# The Modeling of the Fate and Transport of Environmental Pollutants


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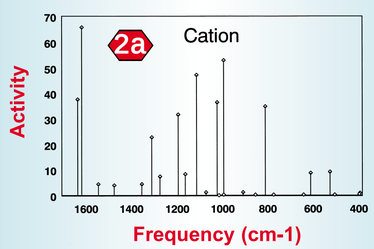
## 1 INTRODUCTION

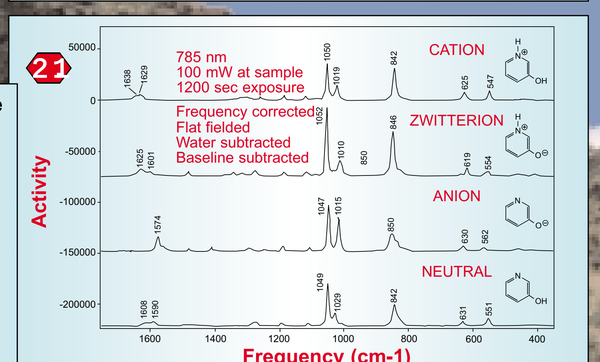
Current models that predict the fate of organic compounds released to the environment are based on the assumption that these compounds exist exclusively as neutral species. This assumption is untrue under many environmental conditions, as some molecules can exist as cations, anions, zwitterions, or neutrals, depending on functionality and pH. We would like to improve this model by quantifying individual species for complex chemicals in water as a function of pH.

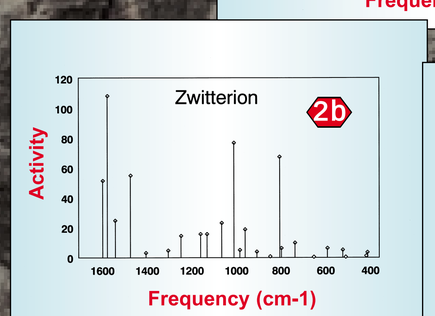
## 2 EXPERIMENTAL

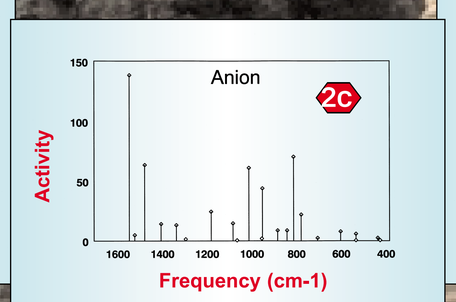
Researchers from the U.S. Environmental Protection Agency, NERL-Athens, Georgia have developed a method for the individual measurement of simultaneously occurring, unimolecular, site-specific "microequilibrium" constants as in, e.g., prototropic tautomerism and zwitterionic equilbria. Raman spectroscopy is used rather than Infrared spectroscopy because of its transparency to water, which is the solvent in these experiments. Once Raman spectra are acquired for the cation and anion of the species, the mathematical method allows prediction of the zwitterion and neutral spectra, and quantization of these species at varied temperatures and pH.

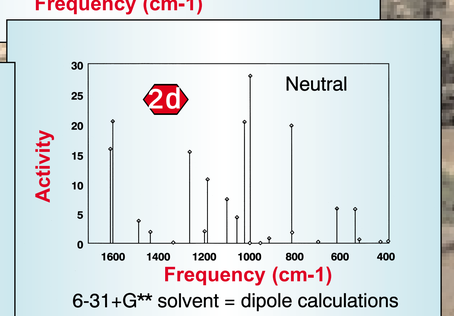
Calculated Raman Spectra for m-OH Pyridine



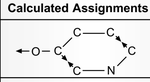
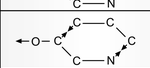
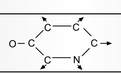
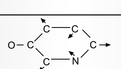
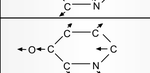




6-31+G** solvent = dipole calculations

## 3 COMPUTATIONAL OBJECTIVE

Computational chemistry can assist this process by simulating the spectra of the particular species. This is accomplished through the frequency calculations using quantum mechanical programs like Gaussian 94. The calculations generate both the frequency of vibration and the activity (or intensity) of that motion. In addition, these calculations give the user an understanding of the exact motion of the vibration, e.g., symmetrical stretch.

