

Resonant Raman Scattering of 4-Nitrothiophenol

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Thiophenol-based molecules are commonly used reporter molecules for various experiments, especially within the scope of surface- and tip-enhanced Raman spectroscopy. Due to their molecular structure, they bind covalently to noble metals and have a huge Raman scattering cross section. Herein, the widely uncharted optical properties of the frequently used probe molecule 4-nitrothiophenol (p-NTP or 4-NTP) are analyzed by resonant Raman spectroscopy. Based on the three different types of samples, it is demonstrated that the molecule exhibits two intrinsic resonances at specific wavelengths. For a wide range of experiments, this is an important information since intrinsic resonances may give rise to an enhancement of the Raman intensity at these specific excitation wavelengths. The Raman cross section of p-NTP in resonance at 1.9 eV (650 nm) to be $6 \times 10^{-26} \text{ cm}^2$ per molecule is also measured.

1. Introduction

Thiophenol-based (TP) molecules are model molecules for a large number of experiments in physics, chemistry, and biology, due to their variety of functionalizing groups with various molecular properties, and their affinity to noble metals.^[1–3] The functionalization of TP-based molecules ranges from small amino groups up to large biological structures, such as peptides.^[4] Depending on the additional group, the molecules suit for fundamental studies, chemical and biological sensing, or surface catalysis.^[5–8] TP-based molecules are also ideal candidates for the functionalization of noble metals, e.g., substrates for surface-(SERS) and tip- (TERS) enhanced Raman spectroscopy.^[4] The functionalization of noble metals occurs via the thiol-group (SH-group) that has a high chemical affinity to this kind of metals ($\approx 200 \text{ kJ mol}^{-1}$).^[9] Other significant properties of TP-based molecules are due to their benzene ring. The molecules are optimal suited for the formation of self-assembled monolayers (SAMs) because of the π - π interactions of the benzene rings^[10,11] and are ideal reporter molecules for Raman and SERS/TERS

detection due to the large Raman scattering cross section of the carbon ring.^[4]

One frequently applied TP-based molecule in a diversity of experimental studies is the designer molecule 4-nitrothiophenol (p-NTP or 4-NTP), also known as 4-nitrobenzenethiol (4-NBT).^[12–19] The p-NTP molecule possesses a large Raman cross section and a photosensitive nitro-group (NO_2) that is attached to the benzene ring in para-position to the SH-group (cf. inset Figure 1). p-NTP is widely used in SERS and TERS experiments to examine photochemical and electrochemical reactions.^[12–14] Furthermore, catalytic processes are monitored at the nanoscale with TERS by using the designer molecule,^[15] and the validations of novel experimental

techniques, such as combined TERS-scattering-type scanning near-field optical microscopy (s-SNOM),^[16] as well as the visualizations of reversible switching processes are done using p-NTP.^[17] Outside the framework of SERS and TERS, the molecule is used to tune the energy levels of nanocrystal quantum dots^[18] and to build electrochemically controllable conjunctions of proteins on surfaces.^[19]

Although p-NTP is one of the most used molecules in SERS, TERS, and other optical experiments,^[12–19] there is, surprisingly, no fundamental study on its optical properties. The Raman resonances of the p-NTP molecule are not sufficiently investigated, although they are of crucial importance in SERS and TERS experiments, as they will affect enhancement factors.^[20,21]

In this article, we use resonant Raman spectroscopy (RRS) to study the excitation energy dependent changes in the Raman intensity. For the experiment, we used three different types of p-NTP samples: A commercially available powder sample, an ethanolic p-NTP solution, and p-NTP bound to a flat (111)-gold film. The powder sample is studied since it is the natural form of the molecule, the dissolved p-NTP is analyzed as intermediate stage of a variety of samples, and the molecule on gold is measured to study the influence of the gold to the molecules' electron transition energy. We found that p-NTP exhibits two Raman resonances in the visible spectral area at which the Raman intensity strongly increases. In addition, we investigated that the resonances occur for all kind of samples. The Raman measurements on the gold sample showed that gold affects the molecules' optical transitions only slightly, compared to the powder sample and the stored solution.

