Coherent phonon coupled with exciton in semiconducting single-walled carbon nanotubes with several chiralities

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Abstract

Dynamics of coherent phonon coupled with exciton in single-walled carbon nanotubes (SWNTs) are investigated by using few cycle pulse laser. Modulations corresponding to the radial breathing mode (RBM) observed in the time traces for the four chiral systems have been analyzed. The vibrational modes of the coherent phonon spectra are identified from the 2D distribution of probe photon energy versus Fourier frequency. Resonance conditions and mode frequencies lead to definite chirality assignments. The present study clarifies that the observed probe photon energy dependence of RBM amplitude is due to both the imaginary and real parts of the third-order susceptibility.

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Selection and/or peer-review under responsibility of the scientific committee of Symposium [Symposium G - Carbon Nanotubes and Graphene: Synthesis, Functionalisation and Applications] – ICMAT

Keywords: single-walled carbon nanotubes, coherent phonon spectroscopy, Few-cycle pulse laser.

Nomenclature

| Symbol | Description |
|--------|-------------|
| SWNT | single-walled carbon nanotube |
| RBM | radial breathing mode |
| CP | coherent phonon |
| NOPA | non-collinear parametric amplifier |
| CoMoCat | Co-Mo catalytic method |
| FT | Fourier-transform |
| MPM | molecular phase modulation |

1. Introduction

Single-walled carbon nanotubes (SWNTs) with one-dimensional nanostructures have unique mechanical, electronic, and optical properties [1–3]. Depending on their chirality, they can exhibit either metallic or semiconducting characteristics [4].
Theoretical and experimental studies have revealed a variety of phonon-assisted peaks, suggesting strong exciton-phonon coupling [5–9], which is often at the heart of many important phenomena in condensed matter physics. Although exciton-phonon coupling in SWNTs is usually studied by Raman spectroscopy [6–14], it is only a sensitive probe of ground-state vibrations. Recently, efforts have been made to investigate coherent lattice vibrations (phonons) in SWNTs by coherent phonon (CP) spectroscopy via femtosecond pump-probe techniques, which can also enable direct measurement of time-domain CP dynamics in excited states [15].

CP dynamics in SWNTs have been studied by several groups using the impulsive excitation method [15-24]. However, there are still some important concerns which need to be addressed, especially the mechanism of CP generation, which is related to coupling between phonon modes and the electronic structure. Using a tunable laser with a 50-fs pulse duration, Lim et al. observed radial breathing mode (RBM) vibrations [16]. The oscillations in the probe transmittance were found to be the result of ultrafast modulation of the optical constants at a frequency $\omega_{\text{RBM}}$ due to band gap ($E_{\text{gap}}$) oscillations induced by changes in the SWNT diameter $d$ ($E_{\text{gap}} \propto 1/d$). It was claimed that the photon energy dependence of the CP signal shows a first derivative behavior. Although they concluded that the two spectral shapes were similar, their results showed that the CP amplitude profile was much steeper than the derivative-based profile, explained in terms of a band-gap oscillation that induces a shift in the transition absorption spectrum. The separations between the two inflection points and between the two peaks in the CP amplitude are calculated to be about 40 meV and 70 meV, respectively, using Fig. 5 of the paper [16]. The two inflection points and the two derivative peaks should be coincident if the spectral shift is the origin of the oscillating signal. In fact, the two values differ by a factor of more than 1.7 times, and thus the real-time traces cannot simply be explained by the spectral shift mechanism.

In the present paper, we report a detailed pump-probe study of CPs in SWNTs using sub-10-fs visible pulses. The effects of the CPs on the difference absorbance are fully modeled. The probe photon amplitude profiles are analyzed in terms of the modulation of the excitonic transition probabilities. Since the signal from the pump-probe experiment is generated in a third-order nonlinear process, the real and imaginary parts of the nonlinear susceptibility can both play roles.

2. Experiment

The SWNT sample was prepared by CoMoCat method [25–27]. The pump and probe light sources were from the non-collinear parametric amplifier (NOPA). The pump source of this system is a commercially supplied regenerative amplifier (Spectra Physics, Spitfire). The central wavelength, pulse duration, power of the output, and repetition rate of this amplifier were 800 nm, 50 fs, 740 mW, and 5 kHz, respectively. With the use of a compression system composed of a pair of prisms and a pair of chirped mirrors, the system supported a pulse with a pulse duration lightly shorter than 5 fs with constant spectral phase, indicating that the pulses are nearly Fourier-transform limited. The energy of the pump is ~32 nJ. The probe pulse energy is five times weaker than the pump pulse.