## 5 A Comparison of the Calculated Assignments with the Experimentally Predicted Assignments

| Species/Frequency | Calculated Assignments | Experimentally Predicted Assignments |
|---|---|---|
| Cation/1629 (1638)*<br>Zwitterion/1625<br>Anion/1574<br>Neutral/1590 |  | Quadrant stretch |
| Cation/1638<br>Zwitterion/1601<br>Anion/~1565<br>Neutral/1608 |  | |
| Zwitterion/1482<br>Anion/1479 | | Semicircle stretch |
| Cation/1185<br>Zwitterion/1187<br>Anion/1188<br>Neutral/1194 | | NH in plane bend  |
| Cation/1050<br>Zwitterion/1052<br>Anion/1047<br>Neutral/1049 |  | Radial in phase |
| Zwitterion/~1030 | Out of plane H bending (slightly different for each species) | |
| Cation/1019<br>Zwitterion/1010<br>Anion/1015<br>Neutral/1029 |  | |
| Cation/842<br>Zwitterion/846<br>Anion/850<br>Neutral/842 |  | Quadrant in plane bend |

*Experimental Assigned Frequency

## 4 COMPUTATIONAL METHODOLOGY

Hartree-Fock calculations were performed for four species of 3-hydroxy pyridine (anion, cation, neutral, zwitterion). These were performed at several different basis sets, which give approximations to the true mathematical description (or wave function) for the molecule. The Hartree-Fock approximation is a non-experimental method for calculating various physical parameters, including energies, structures, and vibrational frequencies. The calculations were initially performed for gas-phase molecules. Since our goal was to compare the spectra with aqueous spectra, the calculations had to be repeated within the context of solvation theory. Solvation theory is a relatively new tool for computational chemistry and still has many limitations, especially when applied to water solutions. Our work used simple theories, which treat the analyte in a cavity (spherical or near spherical) in the midst of the solvent, which is modeled as a dielectric continuum. Water is one of the poorest solvents for this model because of its high polarity and tendency to form hydrogen bonds with the analyte.

## 6 CONCLUSIONS

This is a work in progress, so there remain many details to resolve. The drawbacks of the simulation of Raman spectra for these microspecies in aqueous solution are two-fold: (1) the accuracy of the theoretical method in simulating experimental spectra is dependent upon the particular basis set and method and is presently determined, at best, to be ± 20 $cm^{-1}$ and (2) the current state-of-the-art of solvation theory as incorporated into these theoretical calculations for solvents with large dielectric constants is not very good. Water is a particularly difficult solvent to model because of its tendency to form hydrogen bonds, which are neglected by these simple theories. The consequences of these drawbacks are that it is hard to determine the subtle differences that occur due to the change of charge state. Nevertheless, there are some areas where these theoretical simulations can help clarify what has been determined experimentally. The N-H and O-H motions are specific for two of the species each. For example, the cation of m-OH pyridine has both N-H and O-H motions and the anion has neither. However, these motions occur above 3000 $cm^{-1}$ and experimentally these regions are difficult to map, especially in aqueous solutions. Our calculations on these motions have sparked an interest by the Athens laboratory, and they are currently trying to overcome some of these experimental difficulties to obtain spectra in this region. Another area in which these theoretical calculations can assist in this process is the assignments of specific vibrational motions. Since these assignments come out of a direct consequence of the calculations, they are available for comparison with predictions by experimental methods. As shown in this poster, these predictions are sometimes misassigned, and the computed methods aid in the correct assignments.

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