

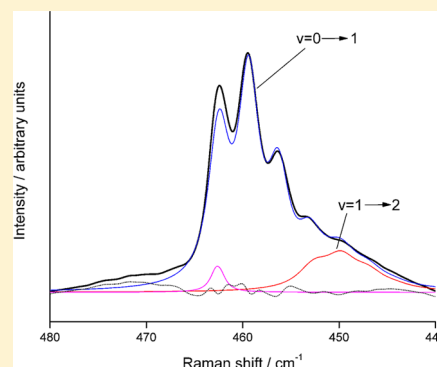
Vibrational Spectroscopy of the CCl_4 ν_1 Mode: Effect of Thermally Populated Vibrational States

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S Supporting Information

ABSTRACT: In our previous article on CCl_4 in this *Journal*, we presented an investigation of the fine structure of the symmetric stretch of carbon tetrachloride (CCl_4) due to isotopic variations of chlorine in $\text{C}^{35}\text{Cl}_x^{37}\text{Cl}_{4-x}$. In this paper, we present an investigation of the contributions from both the $v = 0$ to $v = 1$ excitation and the $v = 1$ to $v = 2$ excitation. We report the calculation of spectral contributions from excited state vibrational transitions (hot bands). All calculations and discussion are appropriate for the undergraduate physical chemistry laboratory as either an independent dry lab or a supplement to a pre-existing vibrational spectroscopy lab.



KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Curriculum, Raman Spectroscopy, Quantum Chemistry, Statistical Mechanics, Hands-On Learning/Manipulatives, Laboratory Instruction

This paper, in conjunction with our previously published work in this *Journal*,¹ is designed to expose students to a more rigorous physical chemistry experiment of investigating the Raman spectrum of carbon tetrachloride (CCl_4). Resources detailing physical chemistry experiments using Raman spectroscopy beyond compound identification do exist;² however, they are relatively few. Even fewer are experiments that incorporate predicting and measuring spectral contributions from thermally populated vibrational states. To our knowledge, this paper is the first to present an undergraduate laboratory experiment that requires students to analyze the intensity contributions due to hot bands in CCl_4 observable with high resolution ($<2 \text{ cm}^{-1}$) in the symmetric stretch peak. The experiment can be used as an independent dry lab or incorporated as a supplement to an existing Raman spectroscopy laboratory. The hot band contributions to the symmetric stretch are in close agreement with theoretical calculations from statistical mechanics. Students can predict the fraction of CCl_4 in the $v = 1$ excited state at a given temperature using the vibrational partition function and see that the empirical results agree with this prediction.

Langseth³ and co-workers first reported the fine structure in the CCl_4 Raman lines in 1931. Shurvell et al. report⁴ CCl_4 spectra at various temperatures from 4 to 300 K, noting that thermal population of the first vibrational excited state contributes to the ν_1 peak increasingly over the range 100–250 K. Further investigation by Hochenbleicher⁵ demonstrated the presence of hot bands with peak splitting similar to the principle CCl_4 peaks but shifted lower in energy due to anharmonicity. Figure 1 is a plot of the harmonic and Morse oscillator potentials on the same graph showing that

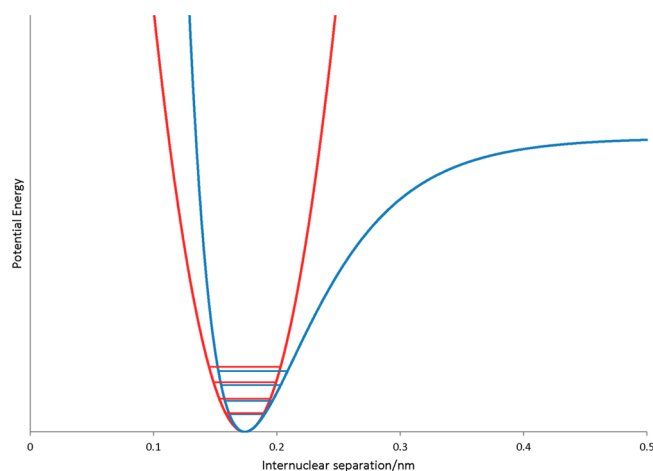


Figure 1. Harmonic (red) and Morse (blue) oscillator potentials for the ν_1 mode of CCl_4 showing the increasing difference between vibrational energy levels as the potential energy increases.

