

Subnanometric Near-Field Raman Investigation in the Vicinity of a Metallic Nanostructure

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We present a near-field Raman investigation in the subnanometric vicinity of a metallic nanotip, where the tip-sample distance is precisely controlled by our newly developed time-gated illumination technique. Using this scheme on an isolated carbon nanotube, we have profiled the spatial decay of evanescent light. We also investigated extremely short-ranged chemical and mechanical interactions between the metal on the tip apex and the molecules of an adenine sample, which are observable only within the subnanometric vicinity of the tip. The results show a near-field Raman investigation with an accuracy of better than a few angstroms. Further, this shows strong promise for superhigh resolution in optical microscopy based on this technique.

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Tip-enhanced Raman scattering (TERS) spectroscopy [1–5] has been established as a powerful optical imaging tool that allows one to optically investigate samples at the nanometric scale. This technique can overcome the diffraction limit of light, and hence a microscopy based on TERS can provide subwavelength optical images far beyond the diffraction limit [6–8], which is attributed to the highly confined evanescent field at the apex of a metal-coated nanotip that is utilized as a probe in this technique. The dominant mechanism for interaction between the tip and the sample is electromagnetism (EM), with an interaction length of the order of a few to a few tens of nanometers. However, because of the presence of metal on the tip, the chemical interaction between the sample molecules and the metal starts to become significant, if the sample is very close to the tip, particularly, at molecular distances [9,10]. Further, if the distance between the sample and the tip is reduced so much that the tip comes in physical contact with the sample, then mechanical interaction between the tip and the sample also starts to play an important role [5,11]. Since the three interaction mechanisms have different interaction lengths, it could be possible to study them individually, if the distance between the tip and the sample in a TERS experiment is precisely regulated with accuracies of the order of subnanometer scale. This is an extremely difficult task, because the nanotip that is usually controlled by atomic force microscopy (AFM) operating either in contact [12] or in tapping [13] mode, cannot be maintained at a preselected fixed distance from the sample during a long measurement. In this Letter, we demonstrate how we can effectively control the tip-sample distance in TERS experiments with extremely high accuracy, even though the tip in our experiment oscillates under the tapping-mode operation of AFM. We demonstrate that the chemical as well as the mechanical interaction distinctly shows up in TERS spectra, when the tip is main-

tained very close to, or pressed against the sample. We achieve this result by time gating the illumination, so that the sample is selectively illuminated only when the tip is at a certain distance from the sample during the repeated cycles of its tapping oscillation. This technique allows us to preselect any desired distance between the tip and the sample, and then maintain that distance for as long exposure as we want, by repeatedly illuminating the sample only for that chosen tip-sample distance during every cycle of tip oscillation. In the first part of this study, we utilized an isolated single-walled carbon nanotube (SWNT) as a sample to profile the distance dependency of EM interaction. In the later part, we used a nanocrystal of adenine to demonstrate clear signatures of chemical and mechanical interactions on TERS spectra for precisely controlled subnanometric tip-sample distances. We also show a one-dimensional scan of an isolated SWNT to emphasize the possibility of super high spatial resolution in an imaging technique based on mechanical interaction in TERS.

Efforts for controlling distance between tip and sample have received some interest in the near past for fluorescence [14,15] and for Raman scattering [16] measurements. These experiments usually involve sheer-force control of the AFM tip, which has poor stability and accuracy of tip position. On the other hand, a time-gated scheme with tapping-mode AFM control can have better control over the tip position. We have recently shown that a synchronous time gating of photon counting can effectively provide a good control over tip-sample distance in TERS measurements [17]. However, this scheme can only analyze the optical signal strength, such as Raman or fluorescence intensity. The chemical and mechanical interactions affect the spectral shapes by inducing both a shift in frequency and a change of intensity of Raman modes. Therefore it is essential to record whole spectrum, rather than just the intensity of a Raman mode. We therefore

developed a new experimental scheme, where, instead of the detector, we apply a synchronous time gating to the illumination system and record entire spectrum by a multi-channel detector. This allows us to record the entire spectrum for any desired tip-sample distance at extremely high accuracy.

