High-Harmonic Spectroscopy of Oriented OCS Molecules: Emission of Even and Odd Harmonics

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We study the emission of even and odd high-harmonic orders from oriented OCS molecules. We use an intense, nonresonant femtosecond laser pulse superimposed with its phase-controlled second harmonic field to impulsively align and orient a dense sample of molecules from which we subsequently generate high-order harmonics. The even harmonics appear around the full revivals of the rotational dynamics. We demonstrate perfect coherent control over their intensity through the subcycle delay of the two-color fields. The odd harmonics are insensitive to the degree of orientation, but modulate with the degree of axis alignment, in agreement with calculated photorecombination dipole moments. We further compare the shape of the even and odd harmonic spectra with our calculations and determine the degree of orientation.

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High-harmonic spectroscopy (HHS) is an emerging tool for studying the electronic structure and dynamics of molecules on femtosecond to attosecond time scales. This method has been used to characterize the electronic structure of static atoms and molecules with an increasing level of detail. While early work used a single-electron model and a plane wave representation of the continuum [1,2], more recent work has established the importance of multielectron effects [3] and the need for a more accurate description of the continuum [4,5]. More recently, HHS has been extended to probing valence electron dynamics during chemical transformations [6], including the observation of the electronic symmetry change occurring at conical intersections [7–9]. These achievements have all been made using partially aligned samples of molecules, be it through impulsive nonadiabatic alignment of ground state molecules [10] or through the anisotropy of single-photon excitation. Such measurements have therefore always been averaged over possible head-to-tail differences of the molecules. In particular, the perspective of measuring attosecond electron dynamics in molecules [11,12], will be greatly extended by orienting the sample, providing access to ultrafast charge migration in molecules [13].

Over the past years, techniques for molecular orientation have made enormous progress and are becoming precious tools for studies of molecular structure and reactive dynamics [14]. Early approaches used static electric fields and were limited to molecules with large electric dipole moments [15]. The combination of a permanent electric field with impulsive stimulated Raman excitation of rotational transitions made orientation accessible for a wider class of molecules [16]. Quantum-state selection of molecules, combined with femtosecond alignment techniques, has reached the highest degrees of orientation reported to date, not only in diatomic [17,18] but even in complex polyatomic molecules [19,20]. These powerful techniques were unfortunately not easily applicable to HHS because of low particle densities resulting from the state-selection step. Recently, all-optical approaches for molecular orientation have been introduced that are compatible with the high particle densities required for HHS [21,22]. As a consequence, HHS of oriented molecules has become possible [23].

In this Letter, we report the first measurements of high-harmonic emission from cold, impulsively aligned and oriented carbonyl sulfide (OCS) molecules. We use a femtosecond laser pulse, superimposed with its phase-controlled second harmonic and observe the emission of even high harmonics when the molecules are oriented. We demonstrate full coherent control over the intensity of the even harmonics by changing the phase delay between the two colors and show that the odd harmonics are insensitive to this variable. These observations show that even harmonics represent a background-free probe of molecular orientation, whereas the odd harmonics are only sensitive to the degree of alignment. We further study the temporal evolution of the odd harmonic intensities around the full rotational revival of the molecule and show that it reflects the electronic structure of the molecule in agreement with *ab initio* quantum scattering calculations. Finally, we compare the shape of the even and odd high-harmonic spectra to our calculations and determine the degree of orientation without assumptions in a single-parameter fit.

