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## HIMANSU MOHAPATRA, Ph.D.

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### Education

**Ph.D. (2002).** Department of Inorganic and Physical Chemistry, Indian Institute of Science – Bangalore, India

**Title of the Thesis:** *Time Resolved Resonance Raman Studies on Photo-induced Electron Transfer Reaction*

**Adviser:** Professor. S. Umamathy

**M.Sc (Master in Science) in Chemistry.** Ravenshaw College-Cuttack, Orissa, India

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### Research experience

#### Postdoctoral Research

- **Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska, U.S.A** 2005-  
april 2009  
*Study of elastic properties and intermolecular interaction in crystalline polymorph of pharmaceutical drugs by Brillouin and Raman Spectroscopy*
- **Institute of Analytical Science, Dortmund, Germany** 2003-2004  
*Near-field optical Raman microscopy*

#### Ph.D

- **Indian Institute of Science Bangalore**  
*Time-resolved resonance Raman and density functional theory studies of intermediates involved in photo-induced electron transfer reaction*

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### Research projects accomplished

- Determination of the **elastic constants** of the **monoclinic polymorph** of **carbamazepine** molecular crystal by **Brillouin scattering spectroscopy**.
- Characterization of **Low-frequency intermolecular phonon vibrations** of **flufenamic acid form III** polymorph by Raman spectroscopic studies in the melt and crystal phase.
- A setup that is a combination of **aperture near-field technique** and **Raman spectroscopy** designed and fabricated to study liquid-liquid interface at variable distance from interface with high resolution.
- **Time-resolved Resonance Raman** and **density functional theory (DFT)** studies have been used to study the resonance Raman spectra and structure of intermediates generated in **photo-induced electron transfer reaction** (PET). The mechanism and nature of intermediates generated in PET reaction have been studied from the time resolved changes in the Raman spectra.

- **Nanosecond laser flash photolysis** carried out to obtain the **transient absorption spectra** and study the time evolution of transient intermediates involved in **photo-induced electron transfer reaction**.

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### Experience with experimental techniques and methods

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- Worked with **Ar<sup>+</sup> gas laser** equipped with **inter-cavity etalon** (used as a light source for Brillouin experiment.)
- Worked with **Burleigh Fabry-Perot interferometer** operated in the triple-pass configuration (to resolve the frequency shifts of Brillouin modes.)
- Designed and fabricated a cell to study the Raman spectra of the sample in the melt and vapor phase.
- Implemented procedures for alignment and optimization of optical instruments used in Brillouin setup.
- Selected and purchased CCD detector to be used for very highly sensitive Raman detection.
- Used solution growth technique for **crystal growth**.
- Implemented **optical goniometer** and **single crystal X-ray diffraction** for characterizing the crystal structure and assignment of crystal faces.
- Experience with **Differential scanning calorimetry**.
- Experience in alignment of **fiber optics** based Raman setup and setting up the optical setup of **near-field optical Raman microscope**.
- Fabricated a **Michelson interferometer** setup to control the movement of the near-field tip in nanometer steps.
- Implemented **Q-switched Nd-YAG pulsed lasers** and **tunable optical parametric oscillators for pump-probe time-resolved Raman experiment**.
- Raman detection carried out by **Liquid – Nitrogen cooled CCD** in combination with **SPEX double monochromator**.
- Delay generator used for **timing control** of the pump and probe laser pulses and a photodiode in combination with 500MHz oscilloscope to follow and control the time delay between the pump and probe laser pulses.

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### Experience with computational work

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- Experience in molecular structure and **vibrational frequency calculations** using **abinitio, DFT** and **semi empirical methods**.
- Performed **potential energy distribution calculations** on the normal modes of vibration for organic systems in its ground state as well as transient species.
- Analyzed **bond order parameters** using **natural Bond orbital (NBO)** analysis.

- Carried out mulliken population analysis in connection with the structural changes upon excitation and reduction of organic systems.
- Experience has been gained with popular quantum mechanical suite of programs such as **Gaussian94** and **Mopac (6.0)**.