2. Results and Discussion

We studied the molecules' optical transitions and its effect on inelastic light scattering on three different kinds of p-NTP

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samples by using RRS. In RRS experiments, the energy of the exciting laser is tuned over a broad range while tracking the intensity of the Raman signal. When the laser energy matches the resonance energy (optical transition) of a molecular eigenstate, the Raman intensity increases by several orders of magnitude.^[20,22] Compared to absorption measurements, RRS has the advantage that nontransparent solid samples may be analyzed. We were able to investigate the crystalline p-NTP powder as well as the p-NTP bounded to an Au surface and compare them to the results obtained in solution.

An example of a p-NTP Raman spectrum is shown in Figure 1. The spectrum exhibits three intense vibrational modes that are characteristic for the molecule. The vibration at 1100 cm^{-1} is attributed to the C–H stretching of the benzene ring, the peak at 1343 cm^{-1} appears due to the symmetric stretch of the NO_2 -group, and the mode at 1571 cm^{-1} is generated by the stretch of the carbon ring (C–C stretch).^[23,24]

Typically, SERS and TERS measurements are performed in the visible spectral range around 488, 532, and 633 nm, and near-infrared regime (785 nm). The occurrence of molecular resonances in this spectral range will be of high interest for SERS and TERS, and resonant Raman scattering, since the measured Raman intensity will be additionally enhanced due to this intrinsic resonances, if the energy of the exciting light corresponds to the energy of an optical transition.^[20,21,25] The enhancement of the Raman signal due to molecular resonances leads further to larger Raman cross sections ($d\sigma/d\Omega$).

To find the resonances and to determine the effect of the optical transitions in the visible spectral range on the Raman intensity, we varied the excitation wavelength from 565 to 790 nm, starting with the analysis of the powder sample. In Figure 2a, we show Raman spectra of the powder sample that we measured at various wavelengths. The spectra are calibrated by a diamond reference (see the Experimental Section). The intensity of the Raman modes varies with the energy of the exciting laser. For

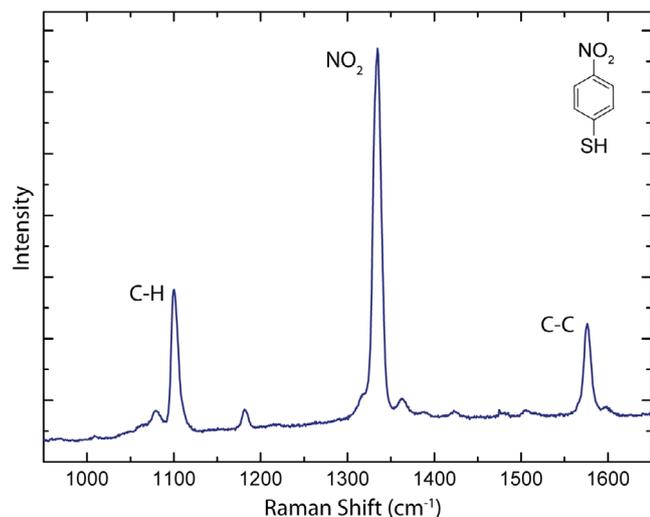


Figure 1. Raman spectrum of p-NTP recorded at $\lambda = 660\text{ nm}$ with its three fingerprint modes: the C–H stretch mode at 1100 cm^{-1} , the symmetric stretch of the NO_2 mode at 1343 cm^{-1} , and the C–C stretch mode at 1571 cm^{-1} . The inset shows the molecular structure of the p-NTP molecule.

increasing wavelengths, the intensity of the Raman modes initially increases and decreases for wavelengths larger than 640 nm. This indicates an intrinsic resonance of the molecule around 640 nm.

