

PAPER • OPEN ACCESS

High-harmonic and terahertz wave spectroscopy (HATS) for aligned molecules

To cite this article: Yindong Huang *et al* 2016 *J. Phys. B: At. Mol. Opt. Phys.* **49** 235601

View the [article online](#) for updates and enhancements.

You may also like

- [HATS-31B THROUGH HATS-35B: FIVE TRANSITING HOT JUPITERS DISCOVERED BY THE HATSOUTH SURVEY](#)

M. de Val-Borro, G. Á. Bakos, R. Brahm et al.

- [HATS-50b through HATS-53b: Four Transiting Hot Jupiters Orbiting G-type Stars Discovered by the HATSouth Survey](#)

Th. Henning, L. Mancini, P. Sarkis et al.

- [HATS-47b, HATS-48Ab, HATS-49b, and HATS-72b: Four Warm Giant Planets Transiting K Dwarfs](#)

J. D. Hartman, Andrés Jordán, D. Bayliss et al.



Easy-to-use and Helium-3 free
cryogenics solutions

LEARN MORE

High-harmonic and terahertz wave spectroscopy (HATS) for aligned molecules

Yindong Huang¹, Chao Meng¹, Jing Zhao¹, Xiaowei Wang¹, Zhihui Lü¹, Dongwen Zhang¹, Jianmin Yuan^{1,2} and Zengxiu Zhao¹

¹Department of Physics, College of Science, National University of Defense Technology, Changsha 410073, Hunan, People's Republic of China

²IFSA Collaborative Innovation Center, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

E-mail: jmyuan@nudt.edu.cn and zhao.zengxiu@gmail.com

Received 22 June 2016, revised 19 September 2016

Accepted for publication 14 October 2016

Published 14 November 2016



Abstract

We present the experimental and theoretical details of our recent published letter Huang *et al* (2015 *Phys. Rev. Lett.* **115** 123002) on synchronized high-harmonic and terahertz-wave spectroscopy (HATS) from nonadiabatically aligned nitrogen molecules in dual-color laser fields. By associating alignment-angle dependent terahertz wave generation (TWG) with high harmonic generation (HHG), the angular differential photoionization cross section (PICS) for molecules can be reconstructed. The angles at which the PICS's minima are located show great convergence between the theoretical predictions and the experimentally deduced results when choosing a suitable internuclear distance. We also show the optimal relative phase between the dual-color laser fields for TWG does not change with the alignment angle at a precision of about 50 attoseconds. This all-optical method provides an alternative for investigating molecular structures and dynamics.

Keywords: high harmonic generation, HATS, orbital imaging, terahertz wave generation

(Some figures may appear in colour only in the online journal)

1. Introduction

Recent advances in laser science have shed new light on the real-time observation and manipulation of the atomic-scale motion of electrons [1]. Taking advantage of the quantum coherence of ultrafast dynamics, ionization, vibrational excitation, band transition and resonance have been traced via modulating the interference between the related quantum pathways for atoms [2–5], molecules [6, 7] or solids [8, 9].

Complete measurements are desired to obtain the full aspects of the dynamics in strong laser fields. So far more than one physical quantity has been measured in coincidence such as ionic fragmentation, electrons or photons. In our previous work, we demonstrated that synchronized high-

harmonics and terahertz-wave spectroscopy (HATS) [3, 10, 11] provides correlated information of terahertz wave generation (TWG) and high-harmonic generation (HHG), which have timescales that differ by more than six orders of magnitude. In the HATS setup, a weak second harmonic field is applied to detune the HHG and TWG from gases by the fundamental pulse. The interference of the radiation between the consecutive half-cycle of the fundamental laser field is controlled by varying the phase-delay between the dual-color fields. It is found that the second harmonic helps to generate even-order harmonics [2] and dramatically enhances the TWG [12]. By monitoring the modulation of HHG and TWG, the information on both radiation and the underlying dynamics can be identified.

Utilizing the HATS technique, the unified picture for TWG and HHG, originating from the rescattering model [13], has been drawn by taking account of the Coulomb force on the continuum electrons [3, 10, 14, 15]. The freed electrons may directly escape or be rescattered from the parent core in



Original content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](https://creativecommons.org/licenses/by/3.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

the oscillating laser field. Due to the Coulomb force acting on the electrons, the photocurrent generated by direct escape is suppressed while that generated from rescattering is enhanced, in comparison with the atomic field-free cases. It has been shown that the rescattering can be further classified as hard collision or soft collision where the former contributes to HHG while the latter dominates TWG.

According to the quantitative rescattering (QRS) theory [16], alignment-dependent HHG from molecules can be viewed as the product of the alignment-dependent ionization rates (AIRs) and the recombination matrix elements. However, the ionized electrons contributing to TWG show less dependence on the spatial distributions once ionized, thus making the alignment-dependent TWG a good measurement object to calibrate the AIRs [15]. Therefore, the angular differential photoionization cross section (PICS) can be deduced from the synchronized angular HATS, due to the principle of the detailed balance between the angular recombination cross section and the PICS. Recently, this idea was tested by reconstructing the angular PICS of a nitrogen molecule, which showed great consistency between our recent experimental results [11] and the theoretical calculations [17].

In this paper, we provide more experimental and theoretical details on the HATS technique for a nitrogen molecule. Meanwhile, we also show that the optimal dual-color relative phase (DRP) for TWG does not change at different alignments in a precision of about 50 as. The DRP induced modulations for terahertz yields from aligned, antialigned and isotropic nitrogen are all similar to the results from an argon atom. Therefore, more precise time domain modulation may be required to directly observe the differences of the optimal phase-delay of terahertz yields from different aligned angles of molecules, due to the angular dependence of the atomic potential [15].

This article is organized as follows. In section 2, we describe our experimental setup in detail. The theory is presented in section 3. In section 4, we show the experimental results and the corresponding discussions. Section 5 contains the conclusions and outlooks.

2. Experimental technology

The schematic of the HATS is sketched in figure 1. Utilizing dual-color fields on aligned molecules, HHG and TWG can be simultaneously measured in one run. The detailed light path has been reported [11].

The experimental setup consists of a 790 nm, 25 fs, 1.5 mJ, 1 kHz Ti:sapphire laser (femtolasers) and a vacuum chambers for HATS. The laser beam is split into three pulses for preparing aligned molecules, generating HATS and recording the terahertz waveform, respectively.