A schematic of our experimental setup is shown in Fig. 1. Figure 1(a) illustrates that the tip-sample arrangement is selectively illuminated only for a particular tip-sample distance. The sinusoidal oscillation of the tip [18] and the synchronized opening of the time gate are shown by the upper and the lower curves, respectively, in Fig. 1(b). One can preselect a desired tip-sample distance and the accuracy in measurement by selecting certain values of the time delay (τ) and the temporal width (Δ), respectively, of the time gate. This is done by feeding a trigger signal extracted from the oscillation of the tip to a pulse generator, which synchronously generates pulsed signal with desired amplitude and width. This pulsed signal controls an optical shutter through an acousto-optic modulator for stroboscopic illumination of the tip-sample arrangement, as illustrated in Fig. 1(c).

We first discuss the tip-sample distance dependency of the EM interaction, which is expected to follow the spatial profile of the evanescent field in the vicinity of the tip apex. We selected SWNTs as a sample in this study, which were synthesized by the direct-injection pyrolytic-synthesis method [19]. The sample was prepared by dispersing SWNTs on a glass substrate, and then selecting an isolated SWNT with length much longer than the focal spot of the

illumination. Raman scattering from the sample was excited with $\lambda = 488$ nm through an oil-immersion objective lens (NA = 1.4) and the scattered signal was recorded by a CCD detector after dispersing by a Raman spectrometer. A commercially available silicon cantilever tip was coated with a 28-nm-thick silver layer by thermal vapor deposition, which was positioned on the sample in the focal spot and was controlled through the tapping-mode operation of an AFM. The pulse generator was set in such a way that for the tapping period of 8 μ s, the temporal width of the time gate, Δ , was 0.2 μ s. The resolution in tip-sample distance, which depends on the absolute position of the tip, was estimated to be about 3 \AA when the tip was closest to the sample. The accuracy in the absolute position of the tip was about 1 \AA . Figure 2(a) displays some of the TERS spectra, marked by A through D, recorded at specified tip-sample distances, d , which is measured from the upper surface of the SWNT. Spectrum A at $d = 0$ nm represents a physical contact between the tip and the sample, whereas spectrum D at $d = 100$ nm represents a far-field spectrum. The prominent Raman peaks appearing in the spectral range of 1550–1620 cm^{-1} , are characteristic Raman modes of SWNTs, known as the G band. The intensities of the peaks in the G band increase drastically as the tip-sample distance decreases, which reflects the near-field enhancement in TERS.

While we have shown only four spectra in Fig. 2(a), we actually measured a large number of spectra for various values of d . The intensity of the G-band signal was found to be consistently increasing with decreasing tip-sample distance, as shown by the data points in Fig. 2(b). In order to numerically confirm the nature of field confinement at the tip apex, we performed a simulation based on the finite-difference time-domain (FDTD) formulation. The tip apex in the simulation was chosen to be 30 nm in size, and it was assumed that 30 nm length of an isolated infinitely long SWNT with a diameter of 1 nm was illuminated with this confined field. The simulation was performed by gradually changing the tip-sample distance and Raman intensity

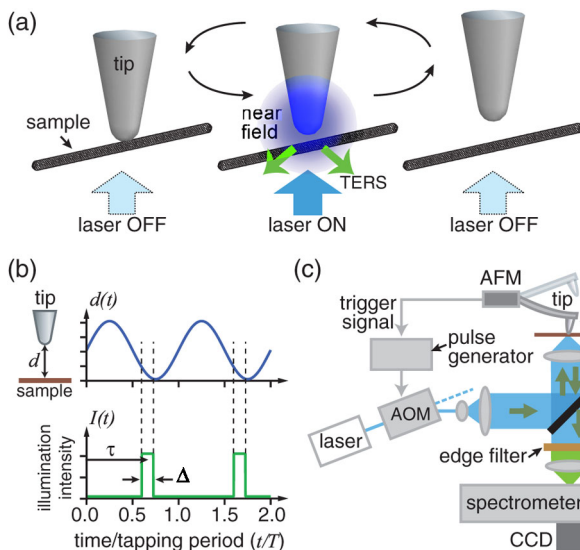


FIG. 1 (color online). (a) The tip-sample arrangement is selectively illuminated only for a predecided tip-sample distance. (b) The sinusoidal oscillation of the tip and the synchronized opening of the time gate are illustrated. The tip-sample distance and the resolution in the distance can be selected by choosing certain values of τ and Δ . (c) The complete system of tip-enhanced Raman spectroscopy using a tapping-mode AFM and acousto-optic modulator for time-gated illumination.