To identify the optical resonances of the molecule by RRS, we plotted the phonon mode intensity (integrated peak intensity) as a function of excitation energy. The RRS profiles for the three fingerprint Raman modes of the p-NTP powder are shown in Figure 2b–d. We found that the p-NTP in its natural powder form exhibits two molecular resonances in the red spectral range for the NO_2 mode (Figure 2b). One resonance is located at 1.68 eV (736 nm) and the second one at 1.93 eV (643 nm). The C–C and C–H stretch modes of the powder p-NTP have identical resonances (Figure 2c,d), implying enhancement by an optical transition. We calculated the Raman cross section for the powder sample when being in resonance at 650 nm and not in resonance at 600 nm, following the study by Reich et al.^[26] using the Raman cross section of the diamond reported in the study by Aggarwal et al.^[27] As result, we found for the resonance case a cross section of $d\sigma/d\Omega(650\text{ nm}) = 6 \times 10^{-26}\text{ cm}^2$ per molecule which is in good agreement with the RRS cross section of dissolved dyes.^[28] Already a shift by 50 nm (0.15 eV) away from the resonance reduces the cross section to $d\sigma/d\Omega(600\text{ nm}) = 9 \times 10^{-27}\text{ cm}^2$ per molecule. Being in resonance leads to a strong increase in the cross section. The challenge when measuring SERS enhancement is that the deposition/bonding of molecules to metals often shifts their resonance energies. It is, therefore, advisable to work with molecules far away from their resonance as Raman probes, which are less affected by changes in resonance energy.

Now, we compare the resonance profiles of the p-NTP powder to the p-NTP solutions: “fresh” and “stored.” “Fresh” means that we measured the sample immediately after the preparation and “stored” that the sample was measured again after storing it for two weeks in the dark. For the comparison, we focused on the Raman intensity changes of the nitro-group, since it is the dominant mode in the Raman spectrum of p-NTP and also detectable for the ethanolic molecule solution, where the ethanol gives rise to a huge background signal, covering the p-NTP Raman signal of the other Raman modes. In Figure 3a, the excitation energy dependent Raman measurements of the freshly prepared ethanolic p-NTP solution are shown. Interestingly, we did not observe resonances in the measured excitation range for the freshly prepared solution (cf. Figure 3a). The Raman intensity of the dissolved molecule increases with excitation energy. Raman measurements for excitation wavelengths below 550 nm showed a strong photoluminescence background from the ethanol, making the detection of the Raman signal impossible.

After storage, a change in the resonance profile of the solution occurs. Figure 3b shows the excitation profile of the ethanolic p-NTP solution that was stored for two weeks in the dark. The Raman intensity of the profile has a first maximum at 1.64 eV (756 nm) and increases further up to its second maximum at 1.88 eV (660 nm). For the fresh solution, these transition energies cannot be observed. Comparing the resonance curve of the stored solution (Figure 3b) with the curve of the p-NTP powder in Figure 2b, it shows that both excitation profiles are very similar. This shows that the sample structure of the precipitated molecules is comparable with the powder sample. The

