

SOLICITACAO DA RENOVACAO DO TERMO DE CONCESSAO PARA PROFESSOR SENIOR

Prof Massuo Jorge Kato

Chefe do Departamento de Quimica Fundamental do IQUSP

Venho através desta encaminhar a V.Sa. minha solicitação de renovação do termo de concessão para Professor Senior junto ao Departamanto de Quimica Fundamental do IQUSP, que implicara na permissão de uso da sala 464 do bloco 4 superior, bem como das facilidades instrumentais do Laboratorio de Espectroscopia Molecular no bloco 4 inferior. Em anexo estou encaminhando o relatório de atividades 2022 – 2024, bem como o plano de atividades para o biênio seguinte,

Atenciosamente



Prof. Paulo Sergio Santos São Paulo ,12 de Maio de 2024

RELATORIO DE ATIVIDADES 2022-2024

Consideracoes Gerais

Na minha visão as atividades de um Professor Senior ,seja em pesquisa,ensino ou extensão devem refletir acima de tudo seu conhecimento da instituição onde atuou por varias décadas,procurando sempre que possível transferir sua experiência para os docentes mais jovens.Reporto a seguir tais atividades.

EXTENSAO

Tendo sido Presidente da Comissao de Biblioteca do IQUSP(Biblioteca do Conjunto da Quimicas) por mais de 30 anos desenvolvi junto com a bibliotecária chefe Sra.Adriana Barros Malheiros um conjunto de atividades para melhor divulgar seus recursos junto ao publico interno e externo.Gravei 3 podcasts na forma de entrevistas disponíveis no site da Biblioteca.No momento esta em andamento o planejamento para destacar o papel da biblioteca como instituição ao longo dos 90 anos da USP,como esse papel evoluiu ao longo do tempo e qual deve ser este papel na atualidade.A titulo de exemplo,já estão sendo contactados como palestrantes ainda para 2024 responsáveis pela administração da Biblioteca Brasileira ,Biblioteca Municipal Mario de Andrade,EDUSP,EDUNESP e EDUNICAMP,num ciclo de palestras e mesas redonda centradas no tema –O Papel das Bibliotecas e Editoras Universitarias nos dias atuais.

ENSINO

Tive a oportunidade de ministrar a disciplina de pos graduação ESPECTROSCOPIA MOLECULAR 2 de 12 creditos envolvendo aulas teóricas e praticas experimentis.Um dos objetivos centrais desta disciplina eh mostrar as diferenças significativas na abordagem teórica de moléculas isoladas e de moléculas em fase condensada,como eh o caso de líquidos por exemplo.Assim sendo , no curso de Espectroscopia Molecular 1 que foi ministrado no ano anterior ,a teoria eh desenvolvida para a situação ideal de moléculas isoladas ,que seria o caso de estado gasoso em baixas pressões.No curso de Espectroscopia Molecular 2 foi dada especial ênfase ao chamado EFEITO DE NÃO COINCIDENCIA RAMAN(NCE).Esse efeito se manifesta sobretudo em cromóforos vibracionais que envolvem grande variação do momento de dipolo elétrico de transição como eh o caso por excelência do grupo carbonila presente em cetonas,aldeídos,ácidos carboxílicos,amidas etc.Um caso que se destaca eh o do ACIDO FORMICO que em solucoes concentradas,onde se encontra majoritariamente na forma do seu dímero cíclico ,dando origem a uma não coincidência enorme da ordem de 80 cm⁻¹ entre as polarizações horizontal e vertical do modo de estiramento C=O no espectro Raman.Os dados experimentais obtidos são de qualidade ainda melhor que aqueles publicados anteriormente.Resolvemos estender o experimento incluindo espécies análogas e redigir um manuscrito voltado para o uso desse experimento num curso avançado de Fisico-Química Experimental,que foi testado no curso de graduação do IQUSP.O texto foi submetido ao JOURNAL OF CHEMICAL EDUCATION cujo editor achou seu conteúdo muito bom mas achou especializado demais para o escopo do periódico.No momento estamos estendendo as medidas para outros ácidos carboxílicos e ousos de solventes não aquosos para submeter o

trabalho a um periódico na área de espectroscopia. Participam desse trabalho as pós-graduandas Clarade Jesus Rangel, Maelly Alves Oliveira e Gabriela Sabença Anversa Reis, alunas matriculadas no curso de Espectroscopia Molecular 2. No presente semestre estou ministrando parte do curso de graduação Introdução a Espectroscopia Molecular para o curso de Química noturno.

Pretendo oferecer novamente o curso de pós-graduação Espectroscopia Molecular 2 no primeiro semestre de 2025.

PLANO DE ATIVIDADES DE PESQUISA 2024-2026

COMPLEXOS DE ÉTERES COROA EM SOLVENTES NÃO AQUOSOS: INTERAÇÕES INTERIÔNICAS

INTRODUÇÃO

O Prêmio Nobel de Química de 1987, concedido a Charles Pedersen, Donald Cram e Jean-Marie Lehn marca o nascimento da Química Supramolecular, mas também um deslocamento de paradigma da Química Orgânica, ou seja de uma química de ligações covalentes para interações não covalentes. Isto fica muito claro ao se considerar os chamados éteres coroa sintetizados por Pedersen e capazes de fixar nas suas cavidades íons de sódio e potássio gerando complexos de altíssima estabilidade. Logo chamou a atenção a solubilidade do permanganato de potássio em benzeno na presença do 18-crown-6, gerando uma solução púrpura em benzeno, conhecida como purple benzene.

