Fourier Transform IR Spectroscopy of Tetrahedral Borate Ions

Introduction

Infrared (IR) radiation comprises the region of the electromagnetic spectrum directly below that of visible light and above that of microwaves. The IR region is typically partitioned into three regimes, which in order of increasing energy are the far-IR, the mid-IR, and the near-IR (Figure 1). The absorption of IR photons, especially those in the mid-IR, can result in transitions between different ***vibrational states*** of molecules and molecular ions. Vibrational information about a substance can provide insights into its geometric structure, its functional group composition, and even the strength of its constituent bonds. As is the case with electronic spectroscopy, the intensity of vibrational transitions can also be used to quantitate analyte concentrations.

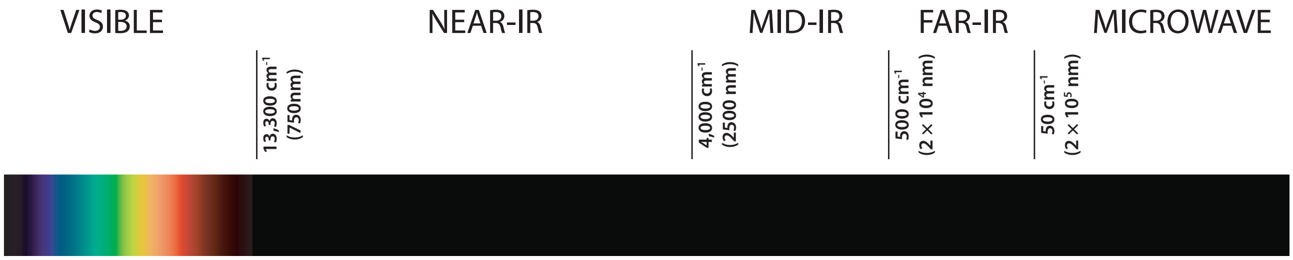


Figure 1. Approximate range of the EM spectrum comprising IR radiation.

Vibrating molecules can be approximated as simple harmonic oscillators. Within this approximation, the vibrational states are described by a single set of vibrational quantum numbers (**v**). These quantum numbers arise from the solution to the Schrödinger equation for a set of vibrating nuclei described by a one-dimensional harmonic oscillator potential, $V(x) = \frac{1}{2}kx^2$. The energies of the vibrational states are quantized as given in Equation 1, where ν is the fundamental vibrational frequency defined by Equation 2. The symbols k and μ refer to the force constant and reduced mass, respectively. One interesting consequence of Equation 1 is that a value of zero for the vibrational quantum number ($\mathbf{v} = 0$) does not correspond to zero energy. This minimum in energy is referred to as the ***zero-point energy***.

$$E_{\mathbf{v}} = h\nu\left(\mathbf{v} + \tfrac{1}{2}\right) \qquad (1)$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (2)$$

The harmonic oscillator approximation is a good model for vibrating atoms in low energy vibrational quantum states. However, the approximation begins to break down at higher values of **v**. Real vibrating atoms in molecules are better characterized by a potential term that takes into account nuclear repulsion as atoms get very close together and bond rupture as atoms get very far apart. In one spatial dimension, such an energy surface is conveniently described by a Morse potential (Figure 2). The energies of the vibrational quantum states for a system described by a Morse potential are altered from those of a harmonic oscillator and contain higher order factors referred to as anharmonic terms (Equation 3).

$$E_{\mathbf{v}} = h\nu\left(\mathbf{v} + {}^{1}\!/_{2}\right) - 2h\nu x_e\left(\mathbf{v} + {}^{1}\!/_{2}\right)^2 + \cdots \qquad (3)$$