The experimental setup consists of an amplified femtosecond titanium:sapphire laser system, an optical setup for generation and synchronization of multiple laser beams, and a vacuum chamber for generation and spectral characterization of high-order harmonic radiation. The laser system [8 mJ, 28 fs, 1 kHz, 3% root-mean-square (rms) variation of the intensity over 1 hour] provides pulses centered at 800 nm which traverse a 50:50 beam splitter. One part of the beam is used to generate a two-color pump beam serving the purpose of aligning and orienting the molecules, whereas the other part is used to generate high-harmonic radiation. The 800 nm pump pulse is sent through a 300 μm BBO crystal for generating its second harmonic, tuned to a conversion efficiency of 15%, followed by two pieces of calcite (1.6 and 0.75 mm) for compensating the group velocity mismatch, and finally through a zero-order half-wave plate which rotates the polarization of the 800 nm and 400 nm beams into the same plane [21]. A similar experimental approach has been reported recently [23]. The two-color beam is aligned parallel to the 800 nm probe beam with a vertical offset of 0.7 cm and the two beams are focused into a molecular beam inside a vacuum chamber using a $f = 40$ cm spherical mirror, as illustrated in Fig. 1. The two-color beam is apertured to $2/3$ of the pump beam diameter to ensure optimal orientation in the probed volume. The molecular beam is generated by expansion of a 33% mixture of OCS in helium through an Even-Lavie valve (ø 150 μm) with a backing pressure of 5 bars. These conditions are chosen and optimized to suppress cluster formation as judged from the contrast of the alignment revivals of the molecules and the suppression of extreme-ultraviolet (XUV) cluster emission lines. The focused probe beam intersects the extremely thin molecular beam 2–3 mm downstream of the nozzle. This configuration minimizes the effects of phase mismatch and reabsorption, leading to the observation of a near-single-molecule response. The high harmonics generated by the probe beam propagate into an XUV spectrometer consisting of a 120 μm wide entrance slit, a concave aberration-corrected grating (Shimadzu, 30–002), and a microchannel-plate detector backed with a phosphor screen. A charge-coupled device camera records the spectral images and transfers them to a computer for analysis. We note that even harmonics from the probe beam have only been observed at intensity levels where the pump beam was significantly ionizing the sample. The weak even and odd harmonics from the pump beam were blocked in the vertical dimension before entering the XUV spectrometer, to eliminate their possible contribution to the measurements.

Carbonyl sulfide is a linear triatomic molecule with a relatively large permanent electric dipole moment (0.71 D). It has been a popular target for experiments on molecular alignment and orientation [16,19,24,25]. However, it has not been studied by HHS previously, nor oriented using the impulsive two-color technique [17], which has so far only been applied to CO [21]. The valence electronic structure of OCS consists of the orbitals with the following symmetries and negative binding energies (equal to the vertical ionization energies within Koopmans' theorem): π, 11.185 eV; π, ~15.5 eV; σ, 16.058 eV; σ, 17.957 eV [26,27]. Theoretical studies of high-harmonic generation in OCS using time-dependent density functional theory have only been reported for intensities of 3.5×10^{14} W/cm^2 and higher [28], making a direct comparison with the present experiments difficult.

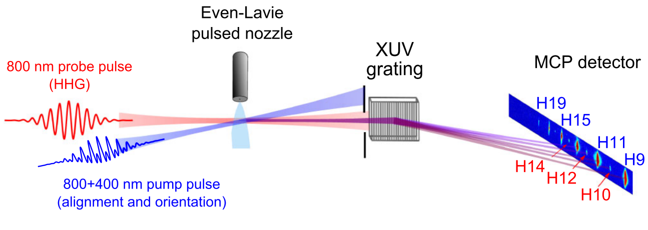

FIG. 1 (color online). Experimental setup for high-harmonic spectroscopy of oriented molecules. The far-field spectrally resolved high-harmonic profile is a false-color logarithmic plot obtained at maximal orientation of the OCS molecules.

Figure 2(a) shows high-harmonic spectra recorded around the full rotational revival of the OCS molecule using a 0.62 mJ two-color (800 nm and 400 nm) pulse that aligns and orients the molecules and a 0.73 mJ, 800 nm laser pulse that generates high harmonics from the sample. We estimate the peak intensities of the pump and probe pulses at their focal points to be 4×10^{13} W/cm^2 and 1.3×10^{14} W/cm^2, respectively. These spectra are obtained by adding the signals from 36000 laser shots. The full red line corresponds to a delay of 82.30 ps between the pump and probe pulses, and shows in addition to the odd harmonics ($H9$–$H21$, i.e., ninth through twenty-first) the presence of weaker even harmonics ($H10$–$H20$). These even harmonics are absent in the spectrum recorded at a delay of 80.5 ps (blue dashed line), where no orientation would be expected. We have thus shown that oriented OCS molecules emit both even and odd harmonics, as would be expected from a non-inversion-symmetric sample [29,30].

