric top molecules such as toluene can be achieved with the combination of a laser pulse and a static field^{33,46}, or a laser pulse and its second harmonic⁴⁷.

Generation of an isolated attosecond burst is possible with a near-single cycle pulse with stable carrier-envelope phase. Phase sensitive detection of the harmonics is possible using two spatially separated sources, which overlap and interfere in the far field^{48,49}. One of the sources contains the oriented sample. The other source is a reference and would contain an isotropic distribution.

An experimental alternative to directly producing an single attosecond burst with to examine the even and odd harmonics produced by a multi-cycle laser pulse. The combination of molecular orientation — a macroscopic asymmetry — and an asymmetric dependence on the angle between the molecular axis and the electric field — microscopic asymmetry — leads to the emission of even harmonics^{44,45}. This is because the macroscopic emissions from successive half cycles of the laser are no longer identical, rather than being identical except for a π phase shift as is the case when only odd harmonics are present. Measurements of the even harmonics, coupled with knowledge of the degree of orientation, allows the microscopic asymmetry to be inferred⁴⁴. In general, the asymmetry will be in both amplitude and phase, and therefore the even harmonics must be measured with a phase sensitive technique. This contrasts with previous reconstructions in which only the amplitudes of the even harmonics were measured; additional information was required from theoretical ionization rates and photorecombination cross sections^{5,44}. Even harmonics can be produced in the reference source by adding the second harmonic of the drive laser^{50,51}, which breaks the odd symmetry of the positive and negative half cycles. Note that although the phase of the reference does not need to be characterized, the relative phase between its even and odd harmonics must be known. Since odd and even harmonics cannot be directly compared, it is worth being precise on the exact meaning of this requirement. The even and odd harmonics, taken separately, each define functions on a common continuous temporal domain via the continuous time Fourier transform. These functions have odd or even periodicity with period $T/2$. Provided the functions decay to zero at some point within a period, a temporal window function may

be applied to isolate a single period. Fourier transforming the functions yields two continuous spectral amplitudes $D_o(\omega)$ and $D_e(\omega)$, which may be directly compared. Knowledge of their relative phase is equivalent to knowing the relative phase of the even and odd harmonics. The sum and difference of $D_o(\omega)$ and $D_e(\omega)$ correspond to the attosecond bursts from positive and negative half cycles respectively, which we denote $D_+(\omega)$ and $D_-(\omega)$. An alternative way of stating the requirement is that the (complex-valued) ratio $r = D_+(\omega)/D_-(\omega)$ be known. For weak second harmonic field strengths, this ratio can be obtained theoretically from a first-order perturbation to the action integral^{50,51}, and it likely that combining the perturbative model with a calibration measurement will allow r to be well characterized across the spectrum.

Experimental considerations aside, Fig. 6 shows the amplitude and phase of the odd and even harmonics in oriented toluene. These correspond to sums and differences of the attosecond bursts from positive and negative half cycles of the laser. Only $0 < \theta < \pi/2$ is shown; the odd (even) harmonics are symmetric (antisymmetric) about $\theta = \pi/2$. In the odd harmonics, the contribution from the HOMO-1 (at $\theta = \pi/2$) is slightly stronger than that from the HOMO (at $\theta \approx \pi/4$). The phase of the odd harmonics is nearly constant with angle, except at low $\theta \approx 0$ where there is a contribution from the C orbital. The even harmonics arise solely from the HOMO and are peaked at $\theta \approx \pi/4$. Their phase, relative to that of the odd harmonics, is $\approx -\pi/2$. This reflects the fact that the asymmetry between positive and negative half cycles is in the amplitude and the phase; an amplitude-only asymmetry would produce even harmonics exactly in or out of phase with the odd harmonics.

3.3 Ortho-xylene HOMO

We now return to the HOMO-only geometry used in section 3.1 (i.e. with the electric field in the nodal plane of the HOMO-1) and consider some different molecules. Figure 7 shows the spectral amplitude and phase of the attosecond burst produced in ortho-xylene in the same format as Fig. 2. The photorecombination cross section was not available for this molecule so we used the plane wave approximation. The amplitude asymmetry is very pronounced, with the emission when tunnelling through the methyl substitutes almost double that through the π orbitals of the benzene ring on the opposite side of the molecule. The phase difference between the half planes $\approx 0.7\pi$.