The alignment pulse prepares the transiently aligned molecules. A half-wave plate is inserted in this light path to change the polarization, in order to vary the alignment angle of molecules. A beam shutter is also placed to continuously turn the alignment pulse on or off, monitoring the long-term

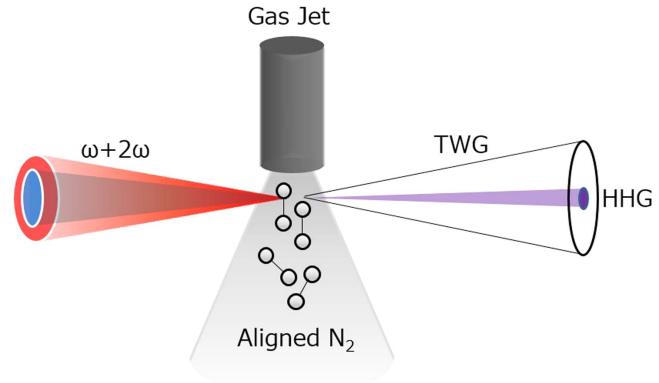


Figure 1. Schematic of the HATS from aligned nitrogen.

stability of the laser intensity and real-time comparing the yields with or without the alignment pulse. By dividing the yields with the alignment pulse to the ones from the isotropic gas, the relative values of HHG or TWG can be obtained, improving the signal-to-noise rate for long laser operation times. The generation pulse passes through a 30 μm β -barium borate crystal (type I) to introduce its second harmonic. The group velocity dispersion of the dual-color field is compensated by a calcite plate and their polarizations are rotated to be parallel by a dual-wavelength wave plate. Owing to the minor differences on the phase velocity between the fundamental pulse and its second harmonic, minor manipulation (about 50 as) on the DRP can be fulfilled by precisely adjusting the transmission length of a pair of fused silica wedges. The time delay (t_d) between the alignment pulse and the generation pulse is controlled by a stepper motor (Newport M-MTM250PP).

The alignment pulse and generation pulse are focused ~ 0.2 mm below and 2 mm before the orifice of the continuous gas jet (0.2 mm in diameter), whose intensities in the interaction area are estimated to be $0.7 \times 10^{14} \text{ W cm}^{-2}$ and $1.5 \times 10^{14} \text{ W cm}^{-2}$, respectively. A concave coated silver mirror is applied in focusing the dual-color generation pulse. A homemade gas jet, prepared by a laser-cut capillary, provides a supersonic expansion of gas with 1 bar backing pressure. The background pressure in the vacuum chamber is typically 10^{-3} mbar with gas supply (10^{-5} mbar without).

A hole-drilled off-axis parabolic mirror reflects the TWG and leaks the HHG at the same time. The harmonics pass through the hole and are recorded by a homemade spectrometer containing a flat field grating and an x-ray CCD camera. The TWG is collinearly focused with the terahertz wave detection pulse through a 1 mm thick (110)-cut ZnTe crystal for electro-optic sampling (EOS) the terahertz waveform. The high-harmonic spectra and terahertz waveforms from aligned and antialigned nitrogen molecules in experiment are present in figure 2. Each high harmonic spectrum is typically acquired by accumulating 10000 laser shots. It takes 300 ms integration time to obtain one point of the terahertz waveform and the standard dynamic range of terahertz detection in our experiment ranges from 40 to 120 dB. Although we do not know the absolute flux of harmonics of different order, the

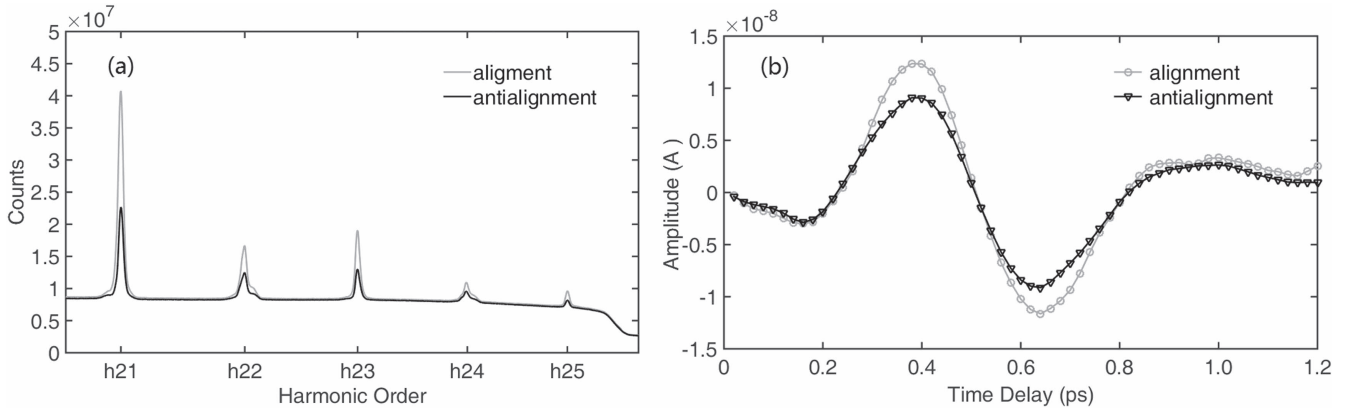


Figure 2. High-harmonic spectra (a) and terahertz waveform (b) recorded at alignment (gray line) and antialignment (black line) moment of nitrogen. The gray cycles and the black triangles in (b) are the data points acquired from the EOS method.

same order harmonic shares the same transition probability of aluminum foil, the same reflection index of grating and the same quantum efficiency of CCD, which makes it possible to compare the angular or temporal properties of each single order of harmonic.

When retrieving the PICSSs of nitrogen during the experiment, the dual-color relative phase of the two-color pulse is fixed at where the TWG yields are maximized to enhance the signal-to-noise ratio for THz wave detection. We have examined optimal DRPs for TWG for nitrogen at the moments when the molecular ensembles are aligned and antialigned. It is found that the optimal DRPs are nearly the same. The same optimal DRPs are found for TWG from isotropic nitrogen molecules and argon atoms as well.