We now turn to the coherent control of the even harmonic emission with the phase delay between the two colors of the pump pulse. We control the delay on the subcycle time scale without affecting the spatial overlap of the two colors by tilting the 0.75 mm thick calcite plate by fractions of a degree away from the vertical using a stepper motor with an angular resolution of 0.01° and a minimal reproducible step of 0.02°. Figure 2(b) shows the resulting modulation of the even harmonic intensities with the temporal delay of the two colors. The intensity of all even harmonics is found to modulate with a period equal to half the optical period of the 400 nm field (0.66 fs) and to display a contrast close to 100%. The electric field of the two-color laser pulse is represented in Fig. 2(c) for three different two-color delays. Orientation is found to maximize according to the degree of asymmetry of the total electric field of the pump pulse which is maximized whenever two maxima or two minima of the two electric fields coincide (i.e., for relative delays of 0 and 0.66 fs). Notably, the intensity of all even harmonics is found to modulate with the same phase, showing the common origin of the symmetry breaking that causes their appearance. The odd harmonics however, show no modulation at all within the signal-to-noise ratio of our measurement.

High-harmonic emission from molecules carries information about their electronic structure in the variation of its amplitude and phase with the alignment of the molecule

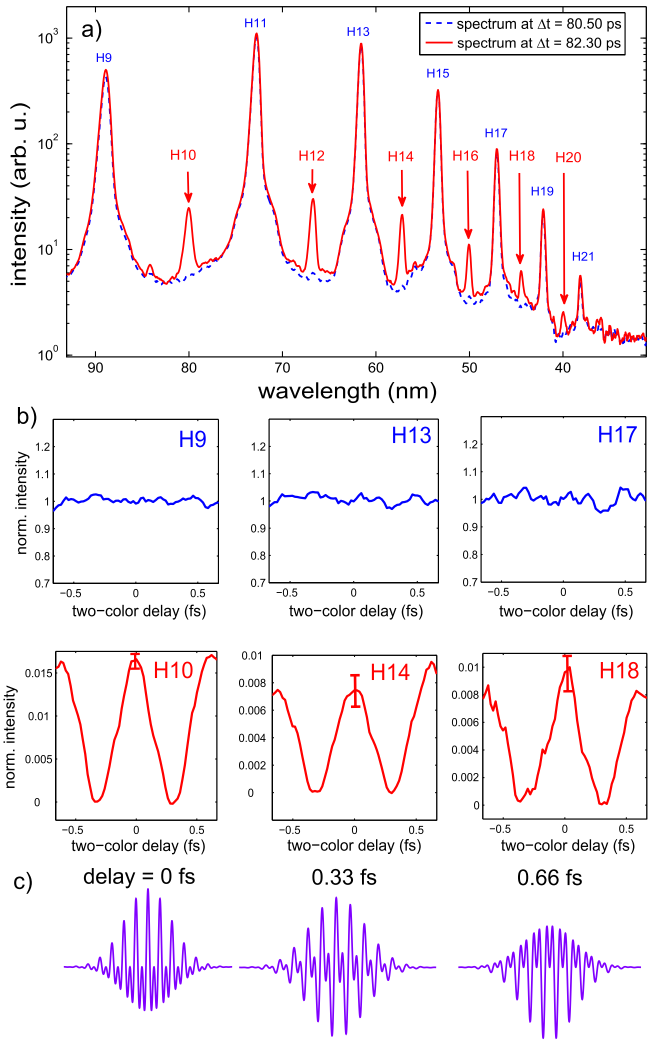

FIG. 2 (color online). (a) High-harmonic spectra recorded at pump-probe delays of 82.3 ps (maximal orientation, red line), showing the presence of the even harmonics $H10$–$H20$ emitted from oriented molecules and 80.5 ps (near-random distribution of molecules, blue dashed line). (b) Variation of the intensity of the odd harmonics (blue lines) and even harmonics (red lines) as a function of the subcycle temporal delay between the 800 nm and 400 nm laser fields forming the pump pulse, measured at a pump-probe delay of 82.30 ps. The intensity of the odd harmonics has been normalized to their value at the left end of the panel and the intensity of each even harmonic $H2n$ has been divided by the intensity at the left end of the panel of the next lower odd harmonic $H2n-1$. The error bars represent rms variations of the measured intensities. (c) Illustration of the electric field of a 800 + 400 nm laser pulse for different two-color delays.