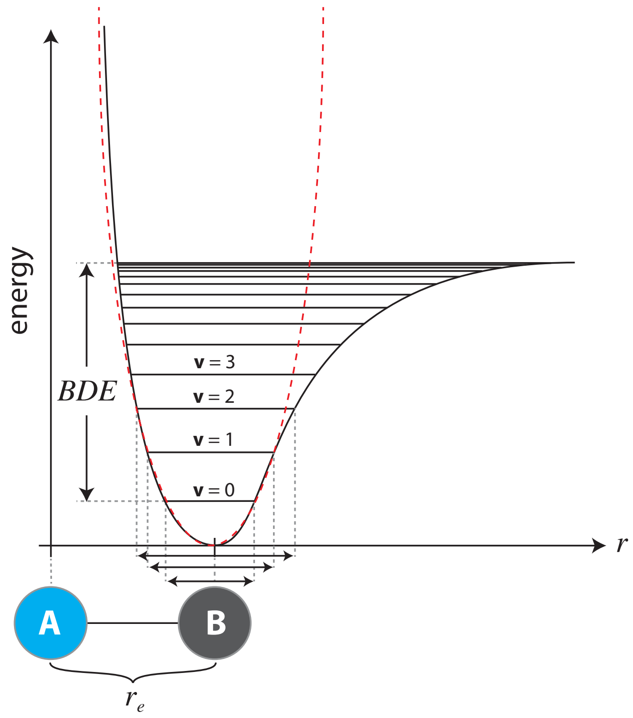
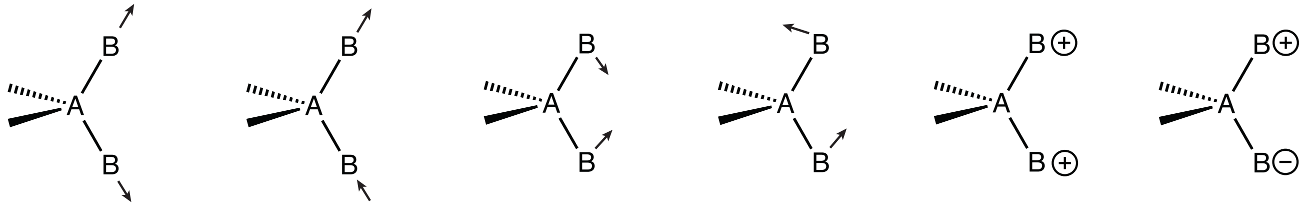


Figure 2. Morse potential for a hypothetical diatomic molecule AB showing the vibrational quantum states (**v**) and their corresponding motions about the equilibrium bond distance (r_e). The harmonic oscillator potential is shown overlaid as a red dashed line.

Vibrational transitions of molecules and ions typically occur from the vibrational ground state (**v** = 0) to the first vibrational excited state (**v** = 1). These types of transitions are known as ***vibrational fundamentals*** and can also be accompanied by rotational transitions (so-called ***rovibrational*** transitions are most relevant to molecules in the gas phase). Higher order excitations (Δ**v** > 1) termed ***vibrational overtones*** are also possible for anharmonic oscillators and can occur across the mid-IR and near-IR regimes.

Although it is convenient to envision molecular vibrations in terms of two vibrating atoms (Figure 2), true molecular motions occur in a variety of ways and can involve multiple atoms. All molecules have 3n degrees of spatial freedom where n is equal to the number of atoms. Of these 3n degrees of freedom, three degrees correspond to translational motion (net displacement along x, y, and z) and three degrees correspond to rotational motion for non-linear molecules. For linear molecules, only two degrees of rotational freedom exist since linear molecules cannot rotate about their principle molecular axes. The result of this analysis is the familiar 3n – 6 (3n – 5 for linear) rule for the total vibrational degrees of freedom. These vibrational degrees of freedom can be described by a fundamental set of atomic motions termed ***normal modes***. Normal modes correspond to irreducible representations within the point group of the molecule and can be discussed in terms of their symmetry.

Each of the normal modes of a molecule is described by a unique Morse potential with a characteristic vibrational frequency (ν). These vibrational frequencies reflect both the strength of the bonds (k) and the masses of the atoms (μ) involved in the atomic motions encompassed by the normal mode. Common descriptors for these atomic motions are shown in Figure 3.



symmetric stretch *asymmetric stretch* *scissoring* *rocking* *wagging* *twisting*

Figure 3. Descriptions for common types of atomic motions involved in normal modes.