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### Publications

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- Himansu Mohapatra and Siva Umopathy. Influence of Solvent on Photoinduced Electron-Transfer Reaction: Time-Resolved Resonance Raman Study. *J. Phys. Chem. A*, 113 (2009) 6904.
- Himansu Mohapatra and Craig J. Eckhardt. The Elastic Constants and Related mechanical Properties of the monoclinic polymorph of the Carbamazepine Molecular Crystal. *J. Phys. Chem. B*, 112 (2008) 2293.
- M. De Serio, H. Mohapatra, R. Zenobi and V. Deckert. Investigation of liquid-liquid interface with high spatial resolution using near-field Raman spectroscopy. *Chemical Physics Letters*. 417 (2006) 452.
- Himansu Mohapatra and Siva Umopathy. Time-resolved resonance Raman studies on Triplet excited state of 2-Methoxy-Naphthalene by photo-sensitization. *Chemical Physics Letters*. 390 (2004) 427.
- H. Mohapatra and S. Umopathy. Time-resolved resonance Raman studies on the radical anion of methyl-1,4-benzoquinone and 2,6-Dimethyl-benzoquinone. *J. Phys. Chem. A*. 106 (2002) 4513.
- M. Puranik, H. Mohapatra, G. Balakrishnan, J. Chandrasekharan, S. Umopathy. Effect of Halogen substitution on the structure and Vibrational spectra of Radical Anions of Benzoquinone. *Asian J. Phys*, 7(2), 189-204, 1999.

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### Manuscript in preparation

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- H. Mohapatra and S. Umopathy. Time-resolved resonance Raman studies on proton-induced electron transfer reaction between triplet 2-methoxynaphthalene and Benzophenone system. *Manuscript under preparation*

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### Presentation

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- Himansu Mohapatra and Craig J. Eckhardt. The Elastic Constants and Related Mechanical Properties of the Monoclinic Polymorph of the Carbamazepine Molecular Crystal, Poster presentation in *54<sup>th</sup> Midwest Solid State conference (2007)* held at University of Nebraska, Lincoln NE, U.S.A.
- Himansu Mohapatra and Craig J. Eckhardt. The Elastic Constants and Related mechanical Properties of the monoclinic polymorph of the Carbamazepine Molecular Crystal, Oral presentation in *Nebraska Academy of Science's 117<sup>th</sup> Annual meeting (2007)* held at Nebraska Wesleyan University, Nebraska, U.S.A.
- Himansu Mohapatra and Craig J. Eckhardt. The Elastic Constants and Related mechanical Properties of the monoclinic polymorph of the Carbamazepine Molecular Crystal, Poster presentation in *American Physical Society (APS) 2007 march meeting* held at Denver, Colorado, U.S.A.
- Himansu Mohapatra and Craig J. Eckhardt. Polymorphism and low frequency Vibrations of Flufenamic Acid Phases, Poster presentation in *Center for Pharmaceutical Processing Research Industrial Advisory Board Meeting (2006)* held at Purdue University, West Lafayette, Indiana, U.S.A.

- H. Mohapatra, M. De Serio, R. Zenobi and V. Deckert. Towards high resolution near-field measurement of the liquid-liquid interface. Oral presentation by H. Mohapatra in *International conference on Raman Spectroscopy 2004 (ICORS 2004)* held at Queensland Australia.
- M. De Serio, R. Zenobi, H. Mohapatra, S. Haiber, V. Deckert. Towards high resolution near-field measurement of liquid-liquid interface. Poster presentation in *8<sup>th</sup> International Conference on Near-Field nano-optics* held at Seoul, South Korea.
- H. Mohapatra and S. Umapathy. Time-resolved Resonance Raman studies on triplet exciplex between 2-methoxynaphthalene and benzophenone. Poster presentation in *Trombay Symposium on Radiation and Photochemistry* held at BARC Trombay, January 2002.