Pretende-se neste projeto utilizando crown éteres com diferentes tamanhos de cavidade preparar os complexos de amônio, lítio, sódio e potássio com o mesmo ânion, como perclorato e sulfato. O mesmo pode ser feito com cálcio e magnésio. Ou seja a formação de par iônico é favorecida tanto pela carga do cátion como do ânion, sendo que no caso de cátions a dependência é também do raio iônico. Por exemplo em água sulfato de magnésio forma pares iônicos estáveis. A dependência com o solvente também deve ser explorada.

Este projeto teve início recentemente com os sistemas permanganato de potássio e manganato de potássio e 18-crown-3 em benzeno. Aqui o objetivo é verificar o efeito da carga aniônica, pois os dois ânions têm essencialmente a mesma geometria. Na sequência pretende-se variar o solvente varrendo uma grande amplitude de constantes dielétricas por exemplo. A escolha desses dois ânions tem uma razão adicional. Ambos têm transições eletrônicas no visível (permanganato púrpura) e manganato verde. Através do efeito Raman ressonante deve ser possível obter espectros Raman de qualidade mesmo em baixas concentrações nos solventes orgânicos. Isso possibilitaria investigar as interações do ânion nu (naked anion) com o solvente sem a intervenção de pares iônicos.

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**THE FORMIC ACID DIMER: STRONG HYDROGEN BONDING
MANIFESTED IN THE POLARIZED RAMAN SPECTRUM**

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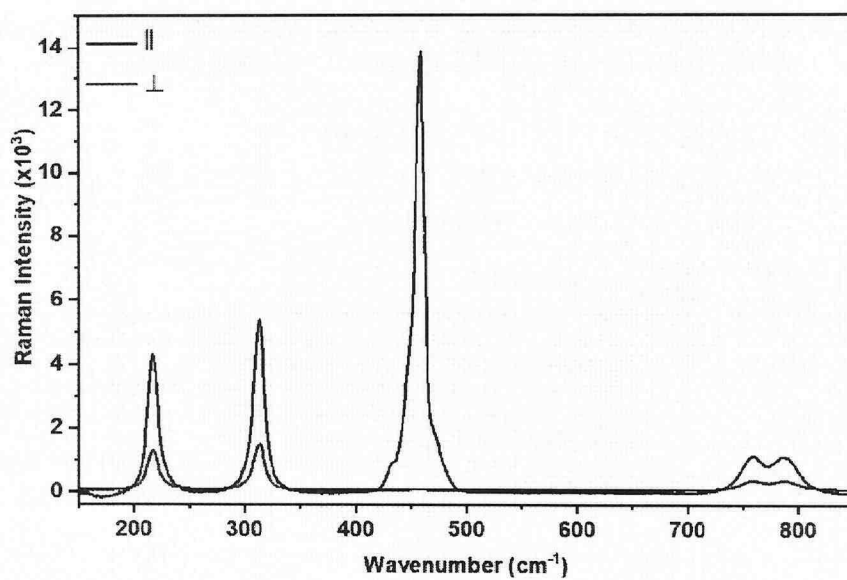


Figure 1. Raman spectrum of neat CCl₄ with parallel (black) and perpendicular (blue) polarizations.

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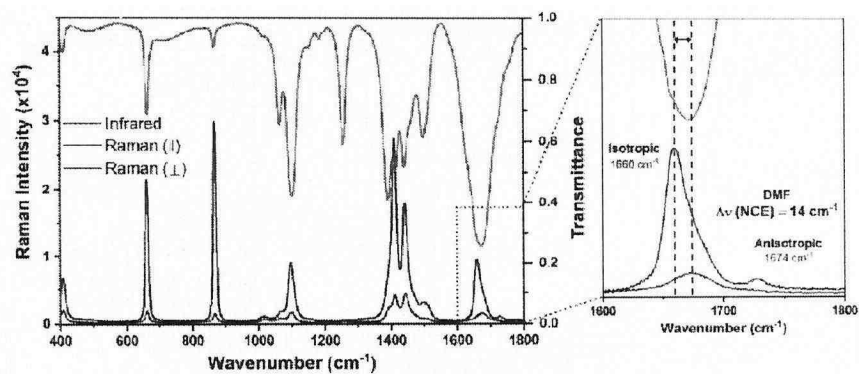


Figure 2. Raman spectrum of neat DMF with parallel (black) and perpendicular (blue) polarization, and IR spectrum of DMF (red).

