ABSTRACT

We study systems in which the resonance Raman process is fast due to the requirement for phonon involvement in the absorption. The resonance enhancement is found to track the isolated molecule, or vapor phase, absorption since the molecule does not have time to exchange energy with its neighbors. This corroborates with studies of pre-resonance, where Heisenberg’s uncertainty principle enforces a rapid process, but differs from resonance on electronically allowed transitions, where the resonance allows a relatively prolonged interaction. High resolution excitation spectroscopy reveals large gains and narrow features usually associated with the isolated molecule. Vibration energies shift as the resonance is approached and the excited state vibration levels are probed. Several multiplets and overtone modes are enhanced along with the strongly coupled ring-breathing mode in aromatic molecules.

Keywords: Resonance Raman, plasmon enhancement, gradient field Raman, nano-antenna, phonon allowed transitions, tunable excitation, excited state spectroscopy

1. INTRODUCTION

Raman spectroscopy is a powerful tool for materials detection and identification, but suffers from low signal level. We have combined two resonance techniques to boost the signal level using: a UV resonance absorption for the excitation wavelength [1,2], and a bowtie nanoscale plasmon resonance antenna that is resonant at the excitation wavelength [3]. The former gives an increase by ~500 times while the latter gives an additional ~30,000 times gain, both on a per-molecule-measured basis. In practice, for bulk samples, the use of the absorption resonance is coupled to a dramatic decrease in the number of molecules measured due to the signal absorption. The actual signal levels measured [4] are not that different for bulk samples. The real gain in signal is achieved when the molecule to be detected is either dispersed as a trace quantity in a nonabsorbing matrix, or when only a tiny volume of sample is present. When combined with nano-antenna enhancement, the latter condition is almost always satisfied, so the resonance excitation technique is advantageous. Although the signal gains are large, the techniques used to obtain them modify the spectra via several mechanisms that are discussed and documented in this paper.

2. RESONANCE RAMAN

Most papers that refer to resonance Raman spectroscopy actually discuss what we would term pre-resonance Raman, since the excitation wavelengths used approach, but do not equal, the peak of the absorption feature. We have found interesting features on resonance. We discuss the benzene case in this paper, although similar results are seen on other molecules such as toluene.

2.1 The absorption feature

Benzene has several absorption features, many of which have been used significantly in the pre-resonance regime. We concentrate on the 'ring back bond' absorption feature at ~260 nm. This is an interesting feature since it is phonon allowed, and indeed couples very strongly to the ring breathing mode (ν2) vibration. This is evident as a series of absorption features repeated towards higher energies (shorter wavelengths) that are separated by this phonon energy of ~990 cm⁻¹. Symmetry forbids the absorption without the presence of a phonon, and we find that this has a dramatic effect on the resonance observed.
2.2 Pre-Resonance Raman

This resonance does not contribute measurably to the pre-resonance Raman enhancement of benzene. Rather, the Raman signal level follows a gain of a higher energy absorption of the standard form given by the A term of the Herzberg-Teller expansion for the polarizability tensor

\[ I_{fi}(\frac{\pi}{2}) = \left( \frac{\pi}{\epsilon_0} \right)^2 (\tilde{\nu}_0 \pm \tilde{\nu}_{fi})^4 J_0 \sum_{\rho, \sigma} [\alpha_{\rho,\sigma}]_{fi}^2 [\alpha_{\rho,\sigma}]_{fi}^* \]  

(1)

with

\[ [\alpha_{\rho,\sigma}] = \frac{1}{hc} \sum_{\nu} \left[ \frac{\mu_{\nu}}{\nu_r - \nu - i\Gamma_r} + \frac{\mu_{\nu}^*}{\nu_r + \nu + i\Gamma_r} \right] \]  

(2)

The (pre) resonance enhancement is due to the denominators approaching zero as the absorption wavelength is approached, with a Lorentzian functional form when one absorption term dominates. There is also another enhancement, a \( \nu^4 \) factor in (1) due to the dipole absorption and emission process. We remove this signal increase to focus on the resonance.

The reason why we do not see pre-resonance at the absorption that we are using, we believe, is due to the requirement for a phonon to be present during the absorption. This requires an internal molecular resonance condition, which can also be considered as a particular relative location of the nuclei within the benzene molecule during a point in the vibration. This configuration would have the symmetry to allow absorption, so is not the average position or lowest energy configuration. It is useful to use this picture when the Raman process happens fast compared to the time for vibration. The resonance forces a rapid process, which limits interactions (losses), thus reduces gamma and hence the range of pre-resonance.