3. Theory

With the assumption of the Born–Oppenheimer approximation, the electronic and nuclear motions can be treated separately. The nuclear movement include the forms of vibration and rotation, while in this paper we only consider the rotation motion. This assumption has been widely applied in modeling the high harmonics from aligned molecules. The influence of terahertz waves on the permanent dipole may affect the rotational wave packet for polar molecules [18, 19], but in our experiment, this can be neglected for the nonpolar property of nitrogen and the weak terahertz wave intensity. Here, the TWG from aligned nitrogen molecules is assumed to be mainly determined by the ionization rates at the generating moment.

Therefore, the measured signals of HHG as well as TWG can be reconstructed by two independent parts, namely the rotation of molecules and the dynamics of electrons. In this section, we present details of obtaining the molecular structures and uncovering the underlying physics.

3.1. Non-adiabatical molecular alignment

The linear molecules can be aligned via ‘kicking’ by the femtosecond laser pulse [20]. Molecules with thermal

distributions of rotational states are coherently excited to form the broad rotational wave packet by the Raman transitions between different angular quantum numbers. This rotational wave packet revives the transient alignment condition several picoseconds after the alignment pulse.

The initial rotational wave packet of the molecules is given by the Boltzmann law at different angular momentum quantum number J and its projection M . Stimulating by the alignment laser field, the transition between different rotational eigenstates can be revealed by solving the time dependent Schrödinger equation, which is the Raman process coupling J with $J, J \pm 2$ states.

After the alignment pulse, molecules continuously rotate at different rotational eigenstates (neglecting the dispersion). By coherently summing all the occupied eigenstates, the rotational wave packet can be acquired for any moment after the alignment pulse technically. Due to the coherence between J and $J \pm 2$, the temporal evolution of HHG presents $1/4$ revivals and can be characterized by the expectation value $\langle \cos^2 \theta \rangle$ for a nitrogen molecule [21, 22], where θ is the angle between the molecular axis and the polarization axis of the alignment pulse in the molecular frame. Recently, high-order fractional revivals have been observed in experiment, corresponding to the coherence between J and $J \pm 4, \pm 6$ even ± 8 [23].

In figure 3, we show the calculated time-dependent expectation values of $\cos^2 \theta$, $\cos^4 \theta$ and $\cos^6 \theta$ for a nitrogen molecule. The parameters for the calculation are obtained from [24–26], the rotational temperature is set at 90 K and the alignment laser is 60 fs, $0.7 \times 10^{14} \text{ W cm}^{-2}$. The general shapes of the expectation values of $\cos^{2n} \theta$ are similar, while the featured differences are the height of base lines and the appearance of high-order fractional revivals.

Note that the population of different rotational states is determined by the intensity of the alignment pulse and the initial rotational temperature [23, 27]. When simulating the experimental results, the determination of these two parameters is crucial for calculating the rotational wave packet. Actually, the laser intensity is a distribution at the transversal surface along the propagation direction at the interaction volumes and the rotational temperature can be roughly

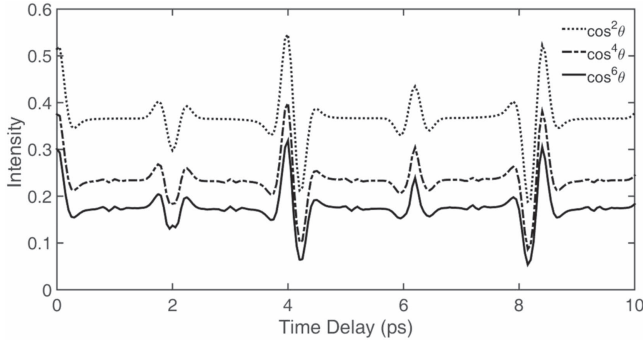


Figure 3. From top to the bottom, the calculated $\langle \cos^2 \theta \rangle$ (dotted line), $\langle \cos^4 \theta \rangle$ (dashed-dotted line) and $\langle \cos^6 \theta \rangle$ (solid line), as functions of the time delay between the alignment and the generation pulses.

estimated by the supersonic expansion property [28]. The rotational temperature of molecules can also be estimated from the Fourier spectrum of the temporal evolutions of high harmonics in experiment [29]. While, by fitting the experimental results, a mathematical procedure has been proposed to precisely determine the laser intensity and the rotational temperature [27].

3.2. Theory of HHG and TWG from aligned molecules

In the following, we present the expressions of the alignment-dependent HHG and TWG from molecules.

HHG has been demonstrated as a fascinating tool for imaging the molecular structure, with the short wavelength of the recombining electron compared to the molecular size [21, 30, 31]. The alignment-dependent high harmonic yields in molecular frame $S_{\text{HHG}}(\Omega, \theta)$, is proportional to the Fourier transform of the induced dipole $D(\Omega, \theta)$ [16],

$$S_{\text{HHG}}(\Omega, \theta) \propto \Omega^4 D^2(\Omega, \theta), \quad (1)$$

with Ω the harmonic frequency. According to the QRS theory, $D(\Omega, \theta)$ is proportional to the rescattering dipole $D_{\text{QRS}}(\Omega, \theta)$, which can be expressed as [17]

$$D_{\text{QRS}}(\Omega, \theta) \approx (W(\Omega)N(\theta)^{1/2})d(\Omega, \theta), \quad (2)$$

where $W(\Omega)$ is the amplitude of the flux of the returning electrons, $N(\theta)$ is the angular ionization rates and $d(\Omega, \theta)$ is the transition dipole.

The recombination process, i.e. the third step for HHG, can be viewed as an inverse of photoionization process, thus the square of the recombination dipole moment $d^2(\Omega, \theta)$ is proportional to the angular differential PICS $\sigma_{\text{PICS}}(\Omega, \theta)$. Deriving from equations (1) and (2) S_{HHG} can be rewritten as

$$S_{\text{HHG}}(\Omega, \theta) \propto \Omega^4 W^2(\Omega) \sigma_{\text{PICS}}(\Omega, \theta) N(\theta). \quad (3)$$

It is worth noting that equation (3) is for the case of a single molecule, and the actual HHG signals include the macroscopic effects. In experiments, the phase-matching for the short trajectory yields is realized by placing the orifice of the gas jet after the focal to minimize the macroscopic effects.