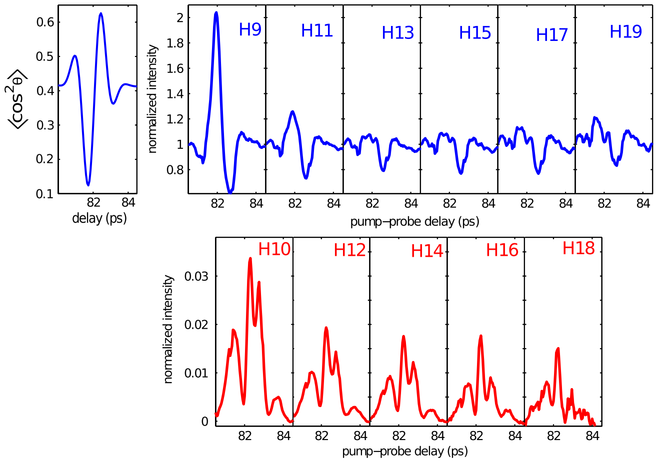

FIG. 3 (color online). Variation of the intensity of the odd harmonics ($H9$–$H19$, blue lines) and even harmonics ($H10$–$H18$, red lines) with pump-probe delay. The intensity of the odd harmonics has been normalized to their value at $\Delta t = 80.5$ ps and the intensity of each even harmonic $H2n$ has been divided by the intensity, at $\Delta t = 80.5$ ps, of the next lower odd harmonic $H2n-1$. The calculated evolution of the degree of axis alignment is shown in the upper left panel.

[31,32]. Figure 3 shows the temporal evolution of the intensity of the odd harmonics ($H9$–$H19$, blue lines) and even harmonics ($H10$–$H18$, red lines), respectively. The intensity of the odd harmonics has been divided by their value at the left end of each panel ($\Delta t = 80.5$ ps) and the intensity of each even harmonic $H2n$ has been divided by the intensity of the next lower odd harmonic $H2n-1$ at a delay of 80.5 ps. We compare this evolution with the degree of axis alignment ($\langle\cos^2\theta\rangle$), obtained by solving the time-dependent Schrödinger equation (TDSE) using the parameters of our experiment together with the rotational constant and polarizability anisotropy of the OCS molecule [20]. The intensity of the odd harmonics is found to modulate in opposition to the degree of axis alignment. This is consistent with the π symmetry of its highest-occupied molecular orbital, as we further discuss below. The maxima and minima of the odd harmonic intensities occur at 81.9 ps and 82.6 ps in all harmonic orders, in close agreement with the minimum and maximum of the calculated degree of axis alignment. The modulation depth is maximal for $H9$ and goes through a minimum for $H13$ before it slightly increases towards the cut off located at $H21$ in the present measurements.

The evolution of the even harmonic intensity is fundamentally different from that of the odd harmonics. Their intensity is nonzero only during the prompt rotational alignment (not shown) and the full rotational revivals, the first of which is displayed in Fig. 3. The intensity evolution can be described as a sequence of two central maxima at 82.3 and 82.7 ps and two peripheric maxima located at 81.4 and 83.7 ps. The most intense maximum at 82.3 ps coincides with the base-line crossing of the odd harmonic intensity, i.e., the time of the rotational revival, whereas the maximum at 82.7 ps occurs just after the global minimum in the odd harmonic intensity, simultaneously with the second local minimum that is visible in the odd harmonics $H11$–$H19$.

We now turn to the interpretation of the observed signals by studying the mechanism of even-harmonic generation.

Let us consider two consecutive half cycles of the 800 nm field generating the high harmonics. Writing the high-harmonic emission at angular frequency Ω triggered by the first and second half-cycles in terms of their complex spectral amplitudes as $d_1(\Omega)$ and $d_2(\Omega)$, the total detected field is $E(\Omega) = d_1(\Omega) - d_2(\Omega)\exp(-iq\omega T/2)$ where q is the harmonic order, ω is the fundamental angular frequency, and $T = 2\pi/\omega$ is the period of the probing laser field. The minus sign results from the odd symmetry of the dipole operator under inversion. For q odd, we thus obtain $E = d_1 + d_2$, whereas for q even, we obtain $E = d_1 - d_2$ [23,33]. Interpreting these results in terms of a polar linear molecule, perfectly aligned and oriented along the polarization of the probing field, we find that the odd harmonics reflect the sum of electric fields emitted by the recollision from the two sides, whereas the even harmonics reflect the difference. Consequently, odd harmonic emission is insensitive to the degree of orientation of the molecule, although it is sensitive to its degree of alignment, as we have shown in the measurements displayed in Figs. 2 and 3. On the contrary, even harmonic emission is exclusively sensitive to the degree of orientation and thus serves as a background-free probe as shown in Fig. 2.