2.3 On-Resonance Raman

Contrary to the lack of a pre-resonant enhancement, a strong resonance is observed at the resonance energy, Fig. 1.

![Figure 1. Several Raman spectra acquired within a 2 nm excitation wavelength range show an increase to a large value at 259 nm, followed by a decrease at larger wavelengths and another increase for the final, 260 nm, spectrum.](image)

The most interesting fact related to the data is that the strong dependence of the Raman signal intensity with wavelength follows the isolated molecule absorption rather than the liquid absorption for this liquid sample. The sample is measured from below through a fused silica window to exclude the possibility of vapor effects above the surface, and the unfocussed laser beam has a low enough intensity that bubble formation is not observed (except when the laser power is
high and is tuned exactly to the isolated molecule peak absorption – which is offset by about two nanometers from the peak of the liquid absorption). The observed laser power dependence appears linear (below), which precludes nonlinear effects such as Raman spectra in a volume that has been excited by a previous laser pulse. The lack of a pre-resonance is consistent with the very narrow Raman enhancement. The gamma, or loss, factor in Eqn. 2 is small, so the resonance peak is very narrow, but very tall. This is potentially a significant benefit for detection.

We attribute the ‘isolated molecule Raman resonance in a liquid’ to the nature of the absorption. If the molecule is isolated, it does not interact with its neighbors. How can this happen in a liquid? The Raman process must be very fast. We are used to thinking of spontaneous Raman processes as fast, since they occur in virtual states relatively far removed from real states and thus possessing very short lifetimes via the Heisenberg Uncertainty Principal. Harmon and Asher [5] give further evidence that the short Raman time is important. They studied pre-resonance Raman enhancement in liquid and vapor phase benzene, in addition to other compounds, and found that the enhancement does not depend upon the phase of the material, in contradiction to the expectation that the enhancement should increase in the liquid state due to the increased local field strength created by the dielectric environment produced by the neighbors. If the dielectric screening is incomplete when the Raman process completes, then the enhancement would be similar to the vapor phase (isolated molecule) enhancement, as they observed. This underscores the ubiquitous importance of the Raman time in understanding the resonance Raman phenomenon. Resonance Raman is usually considered to be a slow process. We suggest that the molecular resonance required for absorption at this particular absorption feature in benzene creates a limit on the Raman time that is not only very fast to preclude neighbor interactions, but also is not related to the laser pulse length or other parameters of the apparatus.

2.4 Energy Resolution

Given the presumed rapid nature of the process and the discussion above concerning Heisenberg’s Uncertainty Principle, one may be tempted to question how the high energy resolution observed in Fig. 1 can be achieved. The answer is that the Raman resonance is related to the magnitude of the Raman signal as a function of excitation energy. It is not the emission from a state with a lifetime that is short. Thus, the Uncertainty Principle does not apply, and the energy resolution can be very high.

3. NANO-BOWTIE ANTENNA PLASMONIC ENHANCEMENT

Plasmonic enhancement was achieved by electron beam lithographic fabrication of small bowtie nano-antennas that are plasmon resonant at the absorption of the molecules used. The bowties were made from two equilateral triangles with height ~80 nm and thickness ~100 nm of aluminum. In the deep-UV wavelength range used, aluminum is the best metal available. The size is determined by the resonance condition. Fig. 2 shows how this varies with wavelength and how we have demonstrated the extrapolation of previous work in the visible into the DUV spectral range.

![Figure 2](image-url) We are here

Figure 2. An extrapolation from the literature [6], we show that our antenna resonance is consistent with the simple model used to determine the resonance of a metal triangle.
3.1 Plasmon Resonance

The plasmon resonance condition for triangles was studied in infrared wavelength range [6], and the triangle height was found to be \( \lambda/(2n) \) for substrate index \( n \). We extrapolated these data into the DUV and found that the same relationship holds for this much smaller wavelength range as well. Instead of using a single triangle, we use two with the tips facing each other and separated by \(~20\) nm. This greatly enhances the electric field in the region between the two triangle tips. It is the source of the increased signal level due to this effect.

3.2 Mode Stiffening

On resonance, the Raman spectroscopy is sensitive to the excited state bonding constants rather than the ground state elastic properties. Thus, it is not surprising to find a shift in the phonon energies as resonance is approached. We display these in Fig. 3 for several resonant modes. The phonon energy shifts are normalized to zero shift at the longest wavelength plotted, 259.25 nm. All modes stiffen as expected for benzene. What is somewhat counter-intuitive is that the ring breathing mode \( \nu_2 \) (and its multiple \( 2 \nu_2 \) with double the shift as expected) stiffen more slowly than the other modes and the combination of \( \nu_2 \) and the other modes.