Vibrational spectroscopy is most commonly employed to observe vibrational fundamentals corresponding to the various normal modes of a molecule. The technique of ***Fourier transform infrared spectroscopy*** (***FTIR***) is particularly useful in this regard and can be performed on solids, liquids, solutions, and gases. FTIR is a multiplex technique that uses an ***interferometer*** to produce time-dependent broadband infrared radiation that interacts with the analyte. The Fourier transform converts the complex absorption information detected by the instrument from the time domain to the frequency domain providing the familiar "IR spectrum" that is usually plotted as percent transmittance versus wavenumber in reciprocal centimeters (cm^{-1}). Normal modes corresponding to the motions of tightly associated atoms (i.e. functional groups) occur at frequencies that display only small changes across a large range of molecules. FTIR spectroscopy is therefore an excellent means of determining functional group composition for many molecules. Vibrational overtones can also be observed by FTIR and can be similarly useful in identifying functional groups.

Much like UV-vis spectroscopy, the most important selection rule for infrared spectroscopy concerns the ***electric dipole***. The transition moment integral for IR absorption is displayed in Equation 4, where μ is the familiar electric dipole moment operator (not reduced mass here!). The symmetry of the vibrational excited state wavefunction ψ_v^k is the same as that of the normal mode in question for a single fundamental and can therefore be used to quickly evaluate if the integral in Equation 4 is non-zero. The value of this integral will dictate whether or not a particular normal mode can be observed by IR spectroscopy.

$$M_v^{j\rightarrow k} \int \psi_v^j \mu \psi_v^k \, d\tau \qquad (4)$$

In this experiment, the FT-IR spectra of several tetrahedral borate anions, BX_4^- (X = H, D, F, and Ph), will be obtained. Using the spectra, we will test predictions about the fundamental vibrational frequencies and normal modes for the molecular ions involved.

Procedure

The experiment will involve four different borate salts, $NaBH_4$, $NaBD_4$, $NaBF_4$, and $NaBPh_4$. Each of the borate anions is approximately tetrahedral giving rise to the four "types" of normal modes shown in Figure 4 for the B-X cores (there are actually $3n - 6 = 9$ total normal modes). Two of these modes are electric dipole allowed and therefore IR active. In the case of tetraphenylborate, many more normal modes are present due to the phenyl groups.

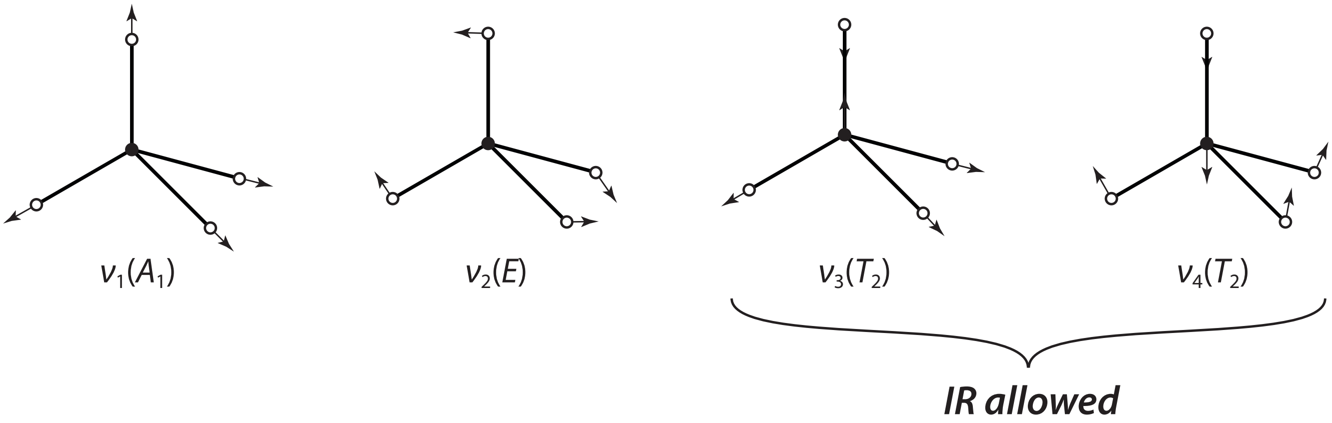


Figure 4. Description of the basic normal modes of a tetrahedral species.