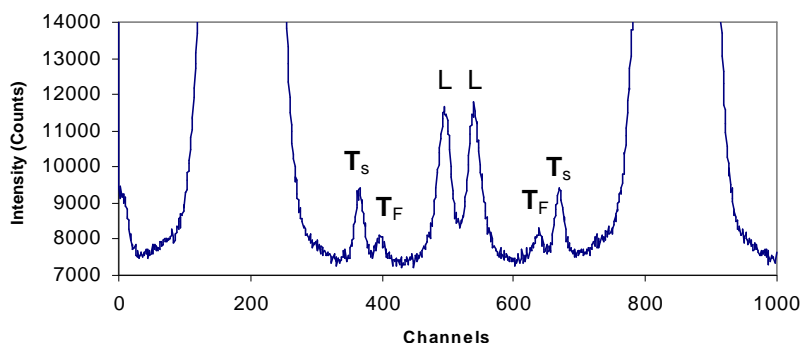
## ADDENDUM – 1

### DESCRIPTION OF THE POSTDOCTORAL RESEARCH PROJECT

#### Department of Chemistry, University of Nebraska-Lincoln

Organic compounds have the ability to crystallize in more than one crystalline form that differs in the arrangement or conformation of the molecule in the crystal lattice; this is referred to as polymorphism. The dissimilar interactions that arise from differences in arrangements of molecules causes variation in the physical properties of polymorphs. Polymorphism is a major issue in drug uptake and tablet processing of pharmaceuticals. This has led to a wide variety of research activities ranging from understanding crystal packing to polymorph prediction. Polymorph stability and ease of formation arise from variations in intermolecular interactions. Thus, knowledge of intermolecular forces is crucial to understanding the phenomenon. A property closely related to intermolecular interactions is the elasticity of the material. A complete picture of the elasticity demands accurate determination of the elements of the elastic constant matrix.

Brillouin scattering has been used to probe the acoustic phonons of the monoclinic ( $P2_1/c$ ) polymorph of the drug, carbamazepine. The propagation of an acoustic phonon is dictated by the elasticity of the medium. By sampling a number of acoustic phonon velocities, the complete set of elastic constants has been derived. The elastic constants relationship to intermolecular interactions and elastic properties has been studied. The results of Brillouin have been used to calculate bulk properties such as bulk modulus and linear compressibility. The linear compressibilities plotted in three crystallographic planes have been used to gain insight into the strength of intermolecular interaction in different directions in terms of the entire compliance tensor. The Brillouin spectrum of monoclinic drug polymorph carbamazepine drug is shown in Figure 1

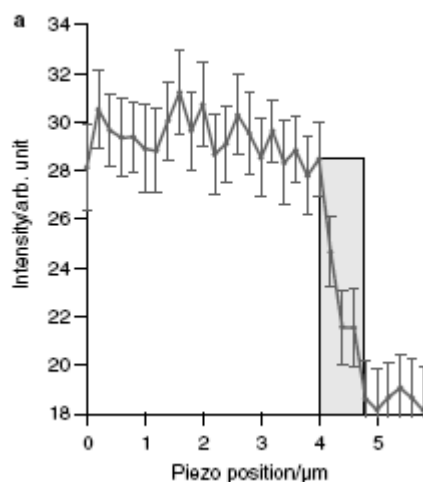


**Figure 1:** VV polarized Brillouin monoclinic ( $P2_1/c$ ) polymorph of the drug, carbamazepine. Scattering is from  $[-0.83043, 0.26007, 0.4926]$  phonon.  $T_s$ ,  $T_f$  and L denote respectively, the slow and fast quasi-transverse modes and quasi-longitudinal modes.