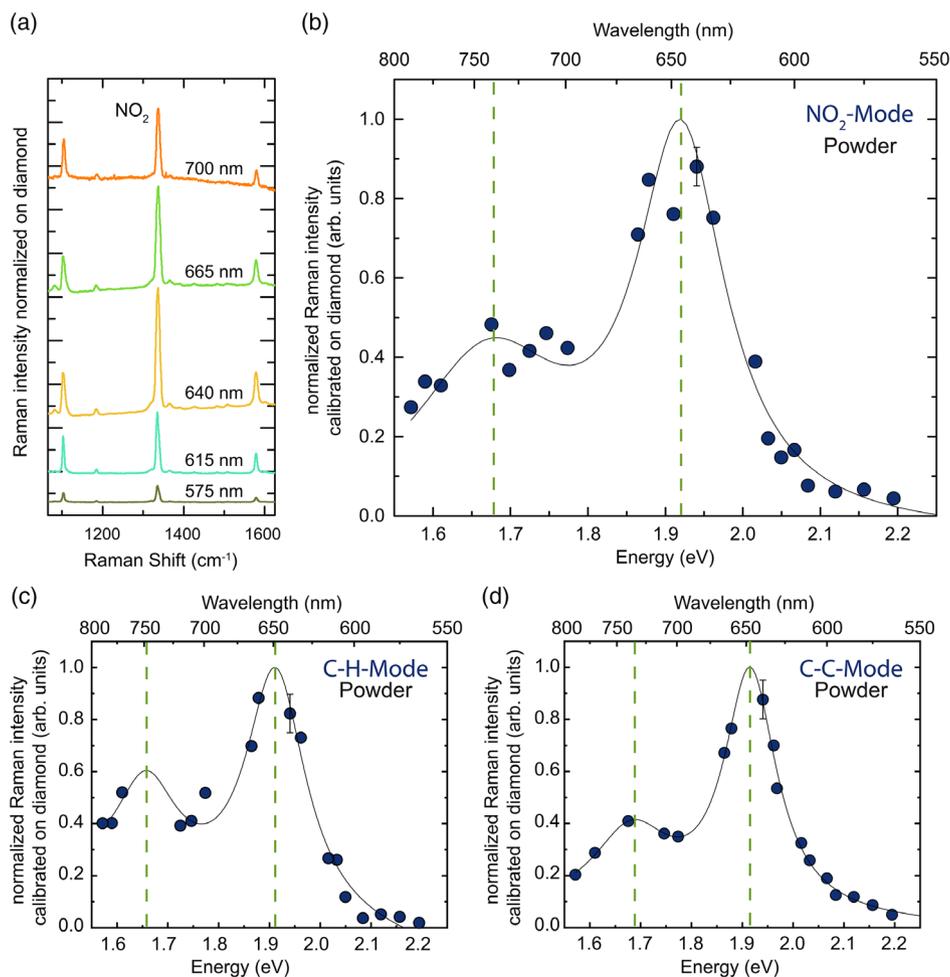


Figure 2. Excitation energy dependent Raman measurements of the powder sample. a) Raman spectra measured at different wavelengths, showing a dependence of the Raman intensity on the excitation wavelength of the laser. b–d) RRS profiles of the different Raman modes NO₂, C–H stretch, and C–C stretch mode showing two transition energies in the red spectral area. The solid line is the sum of two Lorentzians for the fit of the experimental data (blue points). For better comparability, all excitation profiles are normed on their maximum. The enhancement factors have been 16× for the NO₂ mode, 19× for the C–H mode, and 9× for the C–C Mode.

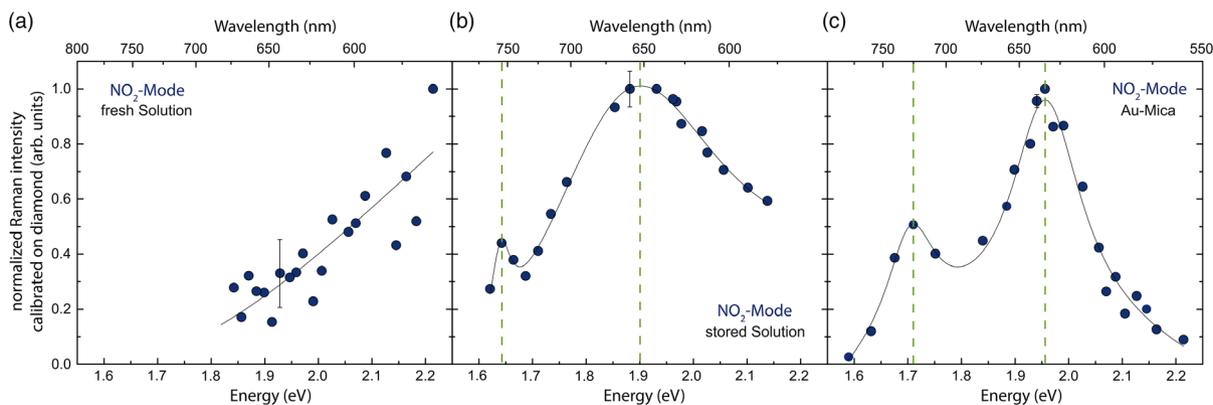


Figure 3. Excitation energy dependent Raman measurements of p-NTP. The Lorentzian areas of the NO₂ modes were plotted as a function of the laser energy for a) the fresh and b) the stored ethanolic p-NTP solution, showing that there is a change in the intrinsic resonances during storage. c) Raman measurements of the p-NTP covalently bond to a (111)-gold film on mica (Au–mica), showing two transition energies in the red, similar to the powder and the stored solution. The solid lines are the sum of two Lorentzians for the fit of the experimental data (blue points). For better comparability, all excitation profiles are normed on their maximum.

broadening of the resonance at 650 nm can be explained by the comparison to the ethanol small NO₂ mode of the p-NTP (smaller volume), which is not only small but also covered by the ethanol, leading to larger fitting errors.