![Figure 3. Mode stiffening is observed as the isolated molecule absorption peak is approached. The zero reference for the phonon energy shift is taken at the highest wavelength plotted, 259.25 nm.](image)

3.3 The Enhanced Modes

Not all Raman active modes are enhanced in resonance Raman spectroscopy. In fact, the \( \nu_1 \) mode at \(~3065\) cm\(^{-1}\) is the strongest for Raman excited with visible radiation, but not observed near the 259 nm resonance. That mode is related to a hydrogen atom vibrating on the outside of the ring, and is not influenced significantly by a bond related to the ring being broken. The modes that are enhanced are those related to the motion of the ring itself, \( \nu_2, \nu_9, \nu_{10} \) and multiplets and combinations with \( \nu_2 \). The strength of the \( \nu_2 \) related modes is not surprising, since it is strongly coupled to the ring motion and also to this particular absorption.
Figure 4. Raman spectra of various types are compared. The upper plot contains a non-resonant Raman spectrum and a resonance Raman spectrum taken without any nearby metal. The lower plot contains a resonance Raman spectrum in the presence of the metal nano-antenna. The plots are shifted so that the horizontal energy axes align, and the green dotted lines relate stronger Raman features in the plots.

3.4 Linearity and Antenna Damage

The intensity of the near-field enhanced resonance Raman of the liquid sample is studied by varying the illumination power. The data in the low power regime is linear, Fig. 5. Arrays of Al bow-tie nano-antennas on a fused silica substrate were brought into perfect contact with liquid benzene. A high repetition rate, picoseconds pulse laser was tightly focused onto one Al nano-antenna and the liquid sample. The laser induced heating or oxidation may play an important role in the stability of the device and thus the time-dependent behavior of Raman signal intensity. If the heat generated in the Al nano-antenna was high enough for diffusion, melting or oxidation to occur for the laser fluence used, changes in Raman signal are expected. Such effects, which increase the spacing between the two antenna arms, can decrease the plasmonic enhancement of the nano-antenna. A simple model in which the antenna is treated as a point heat source with power absorbed from the laser; the fused silica approximated as infinite compared to the nano-antenna, and consideration of their thermal conductivities, $\sim 237\text{Wm}^{-1}\text{K}^{-1}$ for Al, $1.38\text{Wm}^{-1}\text{K}^{-1}$ for silica, and $\sim 0.14\text{Wm}^{-1}\text{K}^{-1}$ for liquid benzene, indicates that the heat conduction into liquid benzene can be ignored. The whole problem can be treated as the heat diffusion from a point source into a half space filled with fused silica. The symmetry of the insulated half space allows the further simplification to a point source with twice the power diffusing into all space with spherical symmetry. Thus, the temperature distribution inside the fused silica can be modeled as,
where the first prefactor 2 results from the twice-power point source, and the second one is from the fact that there are two identical Al triangles under presumably the same laser illumination power. The absorptivity of Al at 258.8 nm excitation is assumed to be a constant value of 8%, the areas for bow-tie antenna and laser focused spot are \( \sim 1 \times 10^4 \text{ nm}^2 \) and \( \sim 2 \times 10^5 \text{ nm}^2 \), respectively. The temperature distribution \( \frac{1}{4\pi k_b R} \) is the solution of the heat conduction in steady state with unit delta function source. When the excitation power is \( \sim 0.69 \text{ mW} \), the temperature at the edge of antenna, \( T(r = 10^{-7} \text{ m}) = 0.92 \times 0.7 \times 10 + 300 \approx 306.4\text{[K]} \). Thus, the temperature rise is negligible, unless the thermal contact between the Al and the substrate is poor. Either this is the case, or the saturation-like behavior of the Raman signal intensity could be attributed to the accumulation of photochemical residue from benzene. A film formed by this adsorption process and can block the further interaction between the benzene and the Al bow-tie antenna.

\[
    T(r) = 2 \times 2 \times \text{Laser Intensity} \times \frac{\text{Bow-tie area}}{\text{Focus area}} \times \text{Absorptivity} \times \frac{1}{4\pi k_b R} + 300\text{[K]},
\]

(3)

Figure 5. Raman integrated intensity is shown as power increases. There is approximately 2 minutes between data points. The incident spot was moved to different bowties twice, as noted in the 10 micron motion annotations on the figure. For the blue part of the curve, the laser power was increased between each point. The laser was left at constant power during the latter, green, points. The same vertical axis applies to all points.