### Institute of Analytical Science Dortmund, Germany

This work employs a near-field aperture probe as illumination source and Raman spectroscopy to obtain vibrational spectra at and near liquid-liquid interface. The near-field tip is dipped into the top liquid, and the cuvette is moved in a stepwise fashion until the tip reaches the interface. The cuvette is mounted on a piezo translator, which allowed movement with a minimum step size of 0.1 nm and a maximum travel range of 12  $\mu\text{m}$ . The Raman light scattered by the liquids is detected by external optics. The aperture probe is based on a tapered optical fiber with metallic coating to obtain an entirely, opaque film on the cone walls and to form a transmissive aperture at the apex. As a result the far-field power emitted by the aperture decreases while strongly confined and enhanced evanescent fields appear at the vicinity of the aperture. Therefore, the small decay length of the evanescent field outside a near-field probe combined with vibrational spectroscopy allows studying structural changes at variable distances from the interface with high resolution.

This technique has been used to study the nature of interface between two immiscible liquids such as  $\text{H}_2\text{O}/\text{CCl}_4$  system and to evaluate the resolution capabilities and the sensitivity of the selected set-up. Figure 2 shows the Raman spectra of  $\text{H}_2\text{O}$  while approaching the interface of  $\text{H}_2\text{O}/\text{CCl}_4$  system.



**Figure 2.** Plot of Raman band intensity of water vs distance (in  $\mu\text{m}$ ) covered by the piezo translator.

## ADDENDUM – 2

### DESCRIPTION OF THE Ph.D. THESIS WORK

In this research work time-resolved resonance Raman (TR3) spectroscopy has been used to study the transient intermediates involved in photo-induced electron transfer reaction. TR3 technique enables the identification of the vibrational structure of the transient intermediates by selectively tuning the probe laser to their transient absorption maximum. Along with this DFT based computational technique has been used to characterize the Raman spectra and support the experimental data. The thesis has been divided into 3 chapters and the outline of each is presented below.

#### **Time-resolved Resonance Raman Studies on Proton-induced Electron Transfer Reaction from Triplet 2-Methoxynaphthalene to Benzophenone System**

Proton induced electron transfer reaction between triplet 2-methoxynaphthalene ( $^3\text{ROME}$ ) and benzophenone system have been investigated using Time resolved resonance Raman (TR3) spectroscopy.  $^3\text{ROME}$  is generated by triplet sensitization of benzophenone system. Figure 3 shows the TR3 spectra of  $^3\text{ROME}$  generated by photosensitization of BP. A comparison of the time resolved resonance Raman (TR3) spectra of  $^3\text{ROME}$  obtained by energy transfer with that of the spectrum obtained in the absence of BP does not indicate any change in vibrational frequencies due to weak charge transfer interaction between ROME and BP, as proposed and expected for a triplet exciplex. Proton induced electron transfer reaction has been investigated using decafluorobenzophenone (DFBP) at probe excitations corresponding to the transient absorption maxima of the cation radical of methoxynaphthalene ( $\text{ROME}^{+\bullet}$ ) and ketyl radical of decafluorobenzophenone ( $\text{DFBPH}^{\bullet}$ ). The TR3 spectra of  $\text{DFBPH}^{\bullet}$  and  $\text{ROME}^{+\bullet}$  are shown in Figure 4 and Figure 5 respectively. The TR3 spectra and structure of  $\text{ROME}^{+\bullet}$  were analyzed with the help of density functional (DFT) computational results. The optimized geometry of  $\text{ROME}^{+\bullet}$  obtained from DFT calculations have shown that the structure of its naphthalene ring deviates from the structure of naphthalene cation radical.

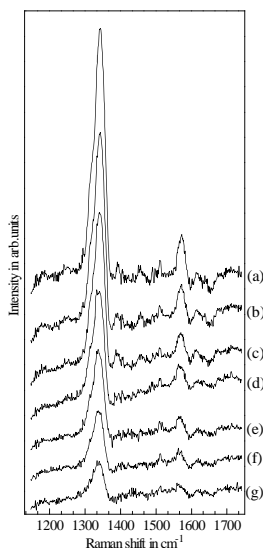
#### **Time-Resolved Resonance Raman Spectroscopic studies on the Radical Anions of Methyl-1,4-Benzoquinone and 2,6-Dimethyl-Benzoquinone.**

