# CHEM 361 L EXPERIMENT 7

## Computational Chemistry V: Dynamics

(revised January, 2026)

*Introduction*

In this experiment, you will model the effect of hydrogen bonding on the spectra and other physical properties of donors and acceptors. In particular, you will calculate the transition species of an amino acid and its zwitterion, alone and in the presence of a single water molecule, using density functional theory (DFT) (1) calculations through Gaussian (2).

The role of the solvent in biochemical processes is a subject receiving much attention. Gas phase spectroscopists are attaching water molecules to amino acids and monitoring the change in the spectrum that results from the formation of such a complex. (3) Theoreticians are determining the number of water molecules necessary for a complex to exhibit the behavior observed in solution. (4) Aqueous glycine is almost completely zwitterionic, whereas gas phase glycine is almost exclusively neutral. (5) You will use DFT calculations to predict the structure of the transition species and determine the activation energy and potential energy surface for the formation of the zwitterion for an isolated amino acid and for a water-amino acid complex.

You may find this software package to be useful in your other IR and hydrogen bonding reports.

*Procedure*

In Gaussview, place the optimized amino acid and its optimized zwitterion in two panes of the same molecule group. Ensure that the atoms in each frame match *exactly*. Calculate the transition state structure using DFT (B3LYP/6-31++g(d,p)), which will require using the QST2 (6) command. The program will calculate the energy as a function of geometry until a local energy maximum is found. Once you have found an energy maximum, calculate the vibrational spectrum of the species. If the vibrational spectrum yields exactly one negative frequency (this is actually an *imaginary* frequency), you have found a saddle point on the potential energy surface connecting two structures. Examine the vibrational mode in question, and verify that its motion connects the amino acid and its zwitterion. If not, restart the optimization with a suggested transition species in the third frame (the command would be QST3 in this case). Calculate the vibrational spectrum of the species resulting from the QST3 calculation and verify that the imaginary frequency belongs to the appropriate mode. {Note: if the frequency calculation for the original uncomplexed zwitterion exhibited a single negative frequency, and that vibration, when animated, shows a proton moving from the nitrogen to an oxygen, then the zwitterion is the transition species} Generate the potential energy surface (PES) for the reaction by performing an intrinsic reaction coordinate (IRC) calculation starting at the transition state structure again using DFT and the same basis set.

Once you have modeled the PES between the neutral and zwitterionic forms of your amino acid, do the same for the amino acid-water(s) complex you optimized in the previous experiment.

*Calculations*

Tabulate the energies and vibrational frequencies of the amino acid, zwitterion, complexes, and transition state species. How does the presence of water influence the activation energy between the neutral and zwitterionic form?

*References*

(1). Becke, A. D. *Journal of Chemical Physics,* **1993**, *98*, 5648; Lee, C.; Yang, W.; Parr, R. G. *Physical Review B,* **1988**, *37*, 785.

(2). Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

(3). “Laser Spectroscopy of Jet-Cooled Biomolecules and Their Water-Containing Clusters: Water Bridges and Molecular Conformation.” Timothy S. Zwier, *Journal of Physical Chemistry A,* **2001**, *105*, 8827-8839.

(4). “Hydration of Valine-Cation Complexes in the Gas Phase: On the Number of Water Molecules Necessary to Form a Zwitterion.” Rebecca A. Jockusch, Andrew S. Lemoff, and Evan R. Williams, *Journal of Physical Chemistry A,* **2001**, *105*, 10929-10942.

(5). “Solvent Effects on Glycine. I. A Supermolecule Modeling of Tautomerization via Intramolecular Proton Transfer” Buelent Balta and Viktorya Aviyente, *Journal of Computational Chemistry,* **2003**, *24*, 1789-1802.

(6). Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comp. Chem.* 1996, *17*, 49; Peng, C.; Schlegel, H. B. *Israel J. Chem.* **1994**, *33*, 449.