anharmonicity causes the transitions from higher vibrational energy levels (e.g., $v = 1 \rightarrow 2$) to be shifted lower in energy than the $v = 0 \rightarrow 1$ transition. In general, lower temperatures depopulate the first vibrational excited state and lessen the peak intensity contributions due to hot bands. This paper shows students how to extract spectral hot band contributions from empirical data of the CCl_4 ν_1 vibrational mode using Lorentzian line shape functions.

THEORY

Thermal Population of Vibrational States

The vibrational partition function from statistical mechanics can be used to calculate the fraction of molecules, f , in a vibrational state, v , at a particular temperature, T , from their vibrational frequency, ν , accordingly:

$$f(v) = \frac{e^{-\beta h\nu[v+(1/2)]}}{q_{\text{vib}}} \quad (1)$$

where q_{vib} is the vibrational partition function, h is Planck's constant, $\beta = (1/k_{\text{B}}T)$, and k_{B} is Boltzmann's constant.

$$q_{\text{vib}} = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \quad (2)$$

Upon an incident field of electromagnetic radiation of sufficient frequency, the molecules in one vibrational state may be excited into a vibrational excited state according to the selection rule $\Delta v = \pm 1$; for example, from the ground state ($v = 0$) to the first excited state ($v = 1$). When the molecule has a thermally populated first vibrational state, the transition from $v = 1$ to $v = 2$ will occur due to a sufficiently populated $v = 1$ state prior to irradiation. Equation 1 suggests a non-negligible fraction of molecules occupy $v = 1$ prior to excitation that will be excited and contribute to the vibrational peak intensity. The vibration depends on the transition dipole moment, μ (expressed below in bold to denote its operator form), and the probability of transition from a state v' to a state v'' is proportional to the square of its expectation value, $\mu_{v',v''}$ over all space, τ :

$$|\mu_{v',v''}|^2 = \left| \int \phi_{v'}^* \boldsymbol{\mu} \phi_{v''} d\tau \right|^2 \quad (3)$$

Using normalized harmonic oscillator wave functions for the above integral

$$\phi_v(x) = (2^v v!)^{1/2} \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2} H_v(\alpha^{1/2} x) \quad (4)$$

where H_v is a Hermite Polynomial specific to the vibrational level v and $\alpha = (4\pi^2 m k/h)^{1/2}$ where m is the reduced mass, k is the force constant and h is Planck's constant. These wave functions yield the following results for μ :⁶

$$\mu_{v,v-1} = \sqrt{\frac{v}{2\alpha}}; \quad \mu_{v,v+1} = \sqrt{\frac{v+1}{2\alpha}} \quad (5)$$

Thus, letting $v = 1$ demonstrates that the $v = 1$ to $v = 2$ transition probability, $|\mu_{12}|^2$, scales as twice that of $|\mu_{01}|^2$. Therefore, the contributions to the peak intensities from the excited state transitions should be twice as intense as the transitions originating from the ground state.

EXPERIMENT

Experimental details have been published elsewhere in this *Journal*.¹

HAZARDS

CCl₄

Extreme caution should be exercised in CCl₄ sample preparation (a sealed NMR tube suffices for our Raman Spectrometer at the University of Portland), as CCl₄ is very toxic and a known carcinogen. It is preferable for the professor

or a trained laboratory assistant to appropriately prepare the CCl₄ in an NMR tube (or equivalent) with the full protection of lab coat, gloves, and goggles under a laboratory fume hood. Once the sample is prepared and sealed, the same sample is easily used for multiple laboratory periods.