Time-resolved resonance Raman spectroscopy (TR3) and density functional calculations have been used to study the effect of asymmetric substitution of the methyl group on the structure and vibrational spectra of the radical anion of benzoquinone. The asymmetrically substituted benzoquinones that have been studied are methyl-1,4-benzoquinone (MBQ) and 2,6-dimethyl-1,4-benzoquinone (2,6 DMBQ) specific vibrational mode assignments have been made to all the vibrational frequencies recorded in the experiment. TR3 spectra of 2,6 DMBQ and MBQ radical anion obtained by reduction of triplet state of quinones by nitrite ion are shown in Figure 6. The coupling between the C=O bonds has been analyzed on the basis of the (DFT results) shift in the vibrational frequency upon isotopic substitution of carbonyl carbon and oxygen atoms. Comparison of isotopic shift and vibrational spectra of the asymmetrically substituted quinone in *in vivo* and *in vitro* will help to understand the interaction of quinones with protein in the photosynthetic reaction center.

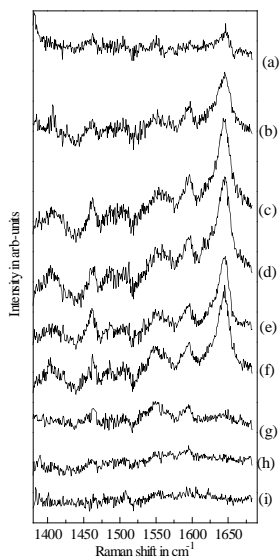
**Time-resolved resonance Raman studies on the solvent effect of Photo-induced electron transfer reaction between triplet fluoranil and tetramethylbenzene**

TR3 and transient absorption spectroscopy have been used to study the effect of solvent polarity on the mechanism and the nature of ion – pair intermediates formed in photo-induced electron transfer reaction between triplet fluoranil ( $^3\text{FL}$ ) and tetramethylbenzene (TMB). Hydrogen transfer has been found to be competing with the electron transfer mechanism. In non-polar media, ketyl radical formation due to hydrogen transfer from TMB to  $^3\text{FL}$  is favored whereas electron transfer mechanism is favored in polar solvents. The nature of primary ion pair intermediates generated in different solvent polarity has been investigated from the structural changes of the acceptor in the ion- pair. In medium polar media, contact ion pair of exciplex nature is more favored and this species eventually decays via intra-ion-pair proton transfer. In polar solvent, complete ionic nature of ion pair (solvent separated ion-pair) has been observed. The nature of ion-pair intermediates in different solvent polarities are shown in Figure 7

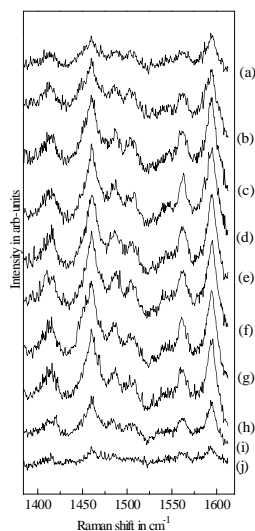
## FIGURES



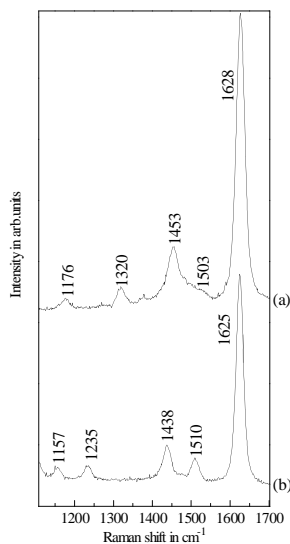
**Figure 3:** TR3 spectra of ROME ( $3 \times 10^{-2}$  M) – BP ( $6.7 \times 10^{-2}$  M) system in acetonitrile obtained at various delay time. Pump only and probe only spectra are subtracted from each of the spectra (pump laser 355 nm probe laser 416 nm): (a) 15 ns (b) 35 ns (c) 55 ns (d) 75 ns (e) 105 ns (f) 135 ns (g) 175 ns.



