

# Determining the Structure of Oxalate Anion Using Infrared and Raman Spectroscopy Coupled with Gaussian Calculations

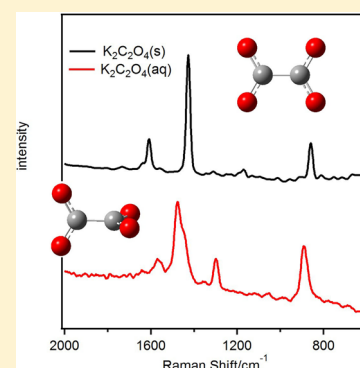
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## Supporting Information

**ABSTRACT:** A laboratory project for the upper-division physical chemistry laboratory is described, and it combines IR and Raman spectroscopies with Gaussian electronic structure calculations to determine the structure of the oxalate anion in solid alkali oxalates and in aqueous solution. The oxalate anion has two limiting structures whose vibrational spectra have distinct differences: planar with  $D_{2h}$  symmetry and nonplanar with  $D_{2d}$  symmetry. In the former case, the IR and Raman spectra are complementary. Students measure the IR and Raman spectra of solid  $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{K}_2\text{C}_2\text{O}_4$ , and  $\text{Cs}_2\text{C}_2\text{O}_4$ , and a nearly saturated aqueous solution of  $\text{K}_2\text{C}_2\text{O}_4$ . They also carry out Gaussian calculations on the oxalate anion to predict the vibrational wavenumbers of both the planar and nonplanar structures and use the results to assign the spectra. By considering their results for the four samples, they decide on the oxalate structure in each and defend their choice in a report. The complexity of the project immerses the students in vibrational spectroscopy so that they learn the subject at a deeper level.

**KEYWORDS:** Upper-Division Undergraduate, Laboratory Instruction, Physical Chemistry, Hands-On Learning/Manipulatives, IR Spectroscopy, Raman Spectroscopy, Molecular Modeling, Molecular Properties/Structure



Research on oxalate compounds is motivated by their widespread importance in nature.<sup>1,2</sup> They are synthesized in most living organisms and have even been suggested as biomarkers for life on Mars.<sup>3</sup> In plants, calcium oxalate production is important in calcium regulation. Also, when particularly high amounts are present in a plant, oxalate's toxicity serves as a defense mechanism against herbivores and some insects.<sup>4</sup> Lichens also produce oxalates, and excreted oxalic acid can react with substrate minerals to form copper, zinc, nickel, and other oxalates.<sup>5</sup>

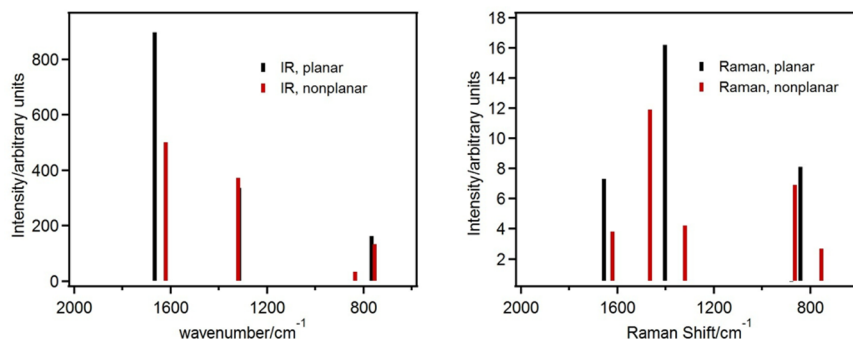
Vibrational spectroscopies can be valuable tools for analyzing oxalate compounds in their natural state because they are noninvasive; there are a number of reports which explore these methods.<sup>1,3,5</sup> More recently, the oxalate anion has been recognized as being well suited for probing the fundamental properties of cation–anion pairs in aqueous solution.<sup>6</sup> This is due to the fact that it has two major structural forms which are similar in energy but different in symmetry. In its isolated state, the lowest energy structure of  $\text{C}_2\text{O}_4^{2-}$  is nonplanar with the  $-\text{CO}_2^-$  groups perpendicular to each other ( $D_{2d}$  symmetry); however, the planar structure ( $D_{2h}$  symmetry) is only on the order of  $10 \text{ kJ mol}^{-1}$  higher in energy and is easily accessed via internal rotation about the C–C single bond. The planar form can be stabilized by cation interactions, and at sufficiently high cation concentrations in solution, some lowering of the  $D_{2d}$  symmetry is evident in the vibrational spectrum.<sup>6</sup> Thus, the oxalate anion can act as a sensor for evaluating the proximity of cations in solution. The similar energies of the two symmetry