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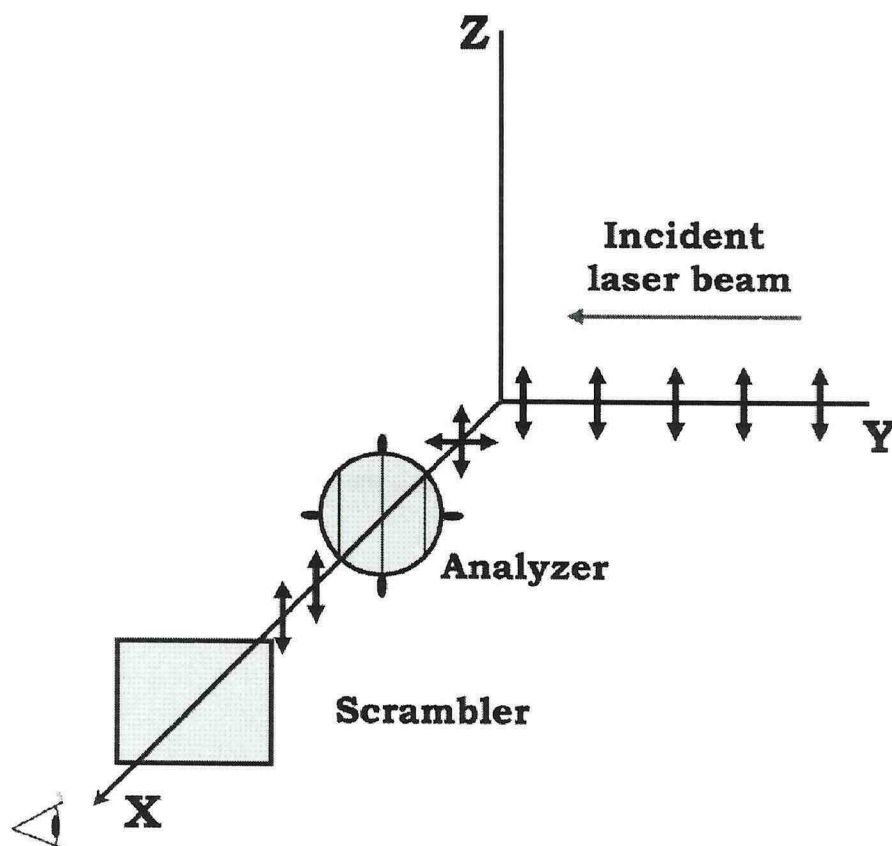


Figure 3. Schematic representation of the disposition of the accessories utilized, considering the sample as the origin of the axes.

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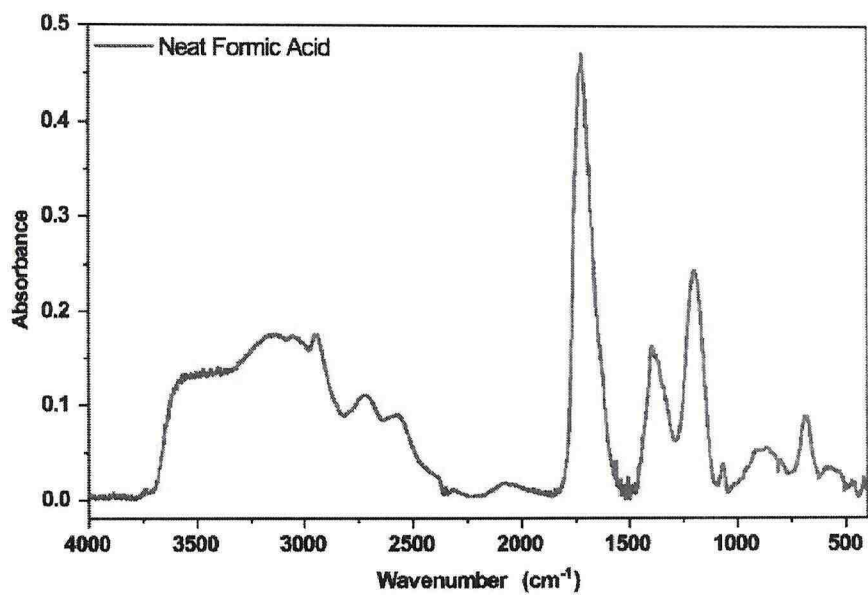


Figure 4. IR spectrum of concentrated formic acid.

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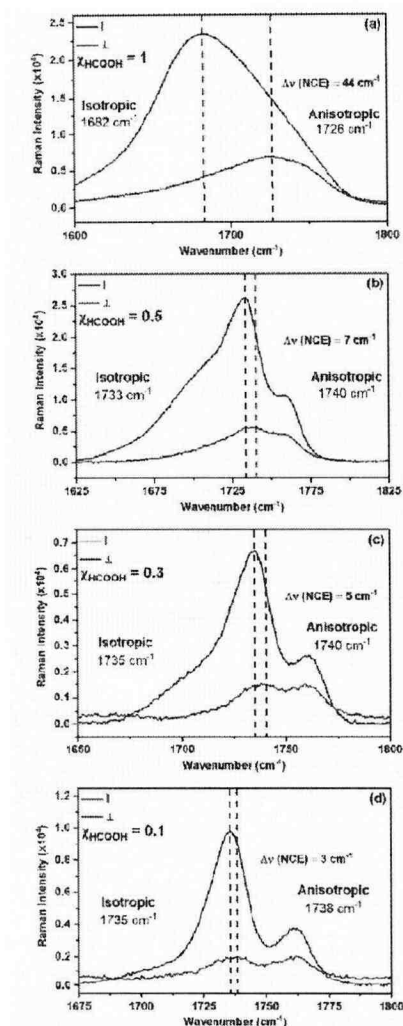


Figure 5. Raman spectrum of concentrated formic acid (83%) with parallel (black) and perpendicular (blue) polarization (a), showing a non coincidence of 44 cm^{-1} in the C=O stretching mode at 1682 cm^{-1} , and with a dilution of (b) 50 (c) 30 and (d) 10 per cent in molar fraction. The intensities of the perpendicular polarization were amplified respectively by a factor of 5, 5, 2 and 7.5.