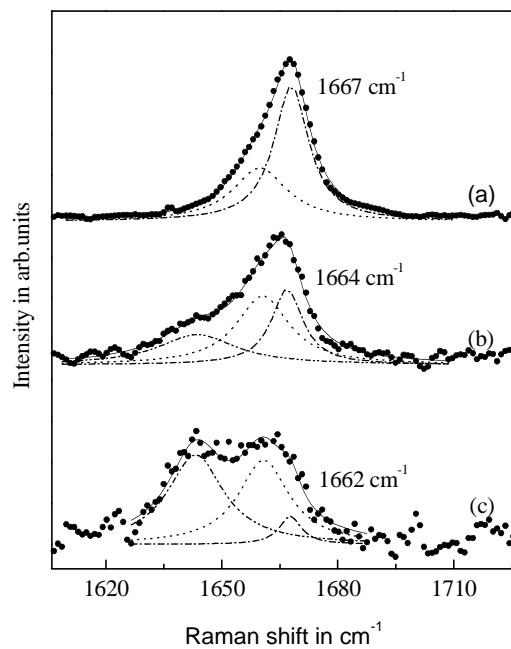
**Figure 4:** TR3 spectra of ROME ( $9 \times 10^{-3}$  M) - DFBP ( $20 \times 10^{-3}$  M) -  $\text{H}_2\text{SO}_4$  (1.0M) system in acetonitrile - water (4:1 v/v) obtained at various delay times, pump only and probe only spectra are subtracted from each of the spectra (pump laser 355nm, probe laser 532nm): (a) 10ns (b) 20ns (c) 40ns (d) 70ns (e) 110ns (f) 210ns (g) 2.2 $\mu$ s (h) 4.2 $\mu$ s (i) probe only.



**Figure 5:** TR3 spectra of ROME ( $9 \times 10^{-3}$  M) - DFBP ( $20 \times 10^{-3}$  M) -  $\text{H}_2\text{SO}_4$  (1.0M) system in acetonitrile - water (4:1 v/v) obtained at various delay times, pump only and probe only spectra are subtracted from each of the spectra (pump laser 355nm, probe laser 600nm): (a) 10ns (b) 20ns (c) 40ns (d)110ns (e) 125ns (f) 175ns (g) 275ns (h) 475ns (l)  $2\mu\text{s}$  (j)  $8\mu\text{s}$ .



**Figure 6:** (a) Time resolved resonance Raman spectra of 2,6-dimethyl-1,4-benzoquinone radical anion from  $1 \times 10^{-3}$  M saturated solution containing  $4 \times 10^{-2}$  M  $\text{NaNO}_2$  (b) Time resolved resonance Raman spectra of methyl-1,4-benzoquinone radical anion From  $1 \times 10^{-3}$  M  $\text{H}_2\text{O}$  solution containing  $4 \times 10^{-2}$  M  $\text{NaNO}_2$  ( $\lambda_{\text{pump}}$  266nm,  $\lambda_{\text{probe}}$  416nm) at 50ns delay between the pump and probe laser. (c) Time resolved resonance Raman spectra of 2,6-dimethyl-1,4-benzoquinone ( $1 \times 10^{-3}$  M)  $\text{H}_2\text{O}$  solution containing  $4 \times 10^{-2}$  M  $\text{NaNO}_2$  and slight amount of sulphuric acid ( $\lambda_{\text{pump}}$  266nm,  $\lambda_{\text{probe}}$  416nm) at 50ns delay between the pump and probe.



**Figure 7:** Time resolved resonance Raman spectra of FL ( $2 \times 10^{-3}$  M) and TMB ( $1 \times 10^{-1}$ ) system in (a)  $\text{CH}_3\text{CN}$  at 20 ns (b) 3:2 (v/v)  $\text{CCl}_4\text{-CH}_3\text{CN}$  at 20 ns (c) 4:1 (v/v)  $\text{CCl}_4\text{-CH}_3\text{CN}$  at 0 ns