Then we recall the theory of TWG in linearly polarized dual-color laser field. Considering the electron ionized at t_i ,

the alignment-dependent drift current density per unit generating time can be expressed as

$$j(\theta; t_i, t) = -n_0(\theta; t_i)w(\theta; t_i) \int_{t_i}^t \frac{e^2 E(t')}{m_e} dt'. \quad (4)$$

where $n_0(\theta; t_i)$ is the transient neutral molecule density, $w(\theta; t_i)$ is the transient ionization rates, $E(t')$ corresponds to the transient laser field, e and m_e is the constant of the electronic charge and mass. Here, we assume the initial velocity of the tunneling electron is zero [15]. Therefore, the residual current density J_R , associating to the electronic motion in the oscillating laser field, can be written as,

$$J_R(\theta, t) = \int_{-\infty}^t j(\theta; t_i, t) dt_i. \quad (5)$$

Taking the form of the current model [32–34], the far-field terahertz amplitude is proportional to the cycle-averaged electric current density $J_R(\theta, t)$,

$$E_{\text{THz}}(\theta) \propto \frac{d\langle J_R(\theta, t) \rangle}{dt} = \langle ev_d(t)n(\theta, t) \rangle, \quad (6)$$

where $v_d(\theta)$ represents the drift velocity of an electron born at t , and $n(\theta, t)$ is the angular ionization rates at t . The cycle average of $n(\theta, t)$ is proportional to the angular ionization rates $N(\theta)$, therefore, the alignment-dependent terahertz yields $S_{\text{THz}}(\theta)$ is proportional to $N(\theta)^2$.

3.3. The minima of angular differential PICSs

Replacing the angular ionization rates with the alignment-dependent TWG, equation (3) can be rewritten as

$$S_{\text{HHG}}(\Omega, \theta) \propto \Omega^4 W^2(\Omega) \sigma_{\text{PICS}}(\Omega, \theta) \sqrt{S_{\text{THz}}(\theta)}. \quad (7)$$

The first two items in the right side of equation (7) are the same for one given harmonic frequency Ω . Therefore, the amplitude of angular PICS can be expressed as,

$$\sigma_{\text{PICS}}(\Omega, \theta) \propto \frac{S_{\text{HHG}}(\Omega, \theta)}{\sqrt{S_{\text{THz}}(\theta)}}. \quad (8)$$

Since S_{HHG} and S_{THz} can be obtained synchronizely, it is straightforward to obtain the angular differential PICS in one run by calibrating the AIR with alignment-dependent TWG.

It is worth noting that the minima of the alignment-dependent high harmonics reflect the harmonic phase jump [35, 36], which is also the reason for the minima of PICSs [16]. For homonuclear diatomic molecules, we can divide the molecular orbital into two parts, namely the ϕ_{sym} and ϕ_{asym} corresponding to the symmetric and antisymmetric partial wave packet. Here, we use the linear combinations of atomic orbitals, ϕ_1 and ϕ_2 , centering at different atoms to construct these two parts, in the form of

$$\begin{aligned} \phi_{\text{sym}}(\vec{r}) &= \phi_1(\vec{r} - \vec{R}/2) + \phi_1(\vec{r} + \vec{R}/2), \\ \phi_{\text{asym}}(\vec{r}) &= \phi_2(\vec{r} - \vec{R}/2) - \phi_2(\vec{r} + \vec{R}/2), \end{aligned} \quad (9)$$

where $\vec{R}$ is the bond length from one atom to the other and $\vec{r}$ is the vector pointing from the center of molecule to an arbitrary position of the molecular wave packet.

The dividing of the orbital into symmetric and antisymmetric parts is based on the symmetry operation of mirror reflection of the nuclei, i.e., $\vec{R} \rightarrow -\vec{R}$. For example, the component of σ_g orbital constructed from atomic s orbitals located at each center is symmetric, while the component constructed from p_z orbitals is antisymmetric, with respect to $\vec{R} \rightarrow -\vec{R}$. Therefore, the molecular wave function $\Psi_{\text{MO}}(\theta)$ can be expressed as

$$\Psi_{\text{MO}}(\theta) = a_1 \phi_{\text{sym}}(\vec{r}) + a_2 \phi_{\text{asym}}(\vec{r}), \quad (10)$$

where the prefactors a_1 and a_2 are the normalization factors of the two parts.

Then, the recombination dipole matrix element in velocity form is

$$\begin{aligned} M_d &= \langle \Psi_{\text{MO}} | -i\nabla_r | e^{i\vec{k}\cdot\vec{r}} \rangle \\ &= 2a_1 k \cos\left(\frac{\vec{k} \cdot \vec{R}}{2}\right) \langle \phi_1(r) | e^{i\vec{k}\cdot\vec{r}} \rangle \\ &\quad - 2ia_2 k \sin\left(\frac{\vec{k} \cdot \vec{R}}{2}\right) \langle \phi_2(r) | e^{i\vec{k}\cdot\vec{r}} \rangle, \end{aligned} \quad (11)$$

where $\vec{k}$ is the wave vector of the returning electron. Denoting q as the relative value between the plane-wave projections on ϕ_1 and ϕ_2 , the interference term $T_{k,\Theta}$ can be simplified as

$$T_{k,\Theta} \propto \cos((kR \cos \Theta)/2 + \Phi), \quad (12)$$

where $\cos \Phi = iqa_1/\sqrt{(iq)^2 a_1^2 + a_2^2}$, and Θ is the angle between $\vec{k}$ and $\vec{R}$.

The two-center interference (TCI) minimum (or maximum) appears when the interference term $T_{k,\Theta}$ changes its sign. Therefore, the corresponding angle for TCI minimum (or maximum) satisfies the following equations,

$$kR \cos \Theta = 2n\pi + \pi - 2\Phi, \quad (13)$$

or

$$R \cos \Theta = \lambda_e \left(n + \frac{1}{2} - \frac{\Phi}{\pi} \right), \quad (14)$$

with n an arbitrary integer. λ_e is the wavelength of the recombining electron, whose kinetic energy is $E_\Omega - I_p$. When gradually varying the value of the returning electronic momentum k , the corresponding minimum angle Θ will also shift, which has been theoretically and experimentally demonstrated for nitrogen [11, 37].

3.4. Deconvolution of the HHG and TWG

In this section, the primed and unprimed notations of the physical quantities indicate the laboratory frame and molecular frame, respectively.

In principle, the measured terahertz and high-harmonic yields in laboratory frame M are the coherent convolution of molecular frame angular emission yields S and the distribution of rotational wave packet ρ [36, 38]. Ideally, both the phase and the magnitude of the molecular frame angular emission can be retrieved self-consistently by fitting the experimental results. It turns out to be a very complex and

challenging task. Therefore, an incoherent sum has been frequently applied instead, for some molecules such as nitrogen and oxygen. Former research has mentioned the error inducing from the incoherent sum [38]. The validity of incoherent deconvolution methods has been discussed in obtaining the molecular frame induced dipole $D(\Omega, \theta)$ for nitrogen [39].