Laser Safety

Laser safety should be incorporated into the laboratory session as suitable for the spectrometer in use. Regardless of available instrumentation, general laser safety should be reviewed with the students. A review of safety mechanisms (shutters, etc.) incorporated into various instrumental designs allows students to become more familiar with a new optical configuration used in chemical analysis.

RESULTS

The Stokes-Shifted Raman Scattering Spectrum

The Stokes-shifted Raman Scattering spectrum in Figure 2 clearly shows the four fundamental vibrational modes for CCl₄

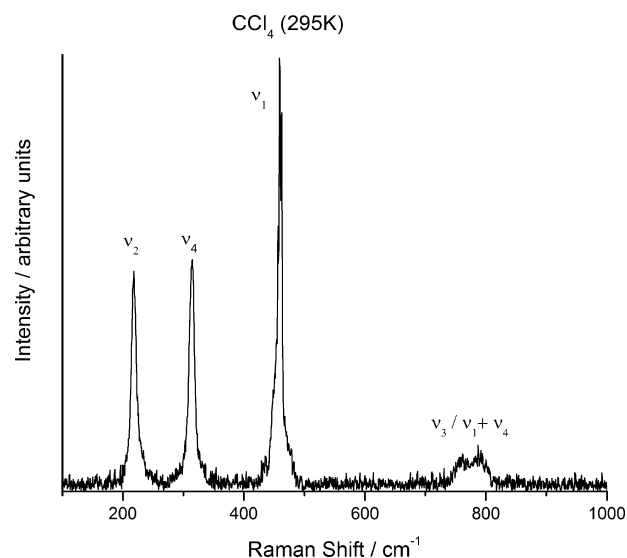


Figure 2. Stokes shifted Raman scattering spectrum for CCl₄ obtained with 1 cm⁻¹ resolution at 295 K.

at 295 K. The symmetric stretch mode, ν_1 , appears at 459 cm⁻¹; the symmetric bend mode, ν_2 , appears at 217 cm⁻¹; and the antisymmetric bend mode, ν_4 , appears at 314 cm⁻¹. A Fermi Resonance⁷ of the ν_3 and the $\nu_1 + \nu_4$ combination band is centered at 776 cm⁻¹ with peaks due to the superposition of these modes occurring at 761 and 791 cm⁻¹. For a comprehensive chart of all normal modes of vibration, see Shoemaker et al. (Table 1, page 432).²

Calculation of Contribution Due to Hot Bands ($v = 1$ to $v = 2$)

Temperatures below 250 K are required to significantly depopulate the excited state vibrational transitions ("hot bands"). These hot bands obscure the peaks of the less abundant isotopic variants of CCl₄ and broaden the low frequency end of the ν_1 peak. The contribution to the spectrum due to thermally excited molecules going from $v = 1$ to $v = 2$ can be extracted from the empirical data using Lorentzian modeling (see [Supporting Information](#)).

Lorentzian peak-fitting deconvolves the empirical data and reveals interesting features not otherwise visible. The following