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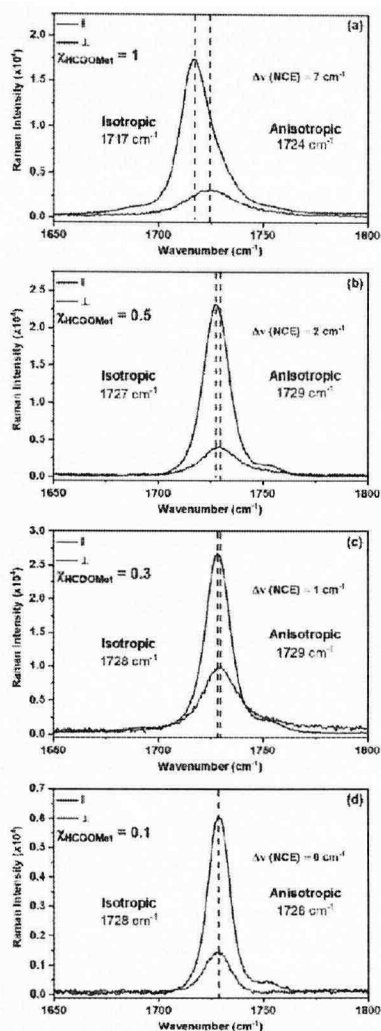


Figure 6. Raman spectrum of neat methyl formate with parallel (black) and perpendicular (blue) polarization (a), showing a non coincidence of 7 cm^{-1} in the C=O stretching mode at 1717 cm^{-1} , and with a dilution of (b) 50 (c) 30 and (d) 10 per cent in molar fraction. The intensities of the perpendicular polarization were amplified respectively by a factor of 15, 2, 10 and 10.

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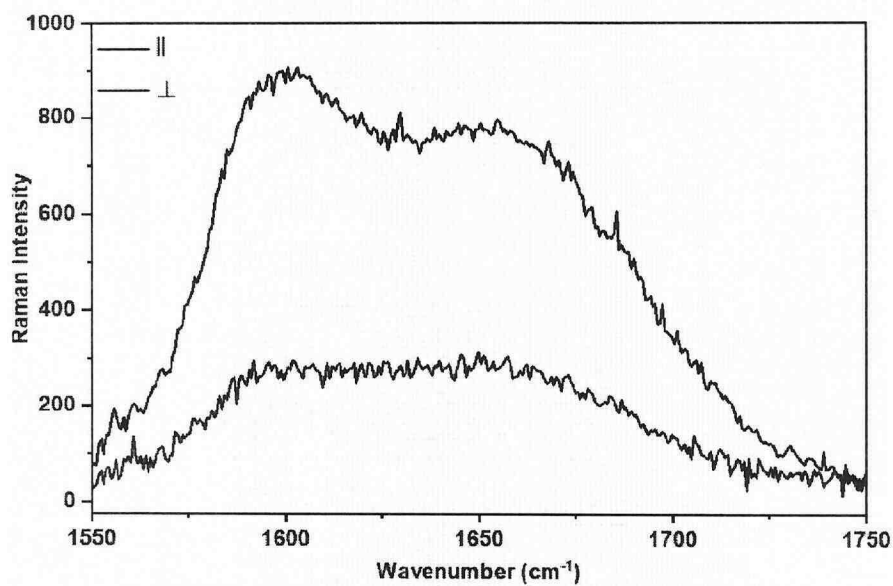
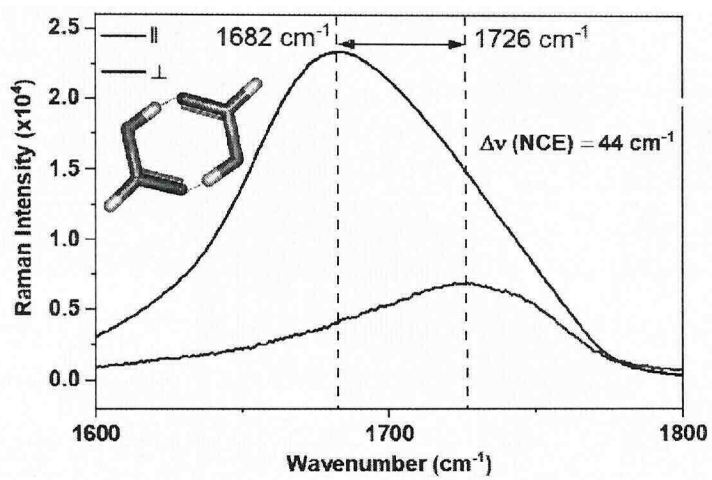


Figure 7. Raman spectra of saturated aqueous solution of sodium formate with parallel (black) and perpendicular (blue) polarization. The intensity of the perpendicular polarization was amplified by a factor of 5.

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THE FORMIC ACID DIMER: STRONG HYDROGEN BONDING MANIFESTED IN THE POLARIZED RAMAN SPECTRUM

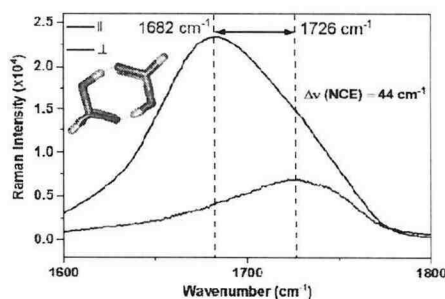
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ABSTRACT

Polarized Raman spectra of CCl_4 , DMF and concentrated formic acid were obtained using standard Raman equipment. The results for DMF and concentrated formic acid are qualitatively different from those of CCl_4 , as the wavenumbers of the parallel and perpendicular spectra are non-coincident for the $-\text{C}=\text{O}$ stretching mode in those molecules. Such non-coincidence is *c.a.* 15 cm^{-1} for DMF and *c.a.* 50 cm^{-1} for formic acid. The intermolecular nature of the effect is confirmed by dilution that causes its disappearance. The IR spectra of the same samples show in all cases the presence of a strong absorption band that is assigned to the $-\text{C}=\text{O}$ stretching mode. As a IR strong band, it involves a large vibrational transition moment, that in the liquid couples to the foreign molecules. In the case of formic acid the huge noncoincidence of *ca.* 50 cm^{-1} can be explained by the presence of its dimer that shows up in the IR spectrum $-\text{OH}$ stretching region.