As with section 3.1, we dissect this result by examining the three steps. The length gauge dipole for the ortho-xylene HOMO (not shown) looks very similar to that of toluene (Fig. 3), except that the lobes produced by the substitution have approximately twice the amplitude. This explains why the emission is stronger in the upper half plane. The HOMO also has ungerade symmetry about xz plane, and this appears as symmetry about $\theta = 0$. Tun-

Fig. 6 Spectral amplitude (top row) and phase (bottom row) of the odd (left column) and even (right column) harmonics produced by a many-cycle laser pulse in oriented toluene. The radial direction corresponds to the photon energy and the angle θ is between the ring-methyl bond axis and the direction of electron motion at ionization. Rotation of the molecule about this bond axis is averaged over. The phase of the even harmonics is shown relative to that of the odd harmonics, and the phase of the odd harmonics is shown relative to that produced by an isotropic distribution. In the phase plots, the color is set to grey where the amplitude is less than 1% of its maximum value. Within each row, the color scale is common to both plots. (c) Amplitude (blue, left y-axis) and phase (red, right y-axis) of the odd (solid) and even (dashed) harmonics at 20 eV.

nelling from the substitution side also produces $\approx \pi$ phase shift, as with toluene. Linear Stark shifting, eq. (10), contributes a phase difference -0.1π and, as with toluene, decreases (increases) the ionization rate when the electron tunnels towards (away from) the methyl group by about 10%. This partially offsets the increased ionization rate when ionizing towards the methyl groups. The plane wave recombination matrix elements are almost entirely unaffected by the substitution, with a phase and amplitude differences of less than 0.1π and 5% respectively between the two directions. Based on the result from toluene and fluorobenzene below, it is likely any asymmetry in the photorecombination matrix element will be similarly small. We tentatively conclude that, as with toluene, the dominant source of amplitude and phase asymmetry in emission from the ortho-xylene HOMO comes from the presence of the lobes around the methyl group which boost the amplitude of tunnel ionization and change its sign.

3.4 Fluorobenzene HOMO

We now consider emission from the fluorobenzene HOMO under identical conditions to the previous section. Fluorobenzene is a revealing example because the shape of the HOMO is very similar to that of toluene, except that the lobes around its fluorine atom are more concentrated than those around the methyl group in toluene. Its length gauge dipole is shown in Fig. 8. As with toluene, the main lobes of the π orbitals on the benzene ring are more concentrated on the substitute side ($2-4$ au in $|\theta| < \pi/2$) compared to the unmodified side ($2-8$ au in $|\theta| > \pi/2$). Unlike in toluene, there are no additional lobes on the substitute side. This is because the orbital is concentrated around the fluorine atom rather than spread around a methyl group. Following the reasoning in section 3.1, we expect tunnel ionization and HHG to be suppressed on the substitute side, but without a phase change. Figure 9 shows the attosecond burst as a function of angle (in the same format as Figures 2 and 7), and this is indeed what the calculation predicts. The amplitude, shown in panel (a), is suppressed by a factor ≈ 4 when the electron leaves from the fluorine side ($|\theta| < \pi/2$). The spectral shape and angular dependence are otherwise similar to the opposite orientation. The phase of positive and negative half cycles is equal to within 0.1π .

4 Summary and conclusion

Using a multichannel model for high harmonic generation incorporating strong field ionization at the level of SFA, laser-induced dynamics and recombination using the input from ab-initio R-matrix calculations, we explored the effect of fluorine and methyl substitutions on HHG in various derivatives of benzene. We found that despite these substitutions having only a minor influence on the overall shape of the HOMO, they dramatically alter the emission in oriented molecules, causing a strong asymmetry in the amplitude and phase between molecules oriented and anti-

Fig. 7 Spectral amplitude (a) and phase (b) of the attosecond burst from a single laser half-cycle in ortho-xylene with the laser field in the HOMO symmetry plane (as shown in Fig. 1); the radial direction corresponds to photon energy and the angle θ is between the bisector of the two ring-methyl bonds and the direction of electron motion at ionization. The phase is plotted relative to the average over all angles (removing the angle-independent attochirp). (c) Amplitude (blue, left y-axis) and phase (red, right y-axis) at 20 eV. Both y-axes have the same scale as the respective color scales in (a) and (b).