The polarization of the pump and probe beams are parallel to each other. In the pump-probe experiment, signal was spectrally dispersed with a polychromator (JASCO, M25-TP) over 128 photon energies (wavelengths) from 1.71 to 2.36 eV (722 to 524 nm). It was detected by 128 sets of avalanche photodiodes and lock-in amplifiers with a reference from an optical chopper intersecting the pump pulse at the 2.5-kHz repetition rate. Details about our sub-5-fs pump-probe experimental setup and working principle of the techniques are described elsewhere [28,29].

3. Results and discussion

3.1. Stationary absorption spectrum of the sample and laser spectrum

Figure 1(a) plots the stationary absorption spectrum of SWNTs with the relevant chirality assignments [25]. The assignments of some absorption bands might be uncertain since they might be shared by more than one type of tubes because of their finite spectral widths. The broadband visible laser spectrum is resonant with the second exciton transitions ($E_{2\text{c}}$) of the tubes in 1.71–2.36 eV range. For the analysis of the real-time data in the latter part of this paper, the absorption spectrum was fitted by the sum of five dominant Voigt functions, which are the convolution of the Gaussian and Lorentzian functions at 2.17 eV, 2.08 eV, 1.91 eV, 1.84 eV and 1.78 eV corresponding to (6,5), (6,4), (7,5), (8,3), and (9,1) tubes, respectively. The properties of tubes (9,1) will not be discussed here due to its weak absorption. Given that the lineshape of the laser spectrum can affect the amount of laser energy absorbed, the “absorbed photon energy spectrum [30,31]” is calculated as shown in Fig. 1(b), which is defined latter by the difference in the spectrum between the probe light before and after passing through the sample.
Fig. 1. (Color online). Laser spectrum (blue line) and stationary visible absorption spectrum of SWNTs (red line) after subtracting the weak background and its Voigt fitting profiles (green lines), illustrating individual $E_{22}$ absorption components in 1.7–2.4 eV spectral range. The chirality assignments are shown together.

3.2. Electronic relaxation and thermalization of excited population.

Fig. 2. (Color online). (a) 2D display of $\Delta A$ ($E_{pr}$, $t$) as functions of probe photon energy, $E_{pr}$, and probe delay time, $t$. The black solid curves are the zero-change lines in the absorbance ($\Delta A = 0$). (b) Time-resolved $\Delta A$ spectra at the delay time points from 50 fs to 1850 fs with a 200-fs integration step.

Figure 2(a) graphs the two-dimensional (2D) difference absorption spectra $\Delta A$ plotted against the probe photon energy $E_{pr}$ and the delay time $t$. The striped oscillatory structures parallel to the time axis represent the modulation of the difference absorbance $\delta \Delta A(E_{pr}, t)$ by CPs. Here $\delta$ is the modulation of the absorbance change $\Delta A(E_{pr}, t)$ due to CPs at a specific probe photon energy $E_{pr}$ and delay time $t$ induced by the spectral shift and transition probability change, which give rise to the horizontal and vertical modulation, respectively. Figure 2(b) plots time-resolved spectra integrated over 200-fs delay-time steps at 10 center probe delay times ranging from 50 to 1850 fs. There are four prominent bleaching bands composed of three peaks and one shoulder, nearly coincident with the relevant $E_{22}$ transitions for the (6,5), (6,4), (7,5), and (8,3) chiral systems in Fig. 1. In addition, there are three isosbestic points near 2.21, 2.02, and 1.94 eV at delay times longer than 250 fs, as indicated by the small squares. The crossing points between neighboring time-resolved spectra are within ±0.03 eV of the average photon energies, except between 0 and 50 fs. Therefore, the relaxation after 200 fs can be described using a simple two-state model composed of a single intermediate state or excited state after photo-excitation, where a conversion from one state to the other is occurring. This behavior can be explained in terms of intraband relaxation from the $E_{22}$ excitonic state to the $E_{11}$ excitonic state, followed by a slower decay from $E_{11}$ to the ground state.
3.3. Fourier-transform (FT) spectra and chirality assignments