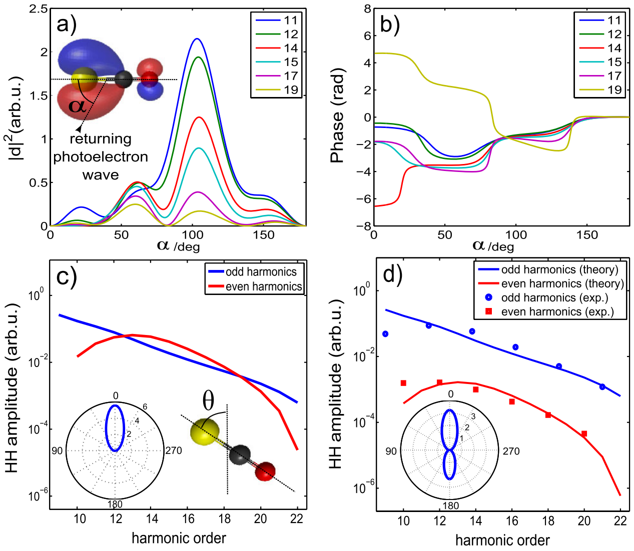

FIG. 4 (color online). (a) and (b) Calculated photorecombination matrix elements for the HOMO of OCS using *ab initio* quantum scattering theory. The inset shows the HOMO of OCS as an isocontour plot and color-coded sign. (c) Predicted high-harmonic spectra for the odd orders (blue line) and even orders (red line) using the matrix elements from (a) and (b) and the axis distribution shown as inset ($\langle\cos^2\theta\rangle = 0.63$, perfect head-to-tail order). (d) Measured and calculated intensities of the odd and even harmonic orders using the axis distribution shown in the inset ($\langle\cos^2\theta\rangle = 0.63$, 16% head-to-tail order), obtained by fitting the head-to-tail order in the calculation to the experimental data.

We further detail this discussion by comparing the experimental results with *ab initio* quantum scattering calculations. Computations are performed for ionization from and photorecombination to the HOMO of OCS (shown as inset in Fig. 4) using the Hartree-Fock method with a correlation-consistent polarized valence-triple-zeta (cc-pVTZ) basis set. All orbitals from this calculation serve as input for the solution of the quantum scattering problem of an electron in the molecular potential for arbitrary energies and angles using EPOLYSCAT [34,35]. The contribution of lower-lying orbitals is expected to be weak in the present experiments because of the large relative differences in ionization energies and the low intensities used. Figure 4(a) shows the calculated squared amplitudes and Fig. 4(b) the phases of the photorecombination matrix elements of selected harmonic orders as a function of the angle between the molecular axis and the direction of the recombining electron. An angle of $\alpha = 0°$ means that the electron recombines with the molecule over its sulfur end. All harmonic orders are found to have two main maxima, one close to 105° and one close to 60°. Whereas the former is dominant for the low harmonic orders ($H9$–$H14$), the two maxima have very similar amplitudes for the higher orders ($H16$–$H21$). The amplitudes of the photorecombination matrix elements are found to drop to zero for angles of 0 and 180 degrees, as expected from the π symmetry of the orbital. Consequently, taking the axis distribution of aligned molecules into account, high-harmonic emission is predicted to be maximized when the molecules are aligned perpendicular to the generating field, in agreement with the observed intensity modulation in Fig. 3. The decreasing amplitude modulation of the calculated matrix elements with increasing harmonic order agrees with the experimentally observed decrease of the modulation depth from $H9$ to $H13$. The phases of the calculated photorecombination matrix elements have been set to zero for $\alpha = 180°$. All phases show three more or less rapid variations as a function of angle, corresponding to the local minima or inflection points in the amplitudes. Both the phase variations and the amplitude minima or inflection points are related to the nodal structure of the HOMO, but the relationship is found to be more complex than in apolar molecules like CO_2 [31].

