

C343: Physical Chemistry Lab II

1 March 2021

2. Simulated Vibrational, Rovibrational and Rotational Raman Spectra

In this lab, we generate a simulated rovibrational and rotational Raman spectrum of a few diatomic molecules using spreadsheet or a computer program. We use the rigid-rotor and harmonic oscillator approximations in generating the spectra. In addition, we also simulate the vibrational spectrum of protonated water dimer using ab initio methods.

- Using spreadsheet or by writing a computer program, generate the simulated rovibrational ($v = 0 \rightarrow v = 1$) spectrum of $^1\text{H}^{35}\text{Cl}$ molecule.
 - There are two stable isotopes of chlorine: ^{35}Cl (75.77%) and ^{37}Cl (24.23%). Considering both the isotopes, generate the simulated rovibrational ($v = 0 \rightarrow v = 1$) spectrum of HCl molecule.
- Using spreadsheet or by writing a computer program, generate the simulated the pure rotational Raman spectrum of N_2 .
- Using HF/6-31G** level of theory find the different conformers of $(\text{H}_3\text{O})^+\text{H}_2\text{O}$ complex (protonated water dimer). What molecular point groups do these conformers belong to? Compute the binding energy with respect to the monomers H_3O^+ and H_2O .
 - Compare the geometrical and vibrational properties of the protonated dimer and water monomer. How do they change when you go from HF/6-31G** to B3LYP/6-31G** level of theory. Assign the below given infrared multiphoton dissociation (IRMPD) vibrational spectra of protonated water.
Reference: *Science* **299**, 1375 (2003).

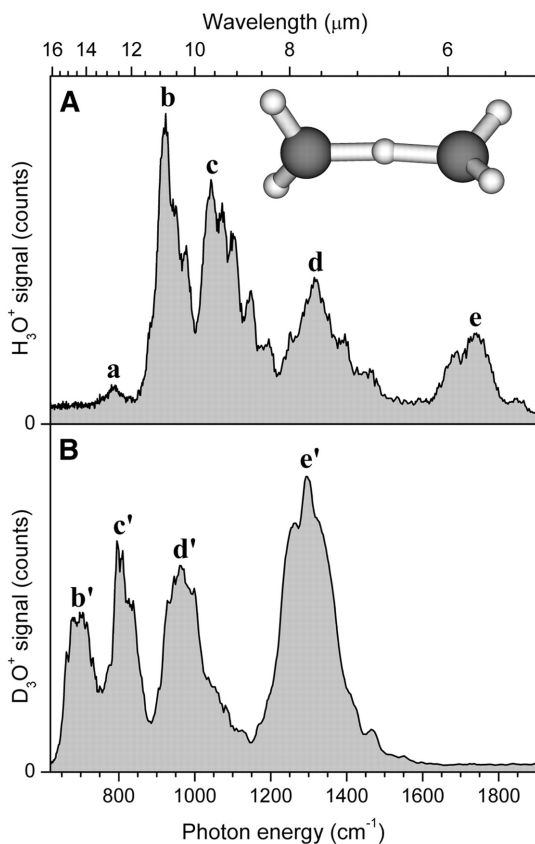


Figure 1: IRMPD spectra of (A) H_5O_2^+ and (B) D_5O_2^+ in the spectral range from 620 to 1900 cm^{-1} . Bands are labeled with lowercase letters. The shown traces are composite spectra, and the data was smoothed. The spectra were measured by monitoring the formation of H_3O^+ (D_3O^+) as a function of FELIX wavelength.

Table 1. Experimental vibrational frequencies [in wave numbers (cm^{-1})] for H_5O_2^+ and D_5O_2^+ and isotope effects determined from IRMPD spectra. The position of each band maximum is underlined.

H_5O_2^+ band	Frequency	D_5O_2^+ band	Frequency	H-D shift
a	<u>788</u>			
b	888, <u>921</u> , 947, 975	b'	<u>697</u>	1.32
c	<u>1043</u> , 1071, 1100, 1145, 1195	c'	<u>795</u>	1.31
d	1252, <u>1317</u> , 1390, ~1460	d'	<u>960</u>	1.37
e	1687, <u>1741</u> , ~1850	e'	<u>1296</u>	1.34