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## Vibrational dephasing and frequency shifts of hydrogen-bonded pyridine–water complexes



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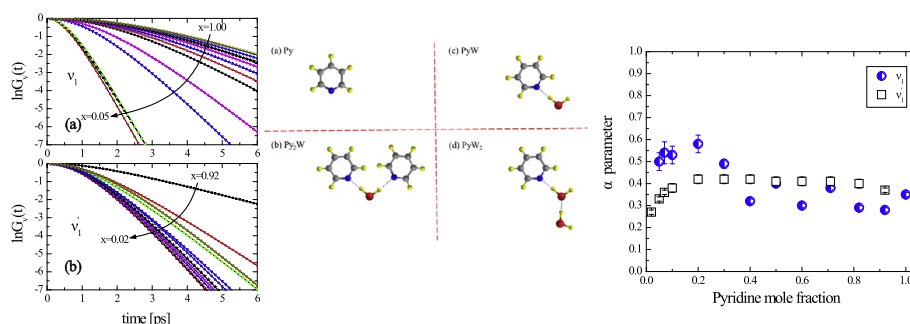
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## HIGHLIGHTS

- The reorientation of pyridine solutions is very slow and only vibrational dephasing is probed.
- Interchange between molecules in the first hydration cell is not the main modulation mechanism.
- The vibrational correlation functions comply with the Rothschild approach.
- The dispersion parameter evolution with dilution indicates strongly interacting system.
- At extreme dilutions, almost all pyridine molecules are involved in hydrogen bonding.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this paper we present the picosecond vibrational dynamics and Raman shifts of hydrogen-bonded pyridine–water complexes present in aqueous solutions in a wide concentration range from dense to extreme dilute solutions. We studied the vibrational dephasing and vibrational frequency modulation by calculating time correlation functions of vibrational relaxation by fits in the frequency domain. The concentration induced variations in bandwidths, band frequencies and characteristic dephasing times have been estimated and interpreted as effects due to solute–solvent interactions. The time-correlation functions of vibrational dephasing were obtained for the ring breathing mode of both “free” and hydrogen-bonded pyridine molecules and it was found that sufficiently deviate from the Kubo model. There is a general agreement in the whole concentration range with the modeling proposed by the Rothschild approach, which applies to complex liquids. The results have shown that the reorientation of pyridine aqueous solutions is very slow and hence in both scattering geometries only vibrational dephasing is probed. It is proposed that the spectral changes depend on the perturbations induced by the dynamics of the water molecules in the first hydration cell and water in bulk, while at extreme dilution conditions, the number of bulk water molecules increases and the interchange between molecules belonging to the first hydration cell may not be the predominant modulation mechanism. The evolution of several parameters, such as the characteristic times, the percentage of Gaussian character in the peak shape and the  $\alpha$  parameter are indicative of drastic variations at extreme dilution revealing changes in the vibrational relaxation of the pyridine complexes in the aqueous environment. The higher dilution is correlated to dif-

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fusion of water molecules into the reference pyridine system in agreement with the jump diffusion model, while at extreme dilutions, almost all pyridine molecules are elaborated in hydrogen bonding. The results are discussed in the framework of the current phenomenological status of the field.

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## Introduction

Vibrational spectroscopy has deserved a special interest among various methods for studying aqueous solutions, because it can provide information for molecular interactions at microscopic, molecular level and in a short time range [1]. The so obtained information is complementary to that obtained from other microscopic observations by, e.g. diffraction methods and NMR, but it has some advantages when species in solution move quickly in a short time. Information obtained by IR and Raman spectroscopies can be related to solvent–solvent, solvent–solute and solute–solute interactions and their modifications in solution induced by changes in concentration, temperature and pressure [2,3].

In solutions containing polyatomic species, changes in their internal vibrations can be correlated to the changes in the structure of ionic hydration, dynamic behavior of solvated water molecules and perturbation on ionic hydration induced by changes in ionic interactions. Vibrational spectroscopy can also offer information of the dynamic behavior of solvent molecules and solute species through the analysis of appropriate time correlation functions of the vibrational data [4–9]. An increase in the concentration induces changes on the band maxima, intensity and half-width of several bands.