GRAPHICAL ABSTRACT



KEYWORDS

Upper-Division Undergraduate, Graduate Education / Research, Laboratory Instruction, Hands-On Learning / Manipulatives, Spectroscopy, Raman Spectroscopy, IR Spectroscopy, Hydrogen Bonding, Liquids, Noncovalent Interactions.

INTRODUCTION

Raman spectroscopy has been the subject of several papers in this Journal, most of them aimed at experiments designed for advanced undergraduate courses. In recent years some rather sophisticated experiments involving the enhancement of the Raman signal (SERS) have also been published.¹

The main focus of Raman spectroscopy is the determination of vibrational transition frequencies in molecules, as well as their intensities. Although the same information can also be obtained via infrared spectroscopy, there is additional information available in the Raman spectrum of neat liquids and solutions.

The incident laser can be polarized with an electric field parallel or perpendicular to the direction of observation. This is accomplished with the use of polaroids and two Raman spectra are obtained, parallel and perpendicular. The ratio of the intensities, I_{\parallel}/I_{\perp} , for each Raman band is called depolarization ratio and given the symbol ρ . Its value gives us direct information about the symmetry of the normal modes of the molecule.^{2,3}

Several years ago a masterful paper on the subject appeared in this Journal.⁴ Notwithstanding the comprehensiveness of that article, there is an additional aspect of depolarization measurements that was out of the scope of the author, more specifically, its relation to intermolecular interactions. The present paper intends to introduce this subject by means of the straightforward measurements of the polarized Raman spectra of formic acid and its derivatives, methyl formate and sodium formate.

This is an important topic that can be used as a prompt to demonstrate the limitations of the isolated molecule model, a widespread assumption used in the fundamental theory of vibrational spectroscopy, that is not always the best model as it is the case for condensed phase, evidenced by the phenomenon in the present paper.^{2,7}

Depolarization Ratio

The measurement of depolarization ratio as well as the theoretical aspects involved has been described in a detailed paper by Denis P. Strommen⁴.

The Raman intensity of a particular band depends on the variation of molecular polarizability with the vibration associated with that band. A straightforward example is of liquid carbon tetrachloride, as shown in Figure 1.

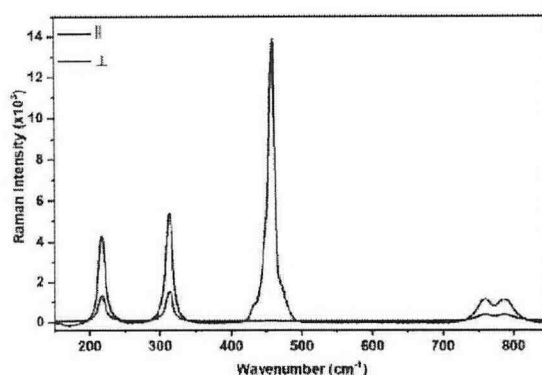


Figure 1. Raman spectrum of neat CCl_4 with parallel (black) and perpendicular (blue) polarizations.

As can be observed for all bands the intensities in the perpendicular polarization are smaller than in the parallel polarization. Even more noticeable is the case of the rather strong band at 459.6 cm^{-1} that virtually disappears in the perpendicular polarization.

The key to the understanding of this result is the molecular polarizability and its variation in each normal mode. Carbon tetrachloride is a molecule of high symmetry (tetrahedral) what reflects in a polarizability tensor that has only diagonal components (α_{xx} , α_{yy} and α_{zz}) responsible for the intensity of totally symmetric modes, as is the case of the mode at 459.6 cm^{-1} , the symmetrical stretching of the C-Cl bonds.

In the perpendicular polarization one observes the contribution of the non diagonal terms of the polarizability, that for a totally symmetric mode is zero, and consequently the intensity of such mode in

the perpendicular spectrum is also zero. The depolarization ratio is defined as $\rho = I_{\perp} / I_{\parallel}$ for each Raman band.

The theory predicts that for a Raman spectrum obtained using a 90° geometry, $\rho = 0.75$ for non polarized bands and ρ smaller than 0.75 for the polarized ones. The case of CCl_4 where $\rho = 0$ is a drastic example due to the high symmetry of the molecule.

Non-Coincidence Effect

As can be observed in Figure 1 and in the vast majority of published Raman spectra, apart from the intensities, the positions of the bands in parallel and perpendicular spectra are the same.

On the other hand, a close examination of the Raman spectrum in the two polarizations of several molecules has revealed a non-coincidence in the positions of bands, particularly for those that are very intense in the IR spectrum, as usually is the case for the C=O stretching mode. This was initially observed in the Raman spectrum of acetone and dimethylformamide (DMF)³ shown in Figure 2.