In our method, the incoherent sum M_{incoh} of the molecular frame angular yields from all solid angles takes the form as [38]

$$\begin{aligned} M_{\text{incoh}}(\alpha'; t_D) &\propto \int_0^{2\pi} d\varphi' \int_0^\pi d\theta' S(\theta, \varphi) \\ &\quad \times \rho(\theta', \varphi'; t_D) \sin \theta', \end{aligned} \quad (15)$$

where θ' (φ') is the polar (azimuthal) angle about the polarization axis of the aligning pulse, $\theta(\varphi)$ is the corresponding angle in molecule frame, α' represents the angle between the polarization directions of the alignment and the generation pulses, $S(\theta, \varphi)$ is molecular frame angular yields of TWG and HHG and $\rho(\theta', \varphi'; t_D)$ is the angular distribution of the rational wave packet at t_D . While, M_{coh} is the coherent convolution of the complex amplitude $A(\theta, \varphi)$ of molecular frame angular emissions and the amplitude of rotational wave packet. We introduce the molecular frame angular phase $\varphi_a(\theta, \varphi)$ for A , thus $A = \sqrt{S} e^{i\varphi_a}$. Then, the total coherent sum M_{coh} can be expressed as

$$\begin{aligned} M_{\text{coh}}(\alpha', t_D) &\propto \left| \int_0^{2\pi} d\varphi' \int_0^\pi d\theta' A(\theta, \varphi) \right. \\ &\quad \left. \times \sqrt{\rho(\theta', \varphi'; t_D)} \sin \theta' \right|^2. \end{aligned} \quad (16)$$

To examine our approach of incoherent convolution, we compare the results calculated by coherent and incoherent convolutions for nitrogen, with the rotational temperature 90 K and the alignment laser intensity $0.7 \times 10^{14} \text{ W cm}^{-2}$. Five different molecular frame angular phases φ_a have been checked with a typical molecular frame emission amplitude, which has a significant minimum. All the molecular frame alignment-dependent amplitudes and phases used for calculation are sketched in figure 4(a). To discuss the comparisons conveniently, we define Δ as the value of the phase jump in each case.

As is shown in figure 4(b), the normalized intensities of coherent sum decrease faster than the incoherent sum, especially when Δ approaches π . Therefore, the incoherent deconvolution method is likely to underestimate the angular yield in the molecular frame as the alignment angle increases, due to the negative value in the amplitude integration. Nevertheless, the major differences concentrate at the magnitude around the angles of the spectral minima, where a sudden phase jump occurs. This gives us confidence that we still can use the incoherent convolution to reconstruct the majority of molecular frame emission properties for nitrogen, and the magnitude discrepancies may appear around the minimum position.

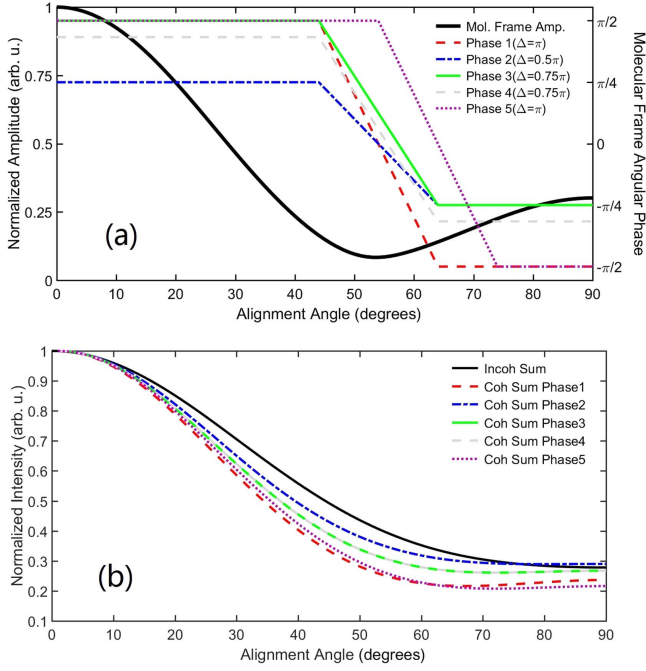


Figure 4. Tests for the differences between the coherent sum and incoherent sum. (a) Typical molecular frame angular amplitude $|A|$ (normalized) and five different phases φ_a versus the alignment angle. (b) The normalized incoherent and coherent convolution results calculated from the molecular frame angular amplitude and phases in (a).

Typically, the molecular frame angular emissions can be deduced by tracing the time-delay (t_D) dependent or the alignment-angle (α') dependent yields in experiment [40]. For homonuclear diatomic molecule, $S(\theta, \varphi)$ only depends on the polar angle θ in molecule frame. Therefore we can simplify it as $S(\theta)$ and expand it by Legendre polynomials. The coordinate transformation between the laboratory and molecule frame is given by [41]

$$\cos \theta = \cos \alpha' \cos \theta' - \sin \alpha' \sin \theta' \sin \varphi'. \quad (17)$$

The angular distribution of the rotational wave packet shares the cylindrical symmetry, therefore $\rho(\theta', \varphi'; t_D)$ can be simplified as $\varrho(\theta', t_D)/2\pi$. Based on the former deductions, the measured terahertz-wave and high-harmonic signal can be expressed as

$$M(\alpha', t_D) \propto \int_0^{2\pi} d\varphi' \int_0^\pi d\theta' S[\theta(\theta', \varphi'; \alpha')] \times \varrho(\theta', t_D) \sin \theta'. \quad (18)$$

Here, we introduce our self-consistent approach to obtain the angle-resolved emission properties in the molecular frame, based on the incoherent convolution method. Firstly, we estimate the potential range of rotational temperature T and the alignment pulse intensity I and try different pairs of them to calculate the rotational wave packet $\varrho(\theta', t_{al})$, with t_{al} the alignment moment. Meanwhile, the molecular frame emissions can be expanded by Legendre polynomials