A 2D map of the Fourier power plotted against the probe photon energy and the vibrational frequency is presented in Fig. 3. The FT plots show two vibrational modes due to RBMs at ~300 cm⁻¹ (~100 fs) and to G modes at 1587 cm⁻¹ (21 fs) [15,19,20], generated by the impulsive excitation for a pulse duration (less than 10 fs) much shorter than all of the vibrational periods. Other vibrational modes are too weak to be resolved. Four RBMs are evident with vibrational frequencies of about 337, 310, 301, and 282 cm⁻¹. The assignment of chirality using only the electronic absorption or Raman spectra is often ambiguous due to spectral congestion [54-58]. In contrast, the intensity of the four dominant double-peaked structures indicated by the double-headed arrows in Fig. 3 corresponds to the first derivative of the electronic absorption spectrum for the different types of tubes [16,17,20]. The central dip in each structure represents the $E_{22}$ transition, since the oscillation is minimal at resonance [20]. However, as will be discussed later, some corrections must be made to this assertion.

The Raman shifts for different RBMs theoretically correspond to the vibrational frequencies of the FT of their CP profiles [32,33]. Consequently, the dips at the intersections of the horizontal and vertical lines in Fig. 3 correspond to the relevant vibrational frequency and electronic resonance transition energy. Using this relationship, the chirality can be assigned for the (6,4), (6,5), (7,5), and (8,3) systems, as indicated in Fig. 3, because only these tubes can simultaneously fulfill these two conditions. Other kinds of tubes may have weak absorption lines in the laser spectral range, but they cannot be efficiently excited. Using broadband high-sensitivity multichannel lock-in detectors, the power spectra of the four systems can be uniquely distinguished for RBMs, even though their absorption spectra overlap as shown in Fig. 1, without the need for time consuming or complex pulse-shaping techniques [17]. Therefore, this method is advantageous for simultaneous analysis of a sample containing many chiral systems. However, the dip position and the peak of the absorption spectrum do not exactly coincide, as will be discussed later. In contrast, for G-mode vibrations, the amplitude profiles for different chiralities overlap and cannot be distinguished. The frequency of the axial G-mode is insensitive to the diameter and chirality of SWNTs and is thus not reflected in the location of the signal in Fig. 3.

3.4. Raman and Raman-like processes in a semi-classical model

Before discussing the origins of CPs in SWNTs in detail, we first consider the mechanism for the appearance of the signals. According to the 2D FT power spectrum in Fig. 3, the power of RBMs is weak at photon energies corresponding to the center of the “absorbed spectrum” for the different chiral systems. Although the exact chirality is difficult to assign for G-mode vibrations, the vibrational spectra have two main components, which are outlined in Fig. 3 with circular ring (upper
panel). They display a similar probe photon energy dependence to that previously reported for a highly purified sample CNT sample with a (6,5) chirality [20]. Here, as discussed previously in Ref [30,31], a similar method is used to analyze the ground state NL processes A and B. The phase relations are

\[ \phi_{\ell}(\omega, \omega) = \arctan(-\omega \omega / \gamma), \]

(1)

\[ \phi_{B}(\omega, \omega) = \arctan(\omega - \omega \gamma), \]

(2)

\[ \phi_{c}(\omega, \omega) = \arctan(\omega / \gamma), \]

(3)

\[ \phi_{s}(\omega, \omega) = \arctan(-\omega \omega / \gamma), \]

(4)

The frequencies \( \omega_{0} \) and \( \omega_{c} \) correspond to the electronic 0–0 transition and vibrational frequency of the system, respectively. As expressed in Eqs. (1–4), the phases of processes B and B’ are opposite, which suggests that the intensity of NL process B will decrease if the intensity of process B’ increases. Since both lie in the same spectral range, the result of this anti-phase relation is that the vibrational spectra due to these two processes will cancel each other.