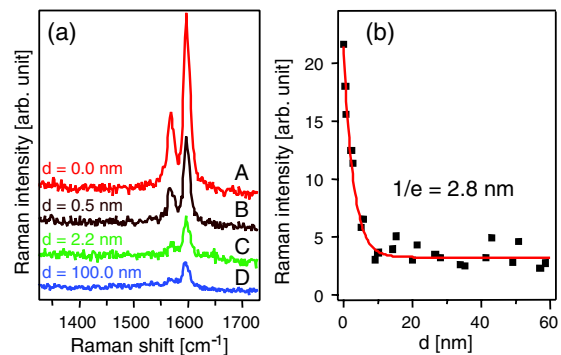


FIG. 2 (color online). (a) Raman spectra of an isolated SWNT at four different indicated tip-sample distances. (b) A plot of integrated Raman intensity of the G-band versus the tip-sample distance d . The solid curve represents a profile obtained from FDTD simulation.

profile was obtained in the z direction. The simulated profile, which shows an exponential decay, is plotted by red curve in Fig. 2(b), and it shows great agreement with the experimental results. The decay length, defined as the value of d where the intensity drops by a factor $1/e$, is a parameter that quantifies the spatial confinement of light at the tip apex and was found to be 2.8 nm, which confirms strongly confined nature of the light field near the tip apex.

In this study, we experimentally observed the spatial behavior of EM interaction between the tip and the sample. However, a clear evidence of chemical or mechanical interaction was not observed. Nevertheless, since this sample shows strong response to EM interaction, we selected this sample for studying the behavior of EM interaction. Next, in order to concentrate on the chemical and mechanical interactions to complement the EM interaction, we selected adenine molecule, because it has stronger affinity with silver, causing a stronger chemical interaction. Also, our experiments showed that it was easy to compress adenine sample by slight push of the tip, making it easier to see mechanical interaction even for a small amount of tip-applied pressure.

Self-assembled adenine nanocrystals [20] were prepared by casting ethanol solution of adenine on a glass substrate, and an isolated nanocrystal was selected as a sample. All experimental parameters were the same as those used for the previous sample. The maximum tip-applied force on adenine nanocrystal during the oscillation of the tip was about 0.4 nN, which was estimated from experimental parameters [21]. The adenine nanocrystal was estimated to be compressed by 1.0 nm under this force. Since d is measured from the upper surface of the sample, it takes a negative value when the sample is compressed under tip-applied pressure in the present experiment.

Figure 3(a) shows a data set of TERS spectra from adenine nanocrystal for the indicated tip-sample distances. The spectra are shown in the spectral range of the ring-breathing mode (RBM) of adenine, which shows a prominent peak at about 721 cm^{-1} . Spectrum A was taken when the sample was compressed under tip-applied force, spectrum B was taken when the tip was in contact with the sample, but the average force applied by the tip on the sample was negligible, and spectrum C was taken when the tip was very close to, but not in contact with the sample. For a comparison, spectrum D was taken for the maximum distance between the tip and the sample, which represents far-field Raman scattering.

The far-field spectrum, shown by D in Fig. 3(a), could be well fitted with one Lorentzian function, whereas the spectra A–C could be best fitted with two Lorentzian functions, showing the presence of two underlying Raman peaks. The peak appearing in spectrum D at 721 cm^{-1} was observed in all spectra at the same frequency position. We term this peak, which corresponds to the unperturbed RBM of adenine, as ω_0 . The other peak appeared at 731 cm^{-1} in spectra C and B, whereas it appeared at 736 cm^{-1} in spectrum A. We term this peak as ω_1 . The dependencies