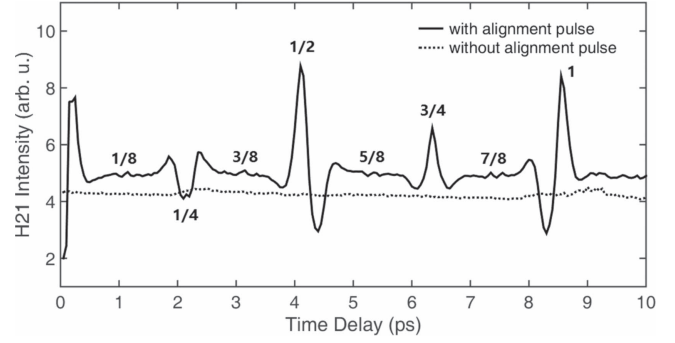


Figure 5. The time-delay dependent modulations of the yields of 21st harmonic from nitrogen with (solid line) or without (dashed line) the alignment pulse. The fractional revivals are indicated at the corresponding time delays.

$$P_i(\cos \theta),$$

$$S(\theta) = \sum_i a_i \times P_i(\cos \theta) \quad (19)$$

where a_i are the unknown expansion parameters. In principle, the higher the expansion order is, the better the fitting accuracy will be. Due to the symmetry of the nitrogen molecule, only the even orders of expansion polynomials should be considered. Therefore, the expansion series $P_{2j}(\cos \theta)$ with j from 0 to 4 are applied in reconstruction of $S(\theta)$. Given the complicated expression form of the Legendre polynomials, it is equivalent to use the Fourier expansion series of $\cos^{2j} \theta$ instead of $P_{2j}(\cos \theta)$. Hence, we can rewrite equation (19) as

$$S(\theta) = \sum_{j=0}^4 c_{2j} \times (\cos^{2j} \theta), \quad (20)$$

with c_{2j} the corresponding expansion parameters. The least square method is performed in searching for different pairs of the temperature and laser intensity $\{I, T\}$ and the corresponding $c_{2j;\{I,T\}}$, by comparing the experimental data at the alignment moment with the fitting results obtained from convoluting $S(\theta)$ with the $\varrho(\theta', t_{al})$.

Secondly, all different pairs of $\{I, T\}$ and the corresponding expansion parameters $c_{2j;\{I,T\}}$ should be used to fit the angular emissions at the anti-alignment moment. The least squares method is applied to find the best fitting series from all the different pairs, denoting as $\{I, T\}_b$ and $c_{2j;\{I,T\}_b}$.

Thirdly, treat the obtained $c_{2j;\{I,T\}_b}$ and $\{I, T\}_b$ as the initial values and retrieve the temporal evolution of the emissions. If we can reproduce the experimental results, all the fitting parameters are self-consistent; if not, a tiny adjustment of the fitting parameters should be attempted until convergent.

4. Experimental results and discussions

4.1. Temporal evolution of HHG and TWG

In figure 5, we show the modulations of the yields of 21st harmonic from nitrogen as a function of the time delay between the alignment and generation pulses. The integral

multiples of the 1/8th revival for nitrogen are marked by their orders. We also show the harmonic signals without the alignment pulse for comparison, which are achieved by closing the beam shutter. Research on nitrogen suggest that the temporal evolution of high harmonics generally follows the modulation of $\langle \cos^4 \theta \rangle$ [42], which is in conformity with our results.

As mentioned above, the general structures of the expecting values for $\cos^2 \theta$, $\cos^4 \theta$ and $\cos^6 \theta$ are similar. However, in figure 5, we still can find some tiny oscillations around the odd times of 1/8th revivals, which corresponds to the high-order coherence between different rotational states. These tiny structures may contribute to the high-order fractional revivals of nitrogen molecule, i.e., the integral multiple of the 1/12th or the 1/16th revivals, which have been reported on carbon dioxide [23, 43]. However, for a nitrogen molecule with a 8.4 ps revival period (one-fifth of carbon dioxide's), the high-order fractional revivals are too close to be separately distinguished.

The comparisons for TWG and HHG from nitrogen around the half revival moments are presented in figure 2 of [11]. Their temporal evolutions are similar to each other when the polarization, the alignment and generation pulses are parallel. Correlated measurements on ion fragments and high harmonics have been conducted for nitrogen [6], showing a consistent trend with ours. These results convincingly demonstrate that our treatment of calibrating the angular ionization rates with alignment-dependent TWG is reliable.

4.2. Shifting minima of the angular PICS

According to the descriptions in section 3.3, the angular differential PICS can be retrieved from the alignment-angle dependent TWG and HHG in the molecular frame. However, the measured signals are recorded in a laboratory frame, thus the deconvolution should be performed to obtain the alignment-dependent terahertz and high-harmonic yields in the molecular frame. Detailed methods are present in section 3.4 and the results of molecular frame angular emissions have been reported before (see figure 3 in [11]).

For HHG from molecules, it is significant that intensity minima can be observed [6, 30, 44], reflecting the phase jump of the recombining electrons [35]. Therefore, recognizing the minima positions from the experimental and theoretical results is a crucial step for the further research on molecular structures.

In figure 6, we show the experimentally deduced results and the theoretical predictions on the minima positions. The projections of the internuclear distance associating to our experimental results are presented, with bond lengths of nitrogen of $R_1 = 0.121$ nm, $R_2 = 0.110$ nm and $R_3 = 0.099$ nm [45]. R_2 is the equilibrium N–N distance for neutral nitrogen.

The theoretical predictions of the simple TCI model (use equation (14) without the additional phase Φ) are shown as dashed and solid black lines for symmetric and antisymmetric wave functions, respectively. Both lines exhibit the shifting trend of the minima positions with the increase of electron

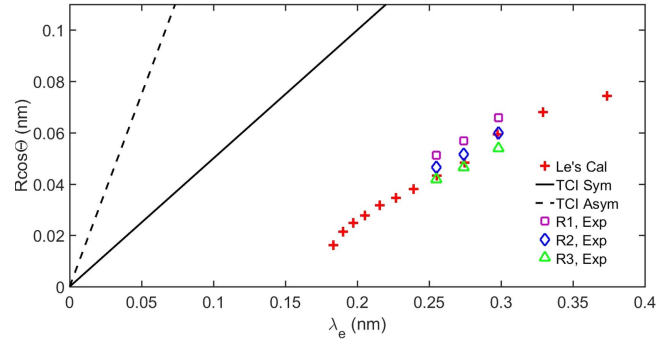


Figure 6. The projection of the internuclear distance is plotted against the electron wavelength for nitrogen. The experimental deduced results are shown in violet squares ($R_1 = 0.121$ nm), blue diamonds ($R_2 = 0.110$ nm) and green triangles ($R_3 = 0.099$ nm). Le's calculations [16] on the minima of the PICS for nitrogen are presented (red crosses) for comparison. The theoretical predictions of the simple TCI model (neglecting the additional phase Φ) are shown as dashed and solid black lines for symmetric and antisymmetric wave functions, respectively.