Fig. 8 Length-gauge dipole matrix element of the fluorobenzene HOMO in the orbital's symmetry plane (as shown in Fig. 1); the angle is between the direction of a departing electron and the carbon-fluorine bond.

oriented to the laser polarization. In particular, the additional lobes in the orbital wavefunction produced by methyl group substitutions were shown to cause a sign flip in the tunnelled electron wavepacket, which is mapped directly into the high-harmonic emission. We discussed how this asymmetry would manifest itself in a phase- and alignment-sensitive HHG spectroscopy experiment. These insights will also enable us to better understand and make quantitative comparison with our existing measurements in isotropic samples.

5 Acknowledgements

We acknowledge the support from Engineering and Physical Sciences Research Council (UK) (EPSRC) grant EP/I032517/1 and the European Research Council (ERC) ASTEX project 290467. ZM and OS acknowledge DFG grant Sm 292/5-1. AH and MI gratefully acknowledge DFG grant DFG IV 152/7-1. DRA acknowledges support from the Imperial College Junior Research Fellowship scheme.

References

- 1 J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pepin, J. C. Kieffer, P. B. Corkum and D. M. Villeneuve, *Nature*, 2004, **432**, 867–871.
- 2 S. Baker, J. S. Robinson, C. A. Haworth, H. Teng, R. A. Smith, C. C. Chirilă, M. Lein, J. W. G. Tisch and J. P. Marangos, *Science*, 2006, **312**, 424–427.
- 3 S. Baker, J. S. Robinson, M. Lein, C. C. Chirilă, R. Torres, H. C. Bandulet, D. Comtois, J. C. Kieffer, D. M. Villeneuve, J. W. G. Tisch and J. P. Marangos, *Phys. Rev. Lett.*, 2008, **101**, 053901.
- 4 O. Smirnova, Y. Mairesse, S. Patchkovskii, N. Dudovich, D. Villeneuve, P. Corkum and M. Y. Ivanov, *Nature*, 2009, **460**, 972–977.
- 5 P. M. Kraus, B. Mignolet, D. Baykusheva, A. Rupenyan, L. Horný, E. F. Penka, G. Grassi, O. I. Tolstikhin, J. Schnei-

Fig. 9 Amplitude (a) and phase (b) of attosecond burst produced by a single laser half-cycle in fluorobenzene with the laser field in the HOMO symmetry plane (as shown in Fig. 1); the radial direction corresponds to photon energy and the angle θ is between the carbon-fluorine bond and the direction of electron motion at ionization. The phase is plotted relative to the average over all angles (removing the angle-independent attochirp), and its color is set to grey where the amplitude is less than 1% of its maximum value. (c) Amplitude (blue, left y-axis) and phase (red, right y-axis) at 20 eV. Both y-axes have the same scale as the respective color scales in (a) and (b).