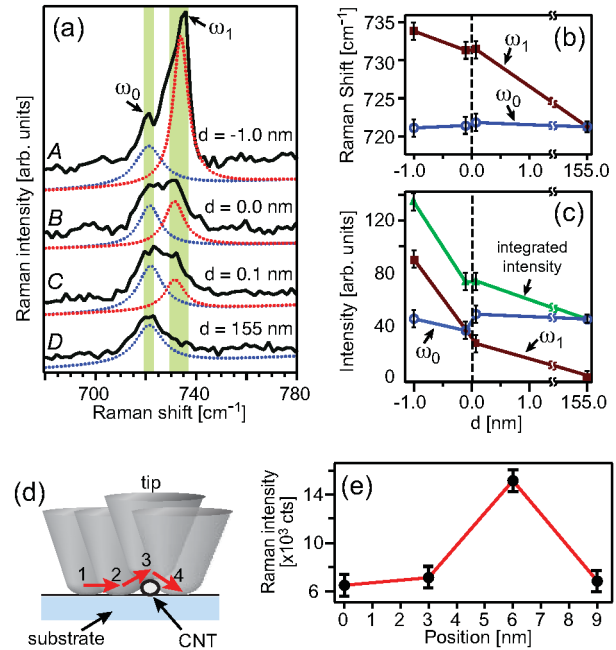


FIG. 3 (color online). (a) Raman spectra of an adenine nanocrystal at indicated tip-sample distances. The peaks marked by ω_0 and ω_1 represent the unperturbed RBM and the frequency-shifted RBM, respectively. Deconvoluted Lorentzian peaks for each spectrum are also shown by the dotted curves. (b) Tip-sample distance dependence of Raman shift, and (c) of the peak intensity, of the two Raman modes ω_0 and ω_1 . The dashed lines indicate the surface of the sample ($d = 0$). An integrated intensity plot is also shown in (c), which represents total enhancement of the RBM. (d) A schematic illustration of 1D scan of an isolated SWNT along a direction perpendicular to its axis. (e) The corresponding TERS intensity increases when the tip is exactly above the SWNT, depicting a spatial resolution of 3 nm.

of frequency positions and intensities of both peaks ω_0 and ω_1 on the tip-sample distance are plotted in Figs. 3(b) and 3(c), respectively. Figure 3(c) also shows the increase of integrated intensity (for combined ω_0 and ω_1 modes) with decreasing tip-sample distance, which represents total near-field enhancement of RBM.

Spectrum D in Fig. 3(a) represents Raman scattering from adenine nanocrystal under no influence of the tip. As the tip came close to the sample at a distance of 0.1 nm, some of the adenine molecules started to chemically interact with silver metal on the tip, and the RBM vibrational frequency of those molecules shifted to 731 cm^{-1} . This shift of 10 cm^{-1} is consistent with our earlier theoretical prediction [9]. At the same time, there were many other adenine molecules within the focal spot, which were not close enough to the tip, and hence they continued to have their RBM frequency at the original position of 721 cm^{-1} . As a result, spectrum C in Fig. 3(a) shows two Raman peaks, ω_0 and ω_1 . When the tip-sample distance was further reduced to $d = 0$ in spectrum B, more adenine molecules came under chemical interaction with the metal on the tip, resulting in slight increase in the intensity of ω_1

mode and slight decrease in the intensity of ω_0 mode, as also shown in Fig. 3(c). Further, when the adenine nanocrystal was pushed by the tip to a value of $d = -1.0$ nm, the corresponding Raman spectrum, presented as A in Fig. 3(a), showed significant changes in both frequency position and peak intensity for the mode ω_1 . These drastic changes could be explained by an additional effect of mechanical interaction due to the uniaxial pressure applied by the tip. It has been shown previously that tip-applied pressure can significantly shift Raman modes [5,11]. As the tip compressed the sample, the contact area between the tip and the sample increased, resulting in an increase in the number of sample molecules in contact with the tip. Because of the contact, these molecules underwent chemical as well as mechanical interactions at the same time [22]. The chemical interaction provided a shift of 10 cm^{-1} to ω_1 , as also seen in spectrum B. The mechanical interaction induced a further shift of 5 cm^{-1} to the RBM of the same molecules, resulting in a total shift of 15 cm^{-1} to ω_1 in spectrum A. The additional shift of 5 cm^{-1} due to tip-applied pressure is consistent with expected amount to pressure-induced shift in the RBM of adenine [9,10]. The increased number of sample molecules in contact with the tip is one of the dominant reasons for an increase of the intensity of ω_1 mode in spectrum A. The other possibility is due to modified resonance condition under tip-applied pressure [11].

