

Looking at Periodic Trends Using Raman Spectroscopy

Purpose	This experiment involves taking Raman spectra of several symmetrical oxyanions. The frequencies of the symmetric stretching vibrations will then allow for an evaluation of periodic trends in bond strength.
References	1 Comstock, M.G.; Gray, J.A. <i>J. Chem. Educ.</i> 1999, 76, 1272-1275. 2 Forseman, J.B.; Frisch, A. <i>Exploring Chemistry with Electronic Structure Methods</i> ; Gaussian Inc.: Pittsburgh, PA, 1993.
Apparatus	Delta Nu Raman Spectrometer and accessories Molecular modeling program such as Gaussian 98W, GaussView, or Gamess 1 mL glass vials Pipettes
Chemicals	Sodium nitrate Potassium carbonate Sodium sulfate Sodium chromate Potassium phosphate (monobasic or dibasic can be used in coordination with the appropriate amount of potassium hydroxide, approx. pH~8-9)
Theory	Raman spectroscopy is the only tool available for studying highly symmetric vibrations because such motions are completely infrared (IR) inactive. ¹ The periodic trend in bond lengths of the oxyanions can be determined by comparing the frequencies of the symmetric stretching vibrations (ν_s) acquired from Raman spectra, quantum calculations, and literature.
Procedure	Quantum Calculations: It is very important to first establish an optimum bond length before performing a frequency calculation. In some programs, however, the two calculations can be performed concurrently. An AM1 or PM3 semiempirical calculation gives a starting estimate for the geometry or bond length. The next step is an ab initio computation such as a Hartree-Fock calculation at the 3-21G* level to optimize bond length and output the symmetric stretching vibrational frequency (ν_s). ¹ Repeat these calculations for each of the five ions in question in this experiment. Laboratory – Part 1 – Preparation of Samples: Prepare a saturated solution of each of the five salts listed above by dissolving the salt in water. As indicated, it may be necessary to add KOH to the solution of potassium phosphate if it is either mono or dibasic until a pH of approximately 8 or 9 is reached. Once the solutions are prepared, pipette a small amount (even a very small volume of liquid can be detected by the instrument) of each solution into a labeled 1 mL glass vial. Be sure to use a clean pipette or pipette tip for each solution. Part 2 – Raman Spectrum Acquisition: Take a Raman spectrum of each of the five samples integrating for 10 seconds. Be sure to print out and carefully label each spectrum.

Treatment of Data

Complete the table below with the ν_1 frequencies from both the quantum calculations and those observed in each Raman spectrum. Also fill in the column listing the optimal bond length for each ion and the experimentally determined force constant. The stretching force constant for a bond between the center atom and one oxygen atom, k , is directly related to the ν_1 band frequency and the mass of the oxygen atom in these highly symmetric ions.

$$k = 4\pi^2 m_o \nu_1^2 \quad (1)$$

Using the wavenumber of the ν_1 band in cm^{-1} and the atomic mass of oxygen $m_o = 15.9995$ amu, equation (1) now becomes

$$k = (5.892 \times 10^{-5}) m_o \nu_1^2 \quad (2)$$

Note that k does not depend on the mass of the center atom as it remains stationary during the symmetric stretching vibration.¹

Ion	Lit. Freq. (cm^{-1})	Calc. Freq. (cm^{-1})	Opt. Bond Length (\AA)	Obsd. Raman Shift (cm^{-1})	Exp. Force Const. (Nm^{-1})
Carbonate	1087				
Nitrate	1060				
Phosphate	938				
Sulfate	983				
Chromate	846				

Questions

- Utilizing the information in the chart above, describe the periodic trend in the bond strength between the center atom and the oxygen atoms in the oxyanions studied.
- Is this trend what you would have expected given your knowledge of chemistry? Explain.