4. GRADIENT FIELD RAMAN

We have shown that a conductor neighboring the molecules can dramatically increase the fields and hence signal level. We have also shown that if phonon-allowed absorptions are used for exciting the resonance Raman, then the molecule behaves as a low-loss isolated molecule with regards to the Raman signal enhancement (although as it would react normally as a liquid for all other, longer time scale, properties). In this section we document another phenomenon, also due to the presence of metal nearby, that changes the Raman spectra.
4.1 Gradient Field Raman

Gradient-Field Raman (GFR) was first observed in the first nano- or tip-enhanced- Raman spectra in the mid 1990’s [7,8], but it wasn’t explained until somewhat later [9], with final details worked out in [10]. Raman-like features in the spectra that relate to strong infrared vibrations are found when a metal is very close to the molecule being studied. This is a different effect form polarization changes that occur near a metal, but relates to the fact that the electric field must be polarized perpendicular to a conducting surface. Since that requirement is a boundary condition, it is quickly relaxed as distance from the surface increases. This creates a strong electric field gradient, much stronger than that in free space, which is limited to a length scale of the order of a fraction of the wavelength of the light. If one takes the qualitative view of Raman spectroscopy as a first photon being scattered and polarizes a molecule, followed by a second photon that Raman scatters off the polarized molecule, then GFR can be described as a first photon being scattered and polarizes a molecule, followed by a second photon whose electric field is modified by the metal so has a different magnitude (in the normal-to-surface-polarized part) at the two ends of the polarized molecule. This means that the Coulomb force on the two ends is different, so differing impulses are imparted by the field and the molecule begins to vibrate. These qualitative ideas are preserved as the mathematical treatment is applied to the problem. In particular, the selection rule is that the vibration has a component in the direction perpendicular to the metal surface, and the strength of the effect is related to the polarizability (as the dipole operator or infrared strength) rather than the derivative of the polarizability (as is Raman). The derivative falls on the field instead, which is large near the surface. It was tested using a near field scanning optical microscope, with the metal coating of the probe providing the nearby metal and the ability of the probe to move to test the gradient character.

The measurements also showed the presence of plasmon generation by the Raman shifted light as it propagates away from the probe. A simple, two parameter no-reflection model described the essential features of the data. The model could not be made to work until an essentially near field attribute was added. Plasmon generation by far-field models did not work, instead, the near field radially polarized 1/r dipole emission term was invoked, which required a different plasmon generation calculation since the polarization is in the direction of ‘propagation.’ With this in place, and using the gradient fields calculated from the Bethe-Boukamp model, the data were quite well described. The two parameters were the metal thickness, which shifted the plasmon absorption on the ‘distance between probe tip and sample’ axis, and an overall scaling factor. The explanation of an additional feature relied on allowing one bounce of some of the light as it escaped from under the probe tip and its metal coating.

4.2 GFR with resonance Raman

The features in the resonance Raman with metal nearby spectrum are labeled in Fig. 4 by vibration mode in color. Black refers to those modes also observed in the data without metal nearby. Blue label those that would not have been observed with sufficient signal to noise in the spectrum without metal nearby. Red labels phonon modes that should have been observed due to their larger signal levels but were not. These are the GFR modes, and the coupling between them and the infrared absorption spectrum is shown in Fig. 6. The good agreement supports this assertion, since the strong infrared modes should be strong in GFR for those molecules that are appropriately oriented with respect to the metal antenna so that the selection rule is satisfied.

5. CONCLUSIONS

We have shown that both Raman time and interactions with the neighboring molecules as well as nearby conductors are important for understanding the spectra and interpreting the resonance. When a phonon allowed absorption is used for resonance, the Raman time is reduced, which can limit interactions with neighbors and make the molecule appear as if it is isolated. This has also been observed in non-resonant Raman. When a metal is nearby (10’s of nanometers), then it impacts the incident field. It can enhance it with a plasma resonance, as done here, and can induce a strong gradient in the component of the electric field normal to the surface, which can engender gradient field Raman, also observed here.

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Figure 6. The resonance Raman peak with nearby metal (nano-antenna) is compared to the infrared spectrum [11] and the far infrared spectrum on the left [12].

REFERENCES