- der, F. Jensen, L. B. Madsen, A. D. Bandrauk, F. Remacle and H. J. Wörner, *Science*, 2015, **350**, 790–795.
- 6 A. Ferre, A. E. Boguslavskiy, M. Dagan, V. Blanchet, B. D. Bruner, F. Burgy, A. Camper, D. Descamps, B. Fabre, N. Fedorov, J. Gaudin, G. Geoffroy, J. Mikosch, S. Patchkovskii, S. Petit, T. Ruchon, H. Soifer, D. Staedter, I. Wilkinson, A. Stolow, N. Dudovich and Y. Mairesse, *Nat. Commun.*, 2015, **6**, 5952.
  - 7 J. P. Marangos, *J. Phys. B: At., Mol. Opt. Phys.*, 2016, **49**, 132001.
  - 8 S. Haessler, J. Caillat and P. Salières, *J. Phys. B: At., Mol. Opt. Phys.*, 2011, **44**, 203001.
  - 9 X. M. Tong, Z. X. Zhao and C. D. Lin, *Phys. Rev. A*, 2002, **66**, 033402.
  - 10 J. Muth-Böhm, A. Becker and F. H. M. Faisal, *Phys. Rev. Lett.*, 2000, **85**, 2280–2283.
  - 11 T. K. Kjeldsen, C. Z. Bisgaard, L. B. Madsen and H. Stapelfeldt, *Phys. Rev. A*, 2003, **68**, 063407.
  - 12 T. K. Kjeldsen and L. B. Madsen, *J. Phys. B: At., Mol. Opt. Phys.*, 2004, **37**, 2033.
  - 13 C. F. de Morisson Faria and X. Liu, *J. Mod. Opt.*, 2011, **58**, 1076–1131.
  - 14 P. Eckle, A. N. Pfeiffer, C. Cirelli, A. Staudte, R. Dörner, H. G. Muller, M. Büttiker and U. Keller, *Science*, 2008, **322**, 1525–1529.
  - 15 L. Torlina, F. Morales, J. Kaushal, I. Ivanov, A. Kheifets, A. Zielinski, A. Scrinzi, H. G. Muller, S. Sukiasyan, M. Ivanov and O. Smirnova, *Nat Phys*, 2015, **11**, 503–508.
  - 16 Y. Mairesse, J. Higuier, N. Dudovich, D. Shafir, B. Fabre, E. Mével, E. Constant, S. Patchkovskii, Z. Walters, M. Y. Ivanov and O. Smirnova, *Phys. Rev. Lett.*, 2010, **104**, 213601.
  - 17 F. McGrath, A. S. Johnson, L. Miseikis, D. Wood, P. Hawkins, D. Austin and J. P. Marangos, *Manuscript in preparation*, 2016.
  - 18 J. L. Hansen, L. Holmegaard, J. H. Nielsen, H. Stapelfeldt, D. Dimitrovski and L. B. Madsen, *J. Phys. B: At., Mol. Opt. Phys.*, 2012, **45**, 015101.
  - 19 A.-T. Le, R. R. Lucchese, S. Tonzani, T. Morishita and C. D. Lin, *Phys. Rev. A*, 2009, **80**, 013401.
  - 20 M. Lewenstein, P. Balcou, M. Y. Ivanov, A. L’Huillier and P. B. Corkum, *Phys. Rev. A*, 1994, **49**, 2117–2132.
  - 21 O. Smirnova, S. Patchkovskii, Y. Mairesse, N. Dudovich, D. Villeneuve, P. Corkum and M. Y. Ivanov, *Phys. Rev. Lett.*, 2009, **102**, 063601.
  - 22 O. Smirnova, S. Patchkovskii, Y. Mairesse, N. Dudovich and M. Y. Ivanov, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 16556–16561.
  - 23 O. Smirnova and M. Ivanov, in *Multielectron High Harmonic Generation: Simple Man on a Complex Plane*, Wiley-VCH Ver-