Methods based on the Fourier transform properties of the measured quantities have some advantages in the analysis. In particular, several advantages have been stressed for the use of self-resolution spectra in order to obtain the number and the parameters of possible component bands included in a complex band profile without introduction of any assumption about these [10]. Nevertheless, problems remain, in general, because of the difficulty to distinguish between an intrinsically asymmetric band and a complex profile containing several bands. In the time domain the dynamic properties of the ions can be studied using the appropriate correlation functions. In Raman scattering the observed intensity is related to the induced dipole transition moment and the relevant magnitude is the first derivative of the molecular polarizability. The isotropic part of the power spectrum is related to the time correlation of the polarizability derivative averaged, while the anisotropic part is concerned with the time correlation function of the anisotropy. That is, the isotropic part is related only to the vibrational correlation function, but the anisotropic part depends on both vibrational and reorientational correlation functions [4].

Analysis of the correlation function allows obtaining relaxation times which in some cases can be related with precise dynamical mechanisms and macroscopic properties [4–7]. Nevertheless, in a general case where homogeneous and inhomogeneous contributions to the line broadening are present, care must be taken before presenting any interpretation for the band-shape analysis and a detailed analysis should be necessary to the frequency and time domains of the spectra [11–14].

Previous studies were focused mainly on liquids composed of simple molecules. This arose from the fact that the Fourier transformation of band profiles requires isolated and intense spectral lines. This requirement restricts the vibrational relaxation studies to a limited number of simple liquids composed of small and mainly symmetric units (molecules or ions), whose spectral fingerprint is characterized by less overlapping lines and hence are easier

to study. Aiming to overcome the problems mentioned above we used a different approach, where severely overlapping spectra can be fitted using a specific function, which has an analytical counterpart in the time domain. The model function does not prejudice in favor of either Lorentzian or Gaussian but can accommodate any form between these two limiting cases [10]. In an effort to introduce a clearer insight in the knowledge of the hydration dynamics and ionic association processes in aqueous solutions, a Raman spectroscopic study has been undertaken for aqueous solutions of pyridine at various concentrations and the pertinent analysis in the frequency domain is reported.

## Theoretical background

Before describing the results obtained and their interpretation it is useful to briefly summarize the necessary theoretical background and to mention the principles followed for the data analysis.

The Fourier transform of the isotropic and anisotropic Raman profiles yields the time-correlation functions of vibrational relaxation and reorientation, respectively

$$G_V(t) = \int_{-\infty}^{+\infty} I_{iso}(\omega) \exp(i\omega t) d\omega \quad (1)$$

$$G_R(t) = \left( \int_{-\infty}^{+\infty} I_{aniso}(\omega) \exp(i\omega t) d\omega \right) / G_V(t) \quad (2)$$

where both  $G_V(t)$  and  $G_R(t)$  describe the time evolution of the system within the picosecond time domain. These time-correlation functions are able to provide information on the microscopic dynamics in a liquid thus elucidating the origin of mechanisms underlying molecular processes. Occurring over the same time scale, vibrational dephasing and reorientation may couple with each other and therefore their separation becomes quite difficult. Owing to this fact, reliable results can be obtained if dephasing and reorientation differ by at least one order of magnitude. This condition is fulfilled for the particular system of pyridine aqueous solutions studied in this work because they consist of massive species of large moments of inertia, thus rendering rotational relaxation slower than vibrational dephasing.

The theory of vibrational dephasing is based on the idea that vibrational phase shifts arise from the changes of the instantaneous vibrational frequency  $\Delta\omega = f(t)$  (vibrational frequency modulation), which are caused by time-dependent molecular interactions (perturbations). The most general expression of the time-correlation function of vibrational dephasing can be written as [15,16]:

$$G_V(t) = \exp \left( - \int_0^t dt' \int_0^{t'} G_{\omega}(t'') dt'' \right) \quad (3)$$

where  $G_{\omega}$  is the time-correlation function of frequency modulation. When  $G_{\omega}$  is a simple exponential, then

$$G_{\omega}(t'') = \exp(-t'') \quad (4)$$

where  $t'' = t/\tau_{\omega}$  is dimensionless time and  $\tau_{\omega}$  is the characteristic frequency modulation time. The Markovian character of the process is determined by the dependence of every next frequency on only

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