Consequently, the vibrational spectra vanish at the center of the “absorbed spectrum”, where intense resonant third-order nonlinear interactions are expected to occur. The degree of cancellation depends on the intensity distribution of the probe spectrum, since the modulation varies with the probe spectral intensities at frequencies \( \omega_{0} - \omega_{c} \) and \( \omega_{0} + \omega_{c} \). If these two intensities are the same, they will exactly cancel each other. When the probe spectrum is broad enough, energy will be exchanged. The modulation at the probe frequency \( \omega_{0} - \omega_{c} \), driven by the resonantly coupled spectral components can trigger oscillations near \( \omega_{0} - 2\omega_{c} \). Likewise, oscillations can be induced at \( \omega_{0} + 2\omega_{c} \). Higher order spectral variations can also occur through cascade processes. However, modulations at \( \omega_{0} \pm 2\omega_{c} \) are not due to high-order molecule-field interactions induced by potential anharmonicities such as overtones. (Here we refer to the CNT system as a “molecule” for simplicity.) On the contrary, the phenomenon arises due to consecutive interactions between the probe and field at different photon energies, even for a harmonic molecular potential. This analysis assumes coherent vibrations in the ground state. Since the interband relaxation occurs with a time constant on the order of 40 fs, the vibrational wavepacket contributing to the modulation of the electronic state is attributed to the ground state [34].

3.5. Probe photon energy dependence of the vibrational amplitudes

The probe photon energy dependence of the vibrational amplitudes (black lines) of RBMs for the three chiralities (6,4), (6,5), and (8,3) is plotted in Figs. 4(a)–(c). The amplitude profile for (7,5) is not shown since it is not strong enough for detailed analysis. Several groups have studied RBM amplitude profiles [16,17,20]. In their work, the probe photon energy dependence of the amplitudes was compared to the first derivative of the absorption spectra (hereafter, this analysis is referred to as a DIF-type analysis). It was argued that the resemblance of the amplitude profiles to the first derivative implies wavepacket motion. This type of analysis is hereafter referred to as a DER-type analysis. However, the physical mechanism does not support that conclusion.

Panels (2) in Fig. 4 show a fit of the probe amplitude profiles with the first derivatives of the relevant stationary absorption components (gray lines) for different chirality. The absorption for each chiral system is obtained from a spectral deconvolution of the stationary absorption spectrum using the Voigt function in Fig. 1(a). The double-peak structure associated with a first-derivative dependence does not produce a good fit [16,17,20]. Even after modifying the absorption components to take into account the errors in fitting the stationary absorption with the analytic function, the disagreement on the pump–probe delay time \( \tau \) [19,23], \( P_{A}(\omega, \tau) = \chi(\omega)E_{pr}^{*}E_{pu}^{*}E_{pu} \times I(\omega)E_{pr}^{*}E_{pu}(\omega) \).

The polarization is generated by a Raman gain/loss process associated with energy exchange between the coherent vibrations and the probe optical field, according to the relation \( \Delta A(\omega, \tau) \propto -\text{Im}[P^{(3)}(\omega, \tau)]E_{pro}^{*}E_{pro} \) [31,35]. In this process, the probe optical field is alternately deamplified and amplified, depending on the phase change of the vibrations. Thus, the probe photon dependence of the FT power is dependent on the spectral distribution of the laser photons absorbed by the sample. In that case, \( \Delta A(\omega, \tau) \propto \delta(\omega)\cos(\omega \tau + \delta). \) We next consider a phenomenological analysis. Since the pump laser is resonant with several chiral species, we first separate the spectra associated with each of these species. For quantitative discussion, the phenomenological description of the probe photon energy dependence \( \Delta A(\omega_{\text{probe}}) \) of the vibrational amplitude can be expressed as [37]

\[ \Delta A(\omega_{\text{probe}} = \omega_{c}) = C_{1s} \left| a(\omega_{\text{probe}}) - a(\omega_{\text{probe}} - \omega_{c}) \right|, \]

(5)

\[ \Delta A(\omega_{\text{probe}} = \omega_{c}) = C_{1s} \left| a(\omega_{\text{probe}}) - a(\omega_{\text{probe}} - \omega_{c}) \right|, \]