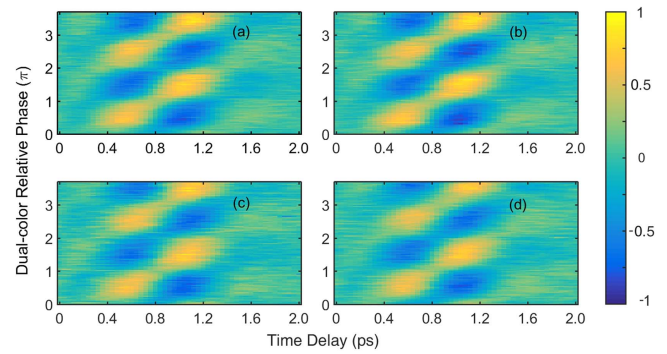


Figure 7. THz time-dependent amplitude (normalized) versus the DRP from nitrogen. (a) and (c) Experimental results from aligned and antialigned nitrogen molecules, respectively; (b) and (d) are the results from isotropic nitrogen molecules by turning off the alignment pulse.

wavelength. The differences between the simple TCI model and the experimentally deduced results implies the influence of the additional phase shift mentioned in equation (14). This phase shift Φ is dependent on the angle and the kinetic energy of the recombined electron.

We also show Le's calculations on the angular PICS of nitrogen for comparison [16]. Great agreements have been found between his theoretical and our experimental results. The wavelength in [16] is the 'effective' electron wavelength, which is acquired from $E_k^{\text{eff}} = E_\Omega$. Here, we shift it by removing the ionization potential of nitrogen, i.e., $E_k = E_\Omega - I_p$. The twisty shapes of the red crosses indicate the participation of s and p_z orbitals [37]. It can be found the blue diamonds with the bond length R_2 , fit better to Le's calculations.

4.3. Optimal phase for TWG

By varying the transmission length of the wedges, we obtain the DRP-modulated TWG from aligned and antialigned nitrogen, while no observable variation on the optimal phase

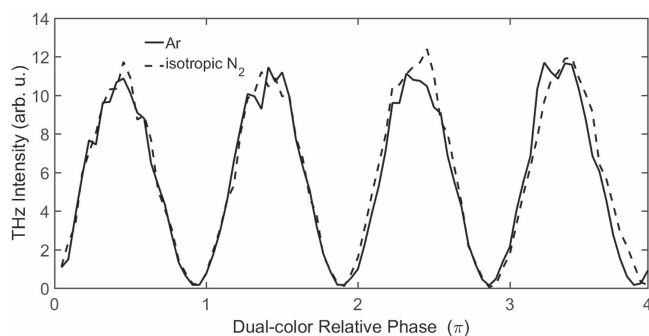


Figure 8. THz intensity versus the relative phase between the ω and 2ω pulses with parallel polarization from isotropic nitrogen molecule (solid line) and argon atom (dashed line).

is found at the accuracy of about 50 as in our experiment. In figure 7, we show the THz waveform versus the DRP. The inverse of the THz waveform at different DRPs indicates the inversion of the current direction. By continuously turning the shutter on and off, the terahertz waveform is traced from nitrogen molecules with or without the alignment pulses. Recently, theoretical work has predicted the difference of the optimal phase for TWG, which is about 17 as between the 0 degree aligned and 90 degree aligned model H_2^+ [15]. Observing this tiny difference is definitely a tough challenge when using current experimental methods. In figure 8, we show the modulations of the THz intensity versus the DRP of argon and isotropic nitrogen under the same experimental conditions. The nearly overlapping lines on modulations indicate the similar motion of electrons from nitrogen and argon, which is determined by the combination of Coulomb potential and the focused dual-color fields.

Argon atom shares a similar ionization potential as the nitrogen molecule, which makes it a suitable comparison when studying the THz generating process. If the electrons, either escaping or rescattering ones, are far from the nuclei which is screened by other electrons, the effect of the Coulomb potential works like a positive core, only slightly adjusting the trajectory. Therefore, to small molecules such as nitrogen, the TWG is almost generated at the same time from different aligned angles. Unless the gating of dynamics is enhanced to a much more precise resolution [46], it is hard to figure out the minor difference on the emission time for TWG. That is the reason why no difference is found in our experiments on the optimal DRPs for the generation of THz from aligned, antialigned, isotropic nitrogen molecules and argon atoms.

5. Conclusions and outlook

In summary, we present the detailed HATS method for aligned N_2 molecules, which exhibits great potential in researching molecular structures and dynamics.

On one hand, HATS, saving separate measurements on AIRs, is introduced as a brand-new method for decoding the structure and dynamics of a molecule in strong laser fields. Due to the importance of AIRs for molecules, applying

alignment-dependent TWG to calibrate the ionization process is indeed a supplement to the contemporary approaches both in theory and experiment. Meanwhile, the qualitative agreements on the minima angles of the PICS between the theoretical and experimental results show the potential applications in investigating the structure and emission properties for much more complicated molecules.

On the other hand, we compare the DRP-modulated TWG from molecules and atoms. Within our experimental precision (50 as), no significant difference on the optimal phase for TWG is observed between nitrogen molecules and argon atoms, regardless of whether they are aligned or not. This means that the Coulomb potential of nitrogen only slightly adjusts the trajectory of the ionized electrons. To exhibit the influence of Coulomb potential on electron dynamics during the TWG process, attempts using larger molecules and enhancements of the detection precision are predictable ways forward in this field, which is still a challenge for experiments.

Acknowledgments

This work is supported by the National Basic Research Program of China (973 Program) under Grant No. 2013CB922203 and the NSF of China (Grants No. 11374366, 11404401 and 11474359). Y H thanks Wenbo Chen, Bin Zhang, Wenpu Dong, Jinlei Liu, Lu Liu and Quan Guo for the constructive discussions.