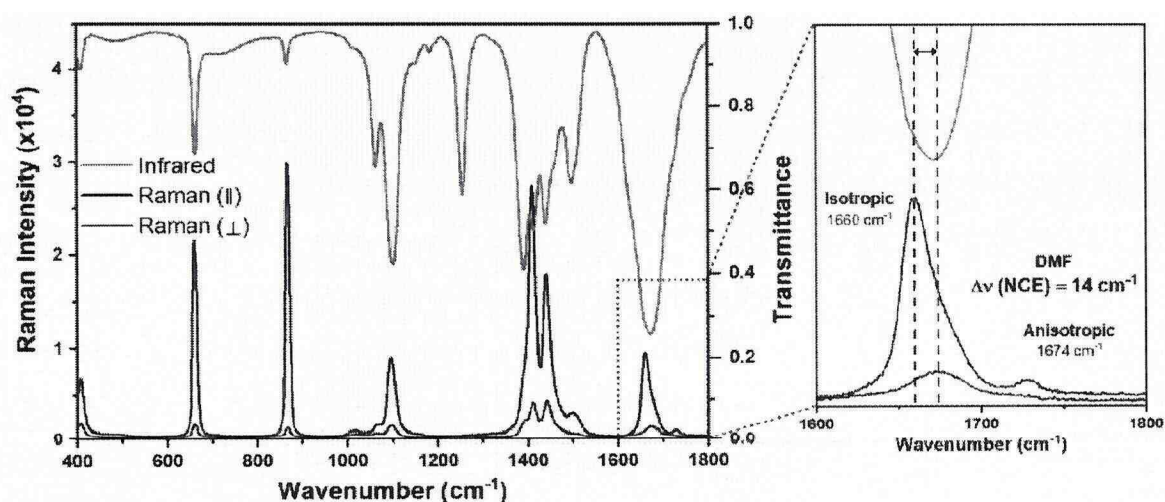


Figure 2. Raman spectrum of neat DMF with parallel (black) and perpendicular (blue) polarization, and IR spectrum of DMF (red).

In DMF, the band at 1675 cm^{-1} shows a difference of 14 cm^{-1} between both polarizations. In the IR spectrum the correspondent band is very intense and coincident with the perpendicular Raman band. The systematic investigation of this Raman non-coincidence effect led to a solid theoretical framework⁵ that can be summarized as follows:

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- The origin of the effect is the coupling of the vibrational transition moments in neighboring molecules with a resonance energy transfer, that affects differently the diagonal and non diagonal components of polarizability, *i.e.* the parallel (isotropic) and perpendicular (anisotropic) spectra.
 - The effect depends on the presence of vibrational chromophores in the molecule, such as carbonyls, whose stretching gives origin to significant vibrational transition moments, and consequently intense bands in the IR absorption spectrum.
 - The magnitude of the effect depends, *inter alia*, on $1/R^2$, where R is the intermolecular distance between chromophores, implying that dilution should eliminate the noncoincidence.

EXPERIMENTAL SECTION

Raman Spectra

Polarized Raman spectra of concentrated formic acid (83%), saturated aqueous solution of sodium formate and neat methyl formate were acquired using the Horiba Jobin-Yvon T64000 spectrometer, equipped with Innova 70C Spectrum a mixed Kr⁺/Ar⁺ (Coherent) laser. All measurements were performed with the 488 nm laser radiation. Detailed information can be found in the **Supporting Information for Instructors** file, as well as a suggestion of material to be given to students prior to the experiment in the **Supporting Information for Students** file.

A simplified scheme of the optical accessories used to obtain all the data is represented in Figure 3. An analyzer (or polaroid) is placed between the sample and the detector entrance, working as a filter for both polarizations. This accessory consists of a plate made of uniformly oriented polymer chains, being capable of selecting only one linear component of the depolarized scattered light. Parallel or perpendicular polarizations can be selected by manually rotating the polaroid by 90°.

As the efficiency of the spectrometer has a certain dependence on the polarization, a scrambler (also known as depolarizer or quarter-wave plate) is positioned before the entrance slit. This optional addition results in the transformation of the linearly polarized light to circularly polarized, eliminating possible biased intensity measurements.

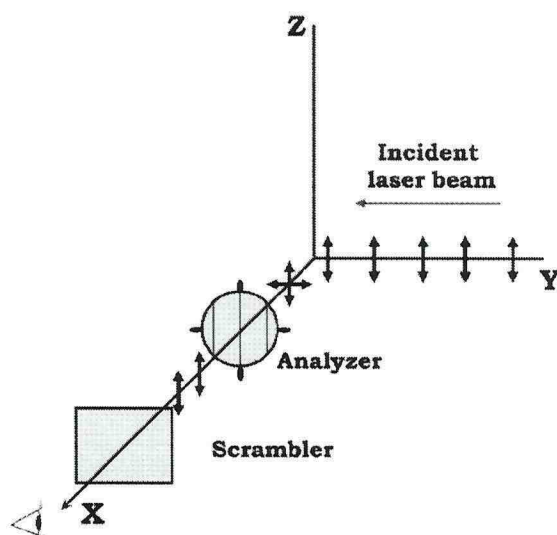


Figure 3. Schematic representation of the disposition of the accessories utilized, considering the sample as the origin of the axes.

IR Spectra

Transmission mode mid-infrared region ($400\text{ cm}^{-1} < \tilde{\nu} < 4000\text{ cm}^{-1}$) absorption spectra of all samples mentioned in the previous section were acquired using the Alpha FTIR spectrometer from Bruker, with resolution of 2 cm^{-1} , using appropriate KRS-5 windows.

Dilution Effect

Concentrated formic acid (83%) was diluted in acetonitrile to molar ratios of 1:1; 1:2.3 and 1:9.

Polarized Raman spectra of the resulting solutions were acquired.

The same was repeated for neat methyl formate.

HAZARDS

Care should be taken while handling all chemicals and materials. Protective equipment should be used at all times.

While making use of laser radiation, careful measures should be taken, such as not looking directly at the laser beam or putting your hands through it.