(6)
Here $C_{1S}$ and $C_{1AS}$ are proportionality constants, $\omega_{\text{probe}}$ is the frequency of the probe, $\omega_v$ is the molecular vibration frequency, $L(\omega)$ is the laser spectrum, $a(\omega)$ is “the absorbed laser spectrum” (which is the frequency distribution of photons being absorbed by the sample, shown by orange lines in panels (1) of Fig. 4), and $A(\omega)$ is the absorbance of the sample at a frequency $\omega$. Equations (5) and (6) correspond to pump/Stokes and pump/anti-Stokes interactions, respectively. The above calculation is based on the assumption that the imaginary part of the third-order susceptibility $\chi^{(3)}$ corresponding to the Raman interaction can be written as $\chi^{(3)}(-\omega_2; \omega_1, -\omega_1, \omega_2) = C_2(a(\omega_2) - a(\omega_2 \pm \omega_1))$. Here $C_2$ is a proportionality constant, the plus and minus signs correspond to the cases of pump/Stokes and pump/anti-Stokes interactions, respectively, and $\omega_2$ and $\omega_1$ are the components of the probe spectrum. The sideband peaks should occur at frequencies corresponding to the difference between the vibrational frequencies [30,31,35].

The energy difference between the sidebands, as numbered in panels (1) of Fig. 4(a), is always found to be close to an integer multiple of the relative RBM frequencies. This observation suggests the presence of overtones in the Raman interactions between the probe pulse and the coherent vibrations. However, these overtones are not induced by anharmonicity but are instead due to cascaded Raman processes as discussed below. Because the spectral distribution of the pump and probe lasers is broad, energy exchange can take place between coherent lattice or molecular vibrations and the probe optical field. The interaction can be between the first Stokes beam and the probe beam (so called “laser” used in the discussion of Raman interaction), or between the first Stokes beam and the second (or higher) Stokes beams via the coherent vibrations.

As a result, the probe photon energy dependence can be compared with the absolute value of the difference between the absorbed photon energy spectrum and the distribution shifted by the vibrational frequency. Hereafter, this analysis is referred to as a DIF-type analysis. Fitting of the amplitude profiles with the difference between the shifted and unshifted absorbed probe energy distributions were carried out for Raman ground-state and Raman-like excited-state interactions. They included higher order contributions with adjustable parameters (due, for example, to the phonon amplitudes). The results are plotted in panels (3) of Fig. 4, corresponding to RBMs for (6,4), (6,5), and (8,3) tubes. It can be seen that the fits are still not good.

3.6. Fitting the amplitude spectrum with contributions from the real and imaginary parts of the third-order susceptibility

![Fig. 4. Probe photon energy dependence of normalized RBM amplitude profiles (AP, black lines) for (a) (6,4), (b) (6,5) and (c) (8,3) tubes, fitted with the absorbed laser spectra (A, orange lines), first-derivative of the stationary absorptions (gray lines, panels 2) and absorbed laser spectra (DER, red lines), the laser spectrum composed of ground-state absorption bleaching, stimulated emission, and induced absorption. This effect results from the change in refractive index caused by the deformation of the lattice and molecular structure during the interaction.](image-url)

In this section, the fit to the probe photon energy dependence of the vibrational amplitude is improved by combining the contributions from the DIF- and DER-type analyses. In the previous papers [24,16–24], based on the DER analysis, the modulation was explained in terms of a sinusoidal electronic energy modulation due to an RBM-induced change in the diameter of a CNT [24,16–24]. In the following, the mechanism involved in the DER-type contribution is more fully discussed.

A change in the refractive index is induced by the molecular phase modulation (MPM) process due to the DER contribution to the modulation [38]. This MPM produces a periodic shift in the probe spectrum. This in turn modulates the time-resolved spectrum composed of ground-state absorption bleaching, stimulated emission, and induced absorption. This effect results from the change in refractive index caused by the deformation of the lattice and molecular structure during the interaction.
coherent vibrations [31], which the electronic distribution instantaneously follows. The index change introduces a modulation of the probe frequency because of the change in the phase of the probe field, whose time derivative is the optical frequency. Consequently, the signal can be approximated as a spectral shift of the probe pulse induced by a kind of “cross-phase modulation” [39], and the probe energy dependence of the phonon amplitude follows the first derivative of the electronic resonance.