Students will record the IR spectrum of each solid salt using ***attenuated total reflectance*** (***ATR***) IR spectroscopy. ATR is a sampling method that measures decreases (attenuation) in the reflectance of an IR beam as it is passes through a crystal that is in close contact with the analyte (Figure 5). Small amounts of IR radiation penetrate the sample at the interface of the crystal in the form of ***evanescent waves***. The absorption of this radiation by the sample decreases the intensity of the reflected beam, which is recorded by the detector. The ATR crystal must maintain intimate contact with the analyte so be sure to completely coat the sample area with solid material (3 to 5 mg). For each sample, a total of 16 scans should be performed. Save all data as .csv files so it can be replotted in Excel or similar software.

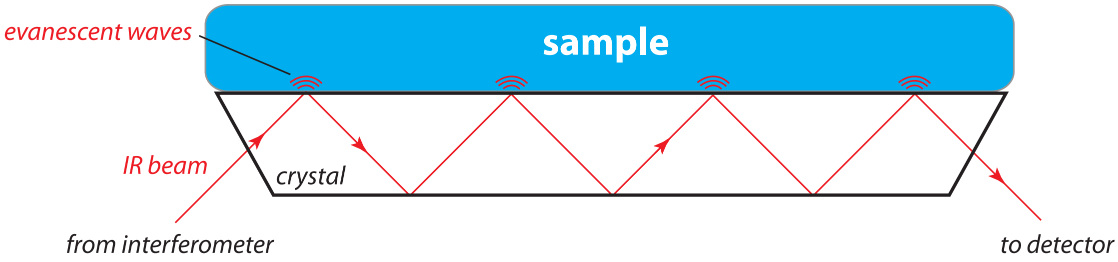
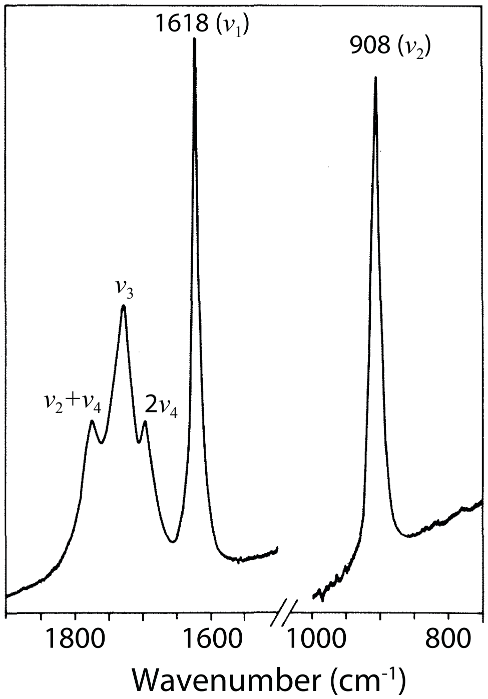


Figure 5. Schematic displaying the operation of an ATR element.

Plot each of the IR spectra and label all peaks with their associated wavenumber values (in cm^{-1}). For $NaBPh_4$, note the intensities of each peak as very strong (*vs*), strong (*s*), medium (*m*), or weak (*w*).