References

- [1] Krausz F and Ivanov M 2009 *Rev. Mod. Phys.* **81** 163
- [2] Dudovich N, Smirnova O, Levesque J, Mairesse Y, Ivanov M Y, Villeneuve D M and Corkum P B 2006 *Nat. Phys.* **2** 781
- [3] Zhang D, Lü Z, Meng C, Du X, Zhou Z, Zhao Z and Yuan J 2012 *Phys. Rev. Lett.* **109** 243002
- [4] Pedatzur O *et al* 2015 *Nat. Phys.* **11** 815
- [5] Zhao J, Yuan J and Zhao Z 2015 (arXiv:1510.07947)
- [6] Kanai T, Minemoto S and Sakai H 2005 *Nature* **435** 470
- [7] Meckel M, Staudte A, Patchkovskii S, Villeneuve D M, Corkum P B, Dörner R and Spanner M 2014 *Nat. Phys.* **10** 594
- [8] Vampa G, Hammond T J, Thire N, Schmidt B E, Legare F, McDonald C R, Brabec T and Corkum P B 2015 *Nature* **522** 462
- [9] Hohenleutner M, Langer F, Schubert O, Knorr M, Huttner U, Koch S W, Kira M and Huber R 2015 *Nature* **523** 572
- [10] Lü Z, Zhang D, Meng C, Du X, Zhou Z, Huang Y, Zhao Z and Juan J 2013 *J. Phys. B: At. Mol. Opt. Phys.* **46** 155602
- [11] Huang Y, Meng C, Wang X, Lü Z, Zhang D, Chen W, Zhao J, Yuan J and Zhao Z 2015 *Phys. Rev. Lett.* **115** 123002
- [12] Cook D J and Hochstrasser R M 2000 *Opt. Lett.* **25** 1210
- [13] Lewenstein M, Balcou P, Ivanov M Y, L'Huillier A and Corkum P B 1994 *Phys. Rev. A* **49** 2117
- [14] Liu J, Chen W, Zhang B, Zhao J, Wu J, Yuan J and Zhao Z 2014 *Phys. Rev. A* **90** 063420
- [15] Chen W, Huang Y, Meng C, Liu J, Zhou Z, Zhang D, Yuan J and Zhao Z 2015 *Phys. Rev. A* **92** 033410

- [16] Le A-T, Lucchese R R, Tonzani S, Morishita T and Lin C D 2009 *Phys. Rev. A* **80** 013401
- [17] Jin C, Bertrand J B, Lucchese R R, Wörner H J, Corkum P B, Villeneuve D M, Le A- T and Lin C D 2012 *Phys. Rev. A* **85** 013405
- [18] Fleischer S, Zhou Y, Field R W and Nelson K A 2011 *Phys. Rev. Lett.* **107** 163603
- [19] Egodapitiya K N, Li S and Jones R R 2014 *Phys. Rev. Lett.* **112** 103002
- [20] Stapelfeldt H and Seideman T 2003 *Rev. Mod. Phys.* **75** 543
- [21] Itatani J, Levesque J, Zeidler D, Niikura H, Pepin H, Kieffer J C, Corkum P B and Villeneuve D M 2004 *Nature* **432** 867
- [22] Itatani J, Zeidler D, Levesque J, Spanner M, Villeneuve D M and Corkum P B 2005 *Phys. Rev. Lett.* **94** 123902
- [23] Lock R M, Ramakrishna S, Zhou X, Kapteyn H C, Murnane M M and Seideman T 2012 *Phys. Rev. Lett.* **108** 133901
- [24] NIST (<http://webbook.nist.gov>)
- [25] Miller K J 1990a *J. Am. Chem. Soc.* **112** 8533
- [26] Miller K J 1990b *J. Am. Chem. Soc.* **112** 8543
- [27] Mikosch J, Bisgaard C Z, Boguslavskiy A E, Wilkinson I and Stolow A 2013 *J. Chem. Phys.* **139** 024304
- [28] Scoles G, Bassi D, Buck U and Lainé D 1988 *Atomic and Molecular Beam Methods* vol 1 (New York: Oxford University Press)
- [29] Yoshii K, Miyaji G and Miyazaki K 2009 *Opt. Lett.* **34** 1651
- [30] Haessler S *et al* 2010 *Nat. Phys.* **6** 200
- [31] Haessler S, Caillat J and Salieres P 2011 *J. Phys. B: At. Mol. Opt. Phys.* **44** 203001
- [32] Kim K Y, Taylor A J, Glowina J H and Rodriguez G 2008 *Nat. Photonics* **2** 605
- [33] Kim K-Y 2009 *Phys. Plasmas* **16** 056706
- [34] You Y, Oh T, Fallahkhair A and Kim K 2013 *Phys. Rev. A* **87** 035401
- [35] Lein M, Hay N, Velotta R, Marangos J P and Knight P L 2002a *Phys. Rev. A* **66** 023805
- [36] Lein M, Hay N, Velotta R, Marangos J P and Knight P L 2002b *Phys. Rev. Lett.* **88** 183903
- [37] Zimmermann B, Lein M and Rost J M 2005 *Phys. Rev. A* **71** 033401
- [38] Yoshii K, Miyaji G and Miyazaki K 2011 *Phys. Rev. Lett.* **106** 013904
- [39] Bertrand J B, Wörner H J, Hockett P, Villeneuve D M and Corkum P B 2012 *Phys. Rev. Lett.* **109** 143001
- [40] Ren X, Makhija V, Le A- T, Troß J, Mondal S, Jin C, Kumarappan V and Trallero-Herrero C 2013 *Phys. Rev. A* **88** 043421
- [41] Pavičić D, Lee K F, Rayner D M, Corkum P B and Villeneuve D M 2007 *Phys. Rev. Lett.* **98** 243001
- [42] Ramakrishna S and Seideman T 2007 *Phys. Rev. Lett.* **99** 113901
- [43] Weber S J, Oppermann M and Marangos J P 2013 *Phys. Rev. Lett.* **111** 263601
- [44] Boutu W *et al* 2008 *Nat. Phys.* **4** 545
- [45] Blaga C I, Xu J, DiChiara A D, Sistrunk E, Zhang K, Agostini P, Miller T A, DiMauro L F and Lin C D 2012 *Nature* **483** 194
- [46] Eckle P, Pfeiffer A N, Cirelli C, Staudte A, Dörner R, Muller H G, Büttiker M and Keller U 2008 *Science* **322** 1525