By adding the contributions from the DIF and DER processes, excellent fits are finally obtained, as shown in panels (4) of Fig. 4. They show the absolute value of the sum (blue lines) of the contributions of the two types of mechanisms for different RBMs with an adjustable relative contribution used as the fitting parameter for DER (dashed lines) and DIF (dotted lines) analyses, before taking absolute values of the sum. We adjusted the relative intensity of different order of phonon peaks taking into accounts of the differences in the signs of amplitudes and add them with the DER profile to make the fitting line shape match the amplitude profile. At first starting with the apparently reasonable ratio to fit with the experimental results of the probe photon dependence of the vibrational amplitude, then to take the sum (over probe photon energy data points) of the squared values of the difference between the fitted and observed and tried to minimize the value by changing the ration by small amount to each the minimum deviation value. Finally we take the absolute value. The fitting profiles of DER and DIF types are already shown in panel (4) of Figure 4 before taking absolute values. For the weight of the DIF and the DER, the fraction (percent) of the contributions from DIF and DER are listed in Table 1.

| Chirality (n,m) | DER-type contrib. (%) | Band Center (cm⁻¹) | Shift amount (cm⁻¹) | Band width (cm⁻¹) | Shift /width | DIF-type contribution (%) | Peak number and its Stokes(-) and anti-Stokes(+) order |
|----------------|-----------------------|--------------------|---------------------|-----------------|-------------|--------------------------|-----------------------------------------------------|
| (6,4)          | −45%                  | 16840              | −30                 | 455.78          | 0.066       | −55%                     | +1 -1 -2 -3                                         |
| (6,5)          | −10%                  | 17510              | −29                 | 801.92          | 0.036       | −90%                     | 1 0 -1 -2                                          |
| (8,3)          | −58%                  | 14821              | −22                 | 327.92          | 0.067       | −42%                     | 1 -1 -2 /                                           |

Table 1. The corresponding parameters used for the fitting of the RBM amplitude profiles, including absorption band center (cm⁻¹), shift amounts (cm⁻¹) for first-derivative fitting, absorption band width (cm⁻¹), DER-type and DIF-type contributions to the amplitudes (%), the Stokes (-) and anti-Stokes (+) order of relevant peaks in amplitude profiles. The zero order Stokes peaks represent the absorbed laser beam.

In the cases of the (6,4) and (6,5) tubes, the contributions from the DER analysis are smaller than those from the DIF analysis. In particular, for the (6,5) tubes, the DIF contribution is 90%. The size of the contribution is reversed for the (8,3) tubes, for which more than half is due to the DIF process. The reason for the higher DIF contribution for the (8,3) tubes is the narrower spectral bandwidth of this system compared to the others. The FWHM of the stationary spectra for the (6,4), (6,5), and (8,3) tubes is found from Fig. 1 to be 64.6, 89.9, and 49.2 meV, respectively. The order of the widths matches the DIF contributions. It can be concluded that both the DIF and DER analyses make significant contributions to the probe photon energy dependence of the absorbance change, in contrast to previous reports [16,17,20]. The physical mechanisms for the DER and DIF contributions are respectively the real and imaginary parts of the third-order susceptibility. Table 3 lists the contributing Stokes and anti-Stokes bands for three different chiral systems. Because of the non-uniform probe spectral distribution, the (6,5) and (8,3) tubes show only anti-Stokes sidebands up to second order, while the (6,4) tubes exhibit both Stokes and anti-Stokes bands. The relative sizes of the DER contributions are further discussed below.

4. Conclusions

CP and electronic relaxation dynamics of SWNTs were investigated in CoMoCat grown ensembles for the four chiral systems (6,4), (6,5), (7,5), and (8,3). It was found that the imaginary and real parts of the third-order susceptibility both play important roles in the modulation of the difference absorbance. The amplitude profiles of RBMs can be well fit by the sum of the first derivative of the absorption due to the real part of the third-order susceptibility and the difference absorption due to the imaginary part of the susceptibility induced by a Raman process, with the relative contributions being adjustable. The imaginary part, given by a DIF contribution in the fit, arises from energy exchange between CPs and the probe optical field. The real part, resulting from a refractive index change due to molecular vibrations, manifests itself as a DER dependence due to the MPM process.

Acknowledgements

The authors would like to acknowledge Drs. H. Kataura, Y. Sakakibara, and Y. Miyata for providing us the sample. This work was financially supported by the International Cooperative Research Project, Ultrashort Pulse Laser Project, Japan Science and Technology Agency.
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