Invoking desired pressure effect by precisely controlling the tip position can be of tremendous benefit in super high resolution imaging, because the pressure effect is much more localized than the enhanced EM field in the x - y plane. While the EM field extends to a size comparable to the tip apex, the tip-applied pressure extends only to the area of physical contact. Owing to the curvature of the tip apex, the contact area in present experiment can be smaller than 1 nm, even if the tip apex is about 30 nm. Therefore, an optical imaging based on precisely controlled tip-applied pressure can provide spatial resolution much better than what is currently obtained in TERS imaging. In order to support our claim, we performed a one-dimensional scan of an isolated SWNT in the direction perpendicular to its axis, while keeping the tip-sample distance within the range where the pressure effects in TERS could be observed. In this scan, the tip was moved at steps of 3 nm, and TERS was measured at 4 consecutive positions as the tip crosses over the SWNT. A schematic of this scan process is shown in Fig. 3(d). For the entire scan, the EM enhancement was almost constant, as the total scan area was much smaller than the extent of the enhanced field. However, as shown in Fig. 3(e), the TERS intensity noticeably increases at position 3, in comparison with positions 1, 2 and 4. This increase of TERS intensity is associated with the pressure effect [11], which is highly localized in x - y plane. The increase of TERS intensity in Fig. 3(e) shows that the SWNT exists at position 3, which is observed with a high spatial resolution of at least 3 nm. The results show strong

promises for super high spatial resolution in imaging technique based on precisely controlled tip-sample distance in TERS.

In conclusion, we have developed a new time-gated technique for stroboscopic illumination in TERS experiments, which effectively allows us to have a precise control over measuring TERS spectrum for a preselected tip-sample distance. Using this scheme, we have demonstrated an exponentially decaying nature of evanescent light near the apex of a metal-coated tip. A precise control of the tip-sample distance with subnanometric accuracy allowed us, for the first time, to experimentally observe the influences of extremely short-ranged chemical and mechanical interactions between the tip and the sample in a TERS measurement. This study opens doors for direct observations, and hence for further studies, of chemical and mechanical interactions in TERS, which range typically within subnanometer scale. Further, it shows strong promise for TERS imaging with super high spatial resolution.

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- [1] Y. Inouye *et al.*, Proc. SPIE Int. Soc. Opt. Eng. **40**, 3791 (1999).
- [2] R. M. Stöckle *et al.*, Chem. Phys. Lett. **318**, 131 (2000).
- [3] N. Hayazawa *et al.*, Opt. Commun. **183**, 333 (2000).
- [4] B. Pettinger *et al.*, Phys. Rev. Lett. **92**, 096101 (2004).
- [5] P. Verma *et al.*, Phys. Rev. B **73**, 045416 (2006).
- [6] A. Hartschuh *et al.*, Phys. Rev. Lett. **90**, 095503 (2003).
- [7] T. Ichimura *et al.*, Phys. Rev. Lett. **92**, 220801 (2004).
- [8] T. Yano *et al.*, Appl. Phys. Lett. **88**, 093125 (2006).
- [9] H. Watanabe *et al.*, Phys. Rev. B **69**, 155418 (2004).
- [10] N. Hayazawa *et al.*, J. Chem. Phys. **125**, 244706 (2006).
- [11] T. Yano, Y. Inouye, and S. Kawata, Nano Lett. **6**, 1269 (2006).
- [12] W. Zhang *et al.*, J. Phys. Chem. C **111**, 1733 (2007).
- [13] A. Rasmussen and V. Deckert, J. Raman Spectrosc. **37**, 311 (2006).
- [14] F. M. Huang, F. Festy, and D. Richards, Appl. Phys. Lett. **87**, 183101 (2005).
- [15] P. Anger, P. Bharadwaj, and L. Novotny, Phys. Rev. Lett. **96**, 113002 (2006).
- [16] B. Pettinger *et al.*, Phys. Rev. B **76**, 113409 (2007).
- [17] T. Yano *et al.*, Appl. Phys. Lett. **91**, 121101 (2007).
- [18] J. P. Cleveland *et al.*, Appl. Phys. Lett. **72**, 2613 (1998).
- [19] T. Saito *et al.*, J. Phys. Chem. B **109**, 10647 (2005).
- [20] B. Giese and D. McNaughton, J. Phys. Chem. B **106**, 101 (2002).
- [21] Q. Zhong *et al.*, Surf. Sci. Lett. **290**, L688 (1993).
- [22] T. Ichimura *et al.*, J. Phys. Chem. C **111**, 9460 (2007).