Since p-NTP is often used for SERS studies, we further studied how the bonding of the thiol-group to a noble metal affects the resonance profile of the molecule. We measured p-NTP covalently bound to a (111)-gold film. The excitation profile of the third sample type is shown in Figure 3c. Again, two intrinsic resonances occur in the red spectral regions that are energetically separated by 250 meV. The first resonance has an energy of 1.96 eV (633 nm) and the second of 1.71 eV (724 nm), i.e., they are only slightly blueshifted ($\Delta\lambda = 10$ nm) compared to powder sample (Figure 2b). The shapes of the resonance curve of the powder and the p-NTP on the gold surface are identical. The small shift of the resonance on the gold surface to lower wavelengths can be interpreted by the bounding of the thiol-group to the gold surface.^[29] The Raman resonances of p-NTP in the visible and near infrared have to be considered when evaluating the SERS and TERS enhancement of the p-NTP molecule. A common approach for evaluating SERS enhancement is to compare the SERS intensity of molecules bound to metal nanostructures to the Raman intensity of the molecules in solution (typically, freshly prepared). In view of our results on RRS on a flat gold surface, this approach has to be treated with care.

3. Conclusion

In summary, we analyzed the optical properties of the designer molecule p-NTP which is intensively used as reference, test, and probe molecule for SERS and TERS experiments. We showed that the energetic position of the molecules' intrinsic resonances strongly depends on the preparation and the age of the sample. Due to precipitation of the dissolved molecules over time, the resonance curve of the stored solution behaves similar to the powder sample. The covalent bond of the sulfur to the gold film additionally leads to changes in the transition energies and therefore to changes in the energetic position of the resonances. Our results show that it is important to know the optical properties of molecules before using them as reporter molecules, because they can vary greatly with excitation wavelength. Depending on the field of application, it might be that photoluminescence hampers the measurements or that the Raman signal is too low to be detectable, especially for small sample volumes.

4. Experimental Section

The p-NTP (O₂NC₆H₄SH) powder used in this article was ordered from Tokyo Chemical Industry (TCI). For the 10 mM ethanolic solution, we dissolved the p-NTP powder in ethanol (C₂H₆O) $\geq 99.5\%$ purchased from Carl Roth. The Au sample was prepared via drop casting 2 μ L of the 10 mM ethanolic p-NTP solution onto a (111)-gold film on mica, ordered by Georg Albert-Physical Vapor Disposition.

The resonant Raman measurements on the three different kinds of p-NTP samples were performed by tuning the excitation wavelength in steps of 10 nm from 565 to 785 nm. To cover the broad excitation range, we used two different continuous wave ring lasers. In the excitation range between 565 and 670 nm, we used a dye laser from Radiant Dyes, operated with two

different fluorescent dyes (Rhodamine 6 G (R6G) was used for the wavelengths between 565 and 615 nm. In the excitation range from 620 to 670 nm DCM was used as lasing medium). The measurements in the range of 705–785 nm were performed with a titanium-sapphire (Ti:Sa) laser from Coherent. The laser was focused on the quartz cuvette with the ethanolic p-NTP solution by a 10 \times objective in backscattering configuration. To focus on the powder and the gold film sample, we used a 100 \times objective. The power of the incoming laser was kept constant at 1 mW. The spectra were recorded by a Jobin-Yvon T64000 spectrometer from Horiba in direct path configuration with a silicon charge-coupled detector. Different edge filters were used to cut off Rayleigh scattered light. For the resonance curves, all Raman spectra were fitted by Lorentzian line shapes. The intensities (areas under the peak) were calibrated by diamond, which had a constant Raman cross section,^[30] to account for wavelength-dependent changes in the sensitivity of the Raman setup. We measured the Raman spectra with different wavelengths on the same sample positions, to avoid position-dependent fluctuations in the signal. All measurements were performed at room temperature.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

4-nitrothiophenol, Raman cross section, resonances, resonant Raman scattering

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