Questions

1. A first-order analysis predicts only two peaks for the spectra of $NaBH_4$, $NaBD_4$, and $NaBF_4$. Is this expectation broadly correct based on your experimental data? Explain any discrepancies. Keep in mind the limitations of the spectrometer and the fact that ambient water can contribute to the spectra of hygroscopic solids.
2. The apparent doublet pattern for $NaBH_4$ occurring near 2250 cm^{-1} is believed to arise from the ν_3 fundamental (higher energy peak) and the first overtone of ν_4 ($2\nu_4$, lower energy peak).[1] Is the assignment of the overtone, $2\nu_4$, consistent with the energy of the observed ν_4 fundamental in your spectrum? Explain.
3. Assume that ν_3 for $NaBH_4$ is approximately an isolated B-H stretch and calculate the predicted value for $NaBD_4$ based on the energy of ν_3 obtained from your spectrum of $NaBH_4$. Comment on the validity of this approximation given the results of the calculation, the observed energy for ν_3 in the spectrum of $NaBD_4$, and the nature of the ν_3 normal mode depicted in Figure 4.
4. A trio of peaks should be visible near 1700 cm^{-1} in your IR spectrum of $NaBD_4$. This same trio is also observed in the Raman spectrum of $NaBD_4$ shown below. The highest energy peak of the trio has been assigned to a combination band involving $\nu_2 + \nu_4$.[1] Based on the energy of this combination band and that of ν_4 determined from the value of the first overtone, $2\nu_4$, in your spectrum, calculate the value of ν_2. How well does the calculated value agree with that of the fundamental in the Raman spectrum? Explain.



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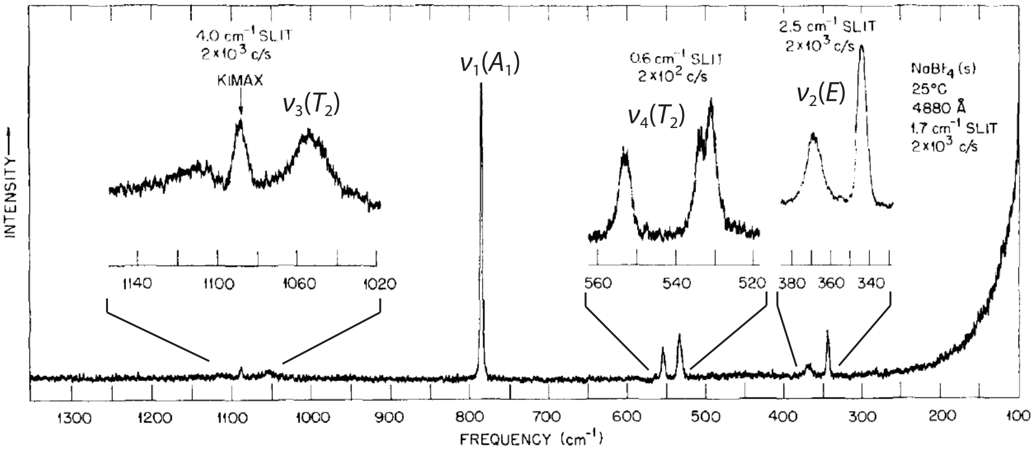
5. Our experimental limitations prevent observation of ν_4 in the case of $NaBF_4$. Assuming that the first overtone of ν_4 is essentially coincident with the fundamental for ν_3, predict the expected energy of ν_4 in wavenumbers. Does the predicted value for ν_4 align with our inability to observe it? Explain.

6. The Raman spectrum of polycrystalline $NaBF_4$ is shown below.[2] All four normal modes are Raman active and can be observed as shown. The apparent splitting of ν_4 and ν_2 into three and two bands, respectively, arises from the decreased site symmetry of the BF_4^- ions in the crystalline lattice. Based on the spectrum, is the position of ν_4 in good agreement with that predicted in Question 6? Should the experimental value be greater or less than that predicted from the first overtone? Explain.



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7. Using online databases and other resources, assign as many functional groups as possible in the spectrum of $NaBPh_4$.

8. How many normal modes are predicted for the BPh_4^- ion? Is such a result consistent with the general differences observed for the IR spectra of BPh_4^- and BH_4^-? Explain.

9. Although not easy to discern, BPh_4^- should demonstrate several normal modes akin to those of BF_4^- involving B-C motion. Do you predict the B-C modes to be at higher or lower energy than those of the corresponding B-F modes? Explain.

References

1. Harvey, K. B.; McQuaker, N. R. Infrared and Raman Spectra of Potassium and Sodium Borohydride. *Can. J. Chem.* **1971**, *49*, 3272-3281.

2. Bates, J. B.; Quist, A. S.; Boyd, G. E. Infrared and Raman Spectra of Polycrystalline $NaBF_4$. *J. Chem. Phys.* **1971**, *54*, 124-126.