- lag GmbH & Co. KGaA, 2014, pp. 201–256.
- 24 A. Etches and L. B. Madsen, *J. Phys. B: At., Mol. Opt. Phys.*, 2010, **43**, 155602.
  - 25 O. Smirnova, M. Spanner and M. Ivanov, *J. Mod. Opt.*, 2007, **54**, 1019–1038.
  - 26 O. Smirnova, A. S. Mouritzen, S. Patchkovskii and M. Y. Ivanov, *J. Phys. B: At., Mol. Opt. Phys.*, 2007, **40**, F197.
  - 27 C. D. Lin, A.-T. Le, Z. Chen, T. Morishita and R. Lucchese, *J. Phys. B: At. and Mol. Opt. Phys.*, 2010, **43**, 122001.
  - 28 A. G. Harvey, D. S. Brambila, F. Morales and O. Smirnova, *J. Phys. B: At., Mol. Opt. Phys.*, 2014, **47**, 215005.
  - 29 D. S. Brambila, A. G. Harvey, Z. Mažín, J. D. Gorfinkiel and O. Smirnova, *J. Phys. B: At., Mol. Opt. Phys.*, 2015, **48**, 245101.
  - 30 B. H. Bransden and C. J. Joachain, *Physics of atoms and molecules*, Prentice Hall, 2003.
  - 31 T. Koopmans, *Physica*, 1934, **1**, 104 – 113.
  - 32 D. Dimitrovski, C. P. J. Martiny and L. B. Madsen, *Phys. Rev. A*, 2010, **82**, 053404.
  - 33 L. Holmegaard, J. L. Hansen, L. Kalhoj, S. Louise Kragh, H. Stapelfeldt, F. Filsinger, J. Kupper, G. Meijer, D. Dimitrovski, M. Abu-samha, C. P. J. Martiny and L. Bojer Madsen, *Nat. Phys.*, 2010, **6**, 428–432.
  - 34 H. Li, D. Ray, S. De, I. Znakovskaya, W. Cao, G. Laurent, Z. Wang, M. F. Kling, A. T. Le and C. L. Cocke, *Phys. Rev. A*, 2011, **84**, 043429.
  - 35 K. Varjú, Y. Mairesse, P. Agostini, P. Breger, B. Carré, L. J. Frasinski, E. Gustafsson, P. Johnsson, J. Mauritsson, H. Merdji, P. Monchicourt, A. L'Huillier and P. Salieres, *Phys. Rev. Lett.*, 2005, **95**, 243901.
  - 36 K. Kimura, *Handbook of HeI photoelectron spectra of fundamental organic molecules: ionization energies, ab initio assignments, and valence electronic structure for 200 molecules*, Japan Scientific Societies Press, 1982.
  - 37 M. Klessinger, *Angewandte Chemie International Edition in English*, 1972, **11**, 525–526.
  - 38 T. Koenig, M. Tuttle and R. Wielesek, *Tetrahedron Lett.*, 1974, **15**, 2537 – 2540.
  - 39 K. Kesper, N. Münzel, W. Pietzuch, H. Specht and A. Schweig, *J. Mol. Str.: THEOCHEM*, 1989, **200**, 375 – 400.
  - 40 J. A. Sell and A. Kuppermann, *Chemical Physics*, 1978, **33**, 367 – 378.
  - 41 R. Murray, M. Spanner, S. Patchkovskii and M. Y. Ivanov, *Phys. Rev. Lett.*, 2011, **106**, 173001.
  - 42 A. Etches, M. B. Gaarde and L. B. Madsen, *Phys. Rev. A*, 2011, **84**, 023418.
  - 43 E. Frumker, C. T. Hebeisen, N. Kajumba, J. B. Bertrand, H. J. Wörner, M. Spanner, D. M. Villeneuve, A. Naumov and P. B. Corkum, *Phys. Rev. Lett.*, 2012, **109**, 113901.
  - 44 E. Frumker, N. Kajumba, J. B. Bertrand, H. J. Wörner, C. T. Hebeisen, P. Hockett, M. Spanner, S. Patchkovskii, G. G. Paulus, D. M. Villeneuve, A. Naumov and P. B. Corkum, *Phys. Rev. Lett.*, 2012, **109**, 233904.
  - 45 P. M. Kraus, A. Rupenyan and H. J. Wörner, *Phys. Rev. Lett.*, 2012, **109**, 233903.
  - 46 B. Friedrich and D. Herschbach, *J. Chem. Phys.*, 1999, **111**, 6157–6160.
  - 47 S. De, I. Znakovskaya, D. Ray, F. Anis, N. G. Johnson, I. A. Bocharova, M. Magrakvelidze, B. D. Esry, C. L. Cocke, I. V. Litvinyuk and M. F. Kling, *Phys. Rev. Lett.*, 2009, **103**, 153002.
  - 48 R. Zerne, C. Altucci, M. Bellini, M. B. Gaarde, T. W. Hänsch, A. L'Huillier, C. Lyngå and C.-G. Wahlström, *Phys. Rev. Lett.*, 1997, **79**, 1006–1009.
  - 49 Bellini, M., Lyngå, C., Tozzi, A., Gaarde, M. B., Hänsch, T. W., L'Huillier, A., Wahlström and C.-G., *Phys. Rev. Lett.*, 1998, **81**, 297–300.
  - 50 N. Dudovich, O. Smirnova, J. Levesque, Y. Mairesse, M. Y. Ivanov, D. M. Villeneuve and P. B. Corkum, *Nat. Phys.*, 2006, **2**, 781–786.
  - 51 J. M. Dahlström, A. L'Huillier and J. Mauritsson, *J. Phys. B: At. Mol. Opt. Phys.*, 2011, **44**, 095602.