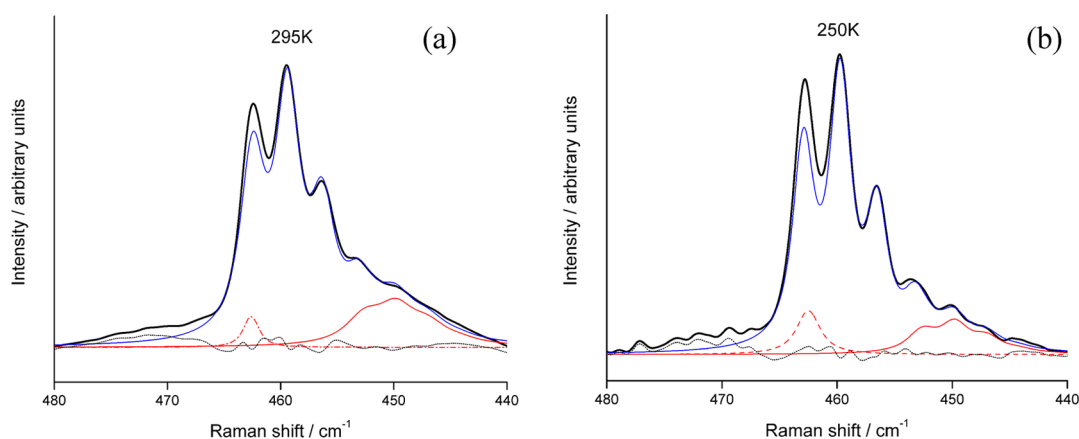


Figure 3. Raman spectra of the ν_1 vibration for (a) 295 K and (b) 250 K (solid black lines) were fit using a Lorentzian line shape function (solid blue lines) where we accounted for the contribution to the spectra due to the $v = 1$ to $v = 2$ transition of thermally excited CCl_4 molecules (solid red lines) and a difference band that we identified as $\nu_3 - \nu_4$ (dashed red lines). All contributions to the experimental peak are accounted for by the modeling as evidenced by the difference plot under the peak (dotted black lines).

equation is the mathematical form of the Lorentzian line shape function

$$I(\nu) = I_0 \frac{w}{(\nu - \nu_i)^2 + \left(\frac{w}{2}\right)^2} \quad (6)$$

where I_0 is the peak intensity, w is the peak full width at half-maximum, and ν_i is the peak position at the maximum intensity. A Lorentzian line shape results from homogeneous effects—factors that affect the sample uniformly. A difference spectrum subtracts all of the simulated or modeled data from the empirical data under a given peak in order to account for all of the contributions to a peak in a spectrum. Figure 3 shows spectra collected at 250 and 295 K of the ν_1 mode of CCl_4 . The peaks were fit using the Lorentzian model for the $v = 0$ to $v = 1$ transition, the hot band transitions and another peak that we propose⁸ is due to the $\nu_3 - \nu_4$ difference band underlying the C^{35}Cl_4 peak at 462.5 cm^{-1} . Thus, it is possible using data in this paper and the Lorentzian model to simulate a CCl_4 spectrum in a computational program, such as Excel (see Supporting Information), and compare this to empirical values obtained independently or those reported here.

The peak positions reported in Figure 3 agree nicely (within 0.5 cm^{-1}) with the thorough Raman spectrum analysis completed by Chakraborty and Verma.⁹ As expected due to the anharmonicity of vibrational transitions, the $v = 1$ to $v = 2$ transition is red-shifted by $\sim 10 \text{ cm}^{-1}$. The hot band peaks fit the empirical data best when the peak intensities predicted from the natural abundance of the chlorine isotopes are used to scale the relative peak intensities of the hot band peaks. This matches the statistical expectation and provides further evidence that this contribution originates from vibrational hot bands. Notably, the hot bands are convolved with the ground state transitions of the less abundant $\text{C}^{35}\text{Cl}_1^{37}\text{Cl}_3$ and C^{37}Cl_4 , which makes them appear broadened and with far greater intensity than is expected. A principal benefit to modeling empirical spectra with a difference spectrum is to identify hidden contributions to peak intensities that cannot be accounted for theoretically. This is achieved by a primary fitting of the empirical spectrum with the Lorentzian of the most significant contribution: the isotopic components of the $v = 0$ to $v = 1$ transition. The statistical populations of each isotopic variant are used to scale the modeled peaks. Beginning