KRS-5 windows are composed of thallium bromide and iodide, and are highly toxic. Users must not attempt to polish the windows by themselves as inhaling the powder produced may cause intoxication.

RESULTS AND DISCUSSION

The effect of noncoincidence in formic acid and related species has been thoroughly investigated by Irish et al.⁶, the abnormally large value of the noncoincidence being assigned to the very strong hydrogen bonding in formic acid molecules leading to the formation of its dimer, a structure that prevails in the neat acid and in its concentrated solutions. The presence of such strong hydrogen bonds in the neat formic acid can be confirmed by examining its IR spectrum in the OH stretching region, as shown in Figure 3.

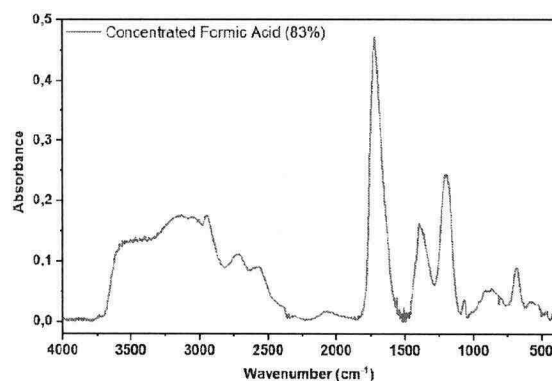


Figure 4. IR spectrum of concentrated formic acid.

Once the hydrogen bonding system is confirmed by the broad band in high-frequency region of the IR spectrum (Figure 4), and knowing that the structure of the dimer favors the vibrational transition moment coupling between the carbonyl groups in each monomer, the effect of dilution was investigated. The dilution experiments were performed to evaluate if the solvent can separate the formic acid molecules and how this affects the NCE.

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3 Figure 5a shows the Raman spectra of concentrated formic acid with parallel and perpendicular
4 polarization exhibiting a 44 cm^{-1} displacement between the two polarizations, which can be attributed
5 to the NCE. In Figure 5b-d the Raman spectra of formic acid in the same conditions as Figure 5a are
6 displayed but with 0.5; 0.3 and 0.1 dilution, respectively, and can be noted that for the more diluted
7 solutions, the NCE is smaller.
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13 The noncoincidence effect is dependent on the distance between the carbonyl groups in the formic
14 acid dimer, as well as the distance between the dimers. This can be observed by the decrease in the $\Delta\nu$
15 between the two polarizations in the diluted solutions. The effect is within the error margin for the 0.1
16 molar fraction, and can be attributed to the dimer rupture and separation by solvent molecules.
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21 A splitting of the band attributed to carbonyl stretching mode in the diluted solutions can be
22 observed, this fact was already noticed by Irish et al⁶ and indicates that the band in lower frequency
23 refers to the dimer whereas the band in higher frequency is attributed to the formic acid monomer.
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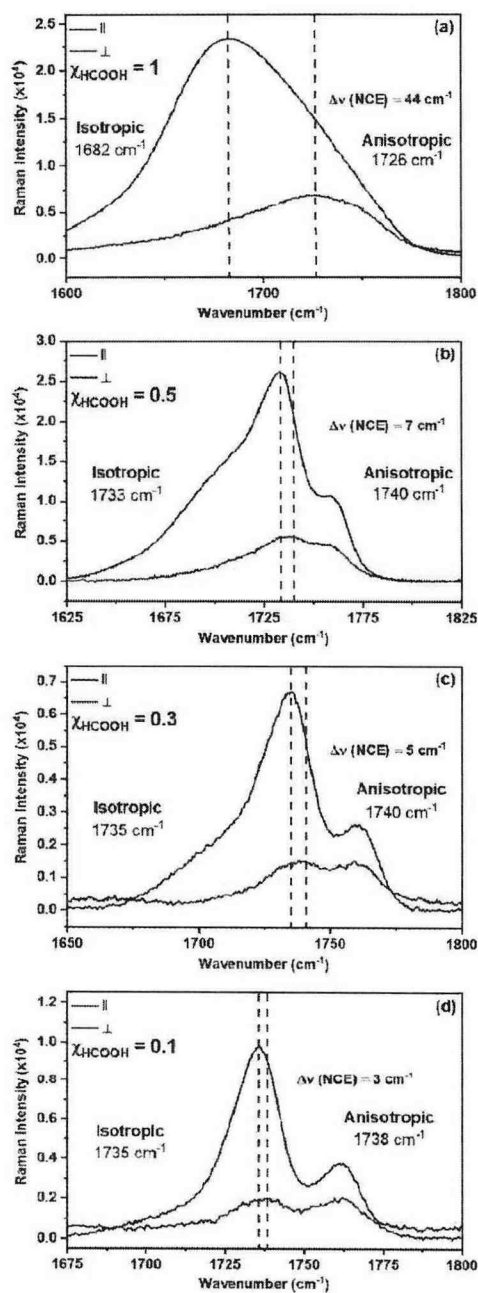


Figure 5. Raman spectrum of concentrated formic acid (83%) with parallel (black) and perpendicular (blue) polarization (a), showing a noncoincidence of 44 cm^{-1} in the C=O stretching mode at 1682 cm^{-1} , and with a dilution of (b) 50 (c) 30 and (d) 10 per cent in molar fraction. The intensities of the perpendicular polarization were amplified respectively by a factor of 5, 5, 2 and 7.5.