In addition to the angular variation of the harmonic yields, we now study the variation of the harmonic intensities with photon energy. As discussed above, the odd and even harmonics result from the sum and difference, respectively, of the electric fields emitted following recombination from the two sides. Consequently, we predict the shape of the odd harmonic spectrum by adding the contributions obtained for recombination from the O- and S-side and the shape of the even harmonic spectrum by calculating their difference. In addition to the complex photorecombination dipole moments, this calculation also requires the relative strong-field ionization yield as a function of angle and the contribution of the Stark effect to the phase of the harmonics [36,37]. The former has been measured in an elegant experiment [20] yielding a ratio of 2:1 in favor of removing the electron via the oxygen atom. The experimentally measured angular variation of the strong-field ionization yield was found to peak perpendicular to the molecular axis, in disagreement with theory [25]. We thus use a strong-field ionization rate of the form $w(\theta) \propto 2\cos^6(\theta - 120^\circ) + \cos^6(\theta - 45^\circ)$ for $0^\circ \leq \theta \leq 180^\circ$ which has the shape given by molecular ADK (Ammosov, Delone, Krainov) calculations [25], but with the amplitude asymmetry and the maxima shifted to agree with the experimental observations in Refs. [20,25] ($\theta = 0^\circ$ means ionization via the S atom). The contribution of the Stark effect to the phase of high-harmonic emission is calculated according to Refs. [36,37] using the permanent dipole moments given in [20] and an intensity of 1.3×10^{14} W/cm^2, matching the conditions of the present experiments.

We predict the shape of the even and odd high-harmonic spectra by coherently averaging the high-harmonic emission over the axis distribution obtained from the TDSE calculation described above ($\langle \cos^2\theta \rangle = 0.63$), restricted to one of the two possible orientations (oxygen atom pointing up). The result is shown in Fig. 4(c). The blue line representing the odd harmonic spectrum is structureless, in agreement with the experiment. We note that the simulation assumes a recombining photoelectron wave packet with a flat spectrum and therefore does not contain information about the location of the cut off. The predicted slope thus purely results from the properties of the complex photorecombination dipoles and the Stark shifts. The red line predicts the shape of the even harmonic spectrum.

The calculation shown in Fig. 4(c) assumes perfect head-to-tail order of the molecules, and shows that the intensity of the predicted even harmonics crosses that of the odd harmonics twice as a function of photon energy. By introducing a finite head-to-tail order in the calculation, we now determine the degree of orientation. The adjustment of the predicted to the observed spectrum thus becomes a single-parameter fit. Both the shape and the intensity of the odd harmonic spectrum are independent of this parameter, as is the shape of the even-harmonic spectrum. Only the overall intensity of the even harmonics is modified by the degree of head-to-tail order which can thus be retrieved from the measurement. The obtained agreement between the calculation and experiment is shown in Fig. 4(d). We obtain a value of 0.16 for the head-to-tail order; i.e., 16% of the molecules are oriented. Combined with the calculated axis distribution, this corresponds to a degree of orientation of $|\langle \cos\theta \rangle| = 0.12$.

In conclusion, we have studied high-harmonic generation in aligned and oriented OCS molecules for the first time. We have observed the emission of even harmonics from the oriented molecules. The temporal variation of the odd harmonics has been found to reflect the expected alignment dynamics of the molecule. The emission of all odd harmonics has been found to maximize when the molecule is aligned perpendicular to the polarization of the generating field, in agreement with *ab initio* quantum scattering calculations. The emission of even harmonics is restricted to a short time interval around the prompt alignment and full rotational revivals. The shape of the even and odd high-harmonic spectra has been predicted based on a simple calculation relying on *ab initio* quantum scattering and found to be in agreement with the experimental observations. Our results show that orientation adds an important new aspect to high-harmonic spectroscopy by giving access to additional aspects of the molecular structure. This tool will thus become essential in many promising applications, such as the characterization of the electronic structure of polar polyatomic molecules, the study of attosecond time-scale charge migration in molecular chains [13], and the study of electronic dynamics and electronic asymmetries in chemical reactions [6,7].

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