with the peak location of the most abundant CCl_4 molecule ($\text{C}^{35}\text{Cl}_3^{37}\text{Cl}_1$), the peak locations of the other peaks are optimized by incrementing/decrementing the peak splitting parameter and the Lorentzian line width is adjusted to best fit the empirical result. After optimizing this fit using the Lorentzian parameters (detailed in the workbook, see Supporting Information), only the secondary contributions to the empirical spectra remain, which are obvious from the difference plot. The remaining peak of lower frequency in the difference spectrum is due to the hot band and can be fit with a separate Lorentzian using the same procedure: adjust the position of the most abundant peak, adjust the other peak positions, and set the Lorentzian line width. Finally, the difference spectrum reveals the location of the contribution that is possibly from a difference band at 462.5 cm^{-1} , likely due to $\nu_3 - \nu_4$.⁸ The agreement between the experimental and calculated spectra is assessed by minimizing the sum of the squared error (i.e., by minimizing the difference between the empirical spectrum and the calculated values using the Lorentzian line shape models. See excel spreadsheet in Supporting Information for more details).

The advantage of the difference spectrum analysis is clearly demonstrated with the identification of the peak arising at $\sim 462.5 \text{ cm}^{-1}$ which underlies the C^{35}Cl_4 peak. Theory predicts this peak to be 75% of the intensity of the most abundant isotopic variant ($\text{C}^{35}\text{Cl}_3^{37}\text{Cl}_1$). However, the empirical result at both 250 and 295 K shows this relative intensity to be $\sim 85\%$, suggesting that there is an underlying contribution in this region. While it has yet to be reported in the literature, we have reason to believe that this peak could be due to the difference of the ν_3 mode at $\sim 776 \text{ cm}^{-1}$ and the ν_4 mode at $\sim 314 \text{ cm}^{-1}$.⁸ A similar observation has been suggested by Hochenbleicher from Raman studies of CCl_4 vapor⁹ and Chakraborty and co-workers show this peak in the infrared spectrum as well as the summation band $\nu_3 + \nu_4$ in the Raman spectrum.¹⁰

From statistical mechanics, the fraction of molecules in the first vibrational excited state can be calculated at various temperatures (see Supporting Information). Since the transition dipole moment for $v = 1$ to $v = 2$ scales as roughly twice that for the $v = 0$ to $v = 1$ transition, the hot band contributions to the empirical spectra scale accordingly (see Table 1).

At 295 and 250 K, roughly 9.5% and 6.5% of CCl_4 are thermally populated in $v = 1$, respectively. Therefore, the

Table 1. Fractions of CCl₄ in the Thermally Populated $\nu = 1$ and Percent Hot Band Contribution to Peak Intensities

| T/K | Fraction of CCl ₄ in $\nu = 1$ ³⁵ Cl: ³⁷ Cl | | | | | Hot Band Contribution (%) |
|-----|---|--------|--------|--------|--------|---------------------------|
| | 4:0 | 3:1 | 2:2 | 1:3 | 0:4 | |
| 295 | 0.0987 | 0.0975 | 0.0963 | 0.0951 | 0.0937 | 17.98 |
| 250 | 0.0695 | 0.0683 | 0.0671 | 0.0659 | 0.0649 | 12.49 |

expected hot band contributions to the symmetric stretch peak range from 18 to 20% at 295 K and 12–14% at 250 K. The values obtained (see Table 1) from Lorentzian modeling of the hot band contributions in the empirical spectra show close agreement with the expected contribution calculated using statistical mechanics. Thus, through Lorentzian modeling of the empirical data and spectral analysis via the difference between the empirical result and the theoretical model, a more complete and detailed understanding of the CCl₄ symmetric stretch is obtained.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: [10.1021/acs.jchemed.5b00339](https://doi.org/10.1021/acs.jchemed.5b00339).

Excel document for Lorentzian modeling (XLSX)

Document titled “Notes to the Professor” that provides a detailed description of the Lorentzian modeling (DOCX)

Mathematica notebook with statistical mechanical calculations of fractions of thermally excited molecules (PDF)

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Notes

The authors declare no competing financial interest.

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