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3 The parallel and perpendicular Raman spectra of methyl formate were also obtained (Figure 6). In
4 this case no hydrogen bonding is involved and the presence of methyl groups helps to hinder the close
5 proximity of its molecules. As can be observed in this case the NCE is much smaller, *c.a.* 7 cm⁻¹. Again,
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9 with dilution the effect virtually disappears.
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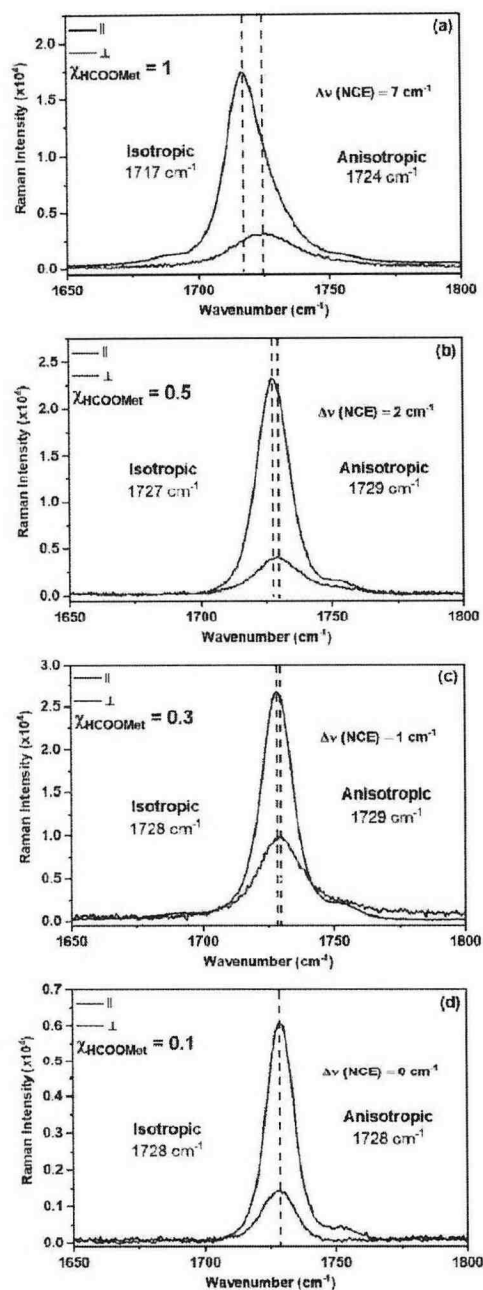


Figure 6. Raman spectrum of neat methyl formate with parallel (black) and perpendicular (blue) polarization (a), showing a noncoincidence of 7 cm^{-1} in the C=O stretching mode at 1717 cm^{-1} , and with a dilution of (b) 50 (c) 30 and (d) 10 per cent in molar fraction. The intensities of the perpendicular polarization were amplified respectively by a factor of 15, 2, 10 and 10.

The salt of formic acid, sodium formate, was also investigated. In this case the interaction between molecules by hydrogen bonding is non-existent, and the addition of negative charge on the oxygens leads to an electrostatic repulsion that prevents the anions from approaching at short distances. This can be seen in Figure 7, the sodium formate saturated solution does not exhibit any NCE at all.

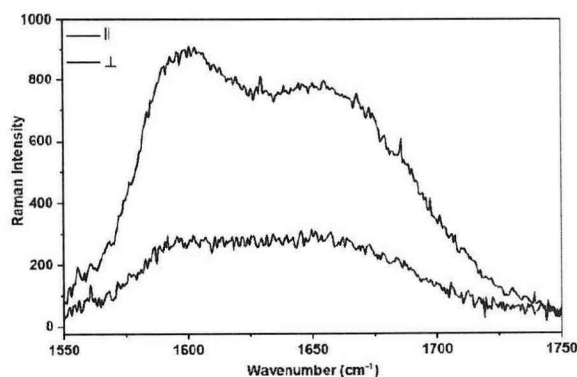


Figure 7. Raman spectra of saturated aqueous solution of sodium formate with parallel (black) and perpendicular (blue) polarization. The intensity of the perpendicular polarization was amplified by a factor of 5.

The displacement between both polarizations are summarized in Table 1. Comparing the values of $\Delta\nu$ for the salt and the ester it is clear that the electrostatic repulsion has a higher contribution to inhibit NCE than steric hindrance.

Table 1. Non-coincidence effect values of the carbonyl stretching band in polarized Raman spectra of formic acid and its derivatives.

	$\Delta\nu$ (cm ⁻¹) *
Formic Acid (83%)	44
Neat Methyl Formate	7
Sodium Formate (Saturated Solution)	0

* $\Delta\nu$ refers to the difference in frequencies of the symmetric carbonyl stretching between each polarization, i.e., perpendicular and parallel.

CONCLUSION

Over the years several experiments aiming at advanced undergraduate courses have been proposed, focusing on different aspects of the technique. In particular, experiments that make use of polarized spectra are just a few, and aimed at the determination of the symmetry of the vibrational modes.

In the present paper an experiment is proposed involving the use of polarized Raman spectra of the formic acid dimer where a very strong intermolecular bonding is present, causing a drastic displacement in the position of the C=O stretching band, due to the noncoincidence effect.

The effect essentially disappears with the dilution since it depends critically on the proximity of neighboring molecules in the liquid. The related species, methyl formate and the formate anion are also investigated to demonstrate how hydrogen bonding in the formic acid dimer affects its polarized Raman spectrum so drastically.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI:
10.1021/acs.jchemed.XXXXXXX. [ACS will fill this in.]

Supporting Information for Instructors (DOCX)

Supporting Information for Students (DOCX)

AUTHOR INFORMATION

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Notes

The authors declare no competing financial interests.

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