forms also mean that there is some variation of the structure within different oxalate compounds.

Infrared and Raman spectra provide complementary information for finding the frequencies of a molecule's vibrational modes. This is particularly evident for molecules having a center of inversion, in which case the Raman and infrared activities of the vibrations are exactly the reverse of each other. When an oxalate ion changes from the nonplanar to planar form, its vibrational frequencies change somewhat, but more interestingly, its structure develops a center of inversion, so certain modes become IR and Raman inactive. The different spectral properties of the two structural forms and the structural variation found in different compounds makes the spectroscopic investigation of oxalate compounds an attractive subject for a student laboratory project. Only a few student projects have been reported that combine IR and Raman spectroscopies. One noteworthy example is a lab developed for upper-division students, which uses cis- and trans-1,2-dichloroethylene to demonstrate the complementary nature of Raman and IR spectroscopies, and also includes the use of electronic structure calculations to aid in interpreting the spectra.<sup>7</sup> Both forms of dichloroethylene are planar, but only the trans form has an inversion center. Since the barrier between the cis and trans forms is very high, there is no ambiguity in the spectral identification.

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**Figure 1.** Predicted intensities of IR (left) and Raman (right) peaks for planar and nonplanar oxalate anion. Gaussian calculations were done using the DFT method with the B3LYP functional and cc-pVDZ basis set.

In this report, we describe a project that focuses on the oxalate anion and its structural dependence on the local environment. Although the structure has  $D_{2d}$  symmetry in its unperturbed state, the planar structure prevails in most solids.<sup>8,9</sup> In the alkali oxalate series, however, the planarity of the oxalate decreases with increasing size of the alkali cation.<sup>8</sup> Therefore, investigating the oxalate compounds gives the students the opportunity of using vibrational spectroscopies to probe environmentally induced structural changes that can occur in a simple anion.

## PROJECT OVERVIEW

This project is designed for an upper-division physical chemistry laboratory course. In our course, the students have three, 3-h lab periods to work, but only two periods are needed to complete the experimental and computational components. The third day is used for analysis and preparation of the report. The project is composed of three parts:

- (1) Calculations of the energies and vibrational wavenumbers of the planar ( $D_{2h}$  symmetry) and nonplanar ( $D_{2d}$  symmetry) forms of  $C_2O_4^{2-}$  using the Gaussian electronic structure program suite with GaussView as the front end.<sup>10,11</sup>
- (2) Measurement of IR spectra for solid  $Na_2C_2O_4$ ,  $K_2C_2O_4$ , and  $Cs_2C_2O_4$ .
- (3) Measurement of the Raman spectra of the same solids as well as a nearly saturated aqueous solution of  $K_2C_2O_4$ .

The solids are used as purchased except that they are vacuum-dried at about 100 °C for a few hours. Nearly saturated solutions of  $K_2C_2O_4$  are prepared by the students.  $Rb_2C_2O_4$  was not included because both the planar and nonplanar forms coexist in the solid, even when it is dried, and analyzing the spectra would add too much complexity to the experiment. After finishing the computations and spectral measurements, the students examine their data to determine the structure of the oxalate in each system. All of their results and analyses go into a complete report in which they are required to develop strong arguments in support of their conclusions. Students work in pairs in our course, but the experiments are straightforward enough for them to work individually, and if resources permit, this is recommended. The full project instructions are presented in the [Supporting Information](#).

## METHODS AND SAMPLE RESULTS

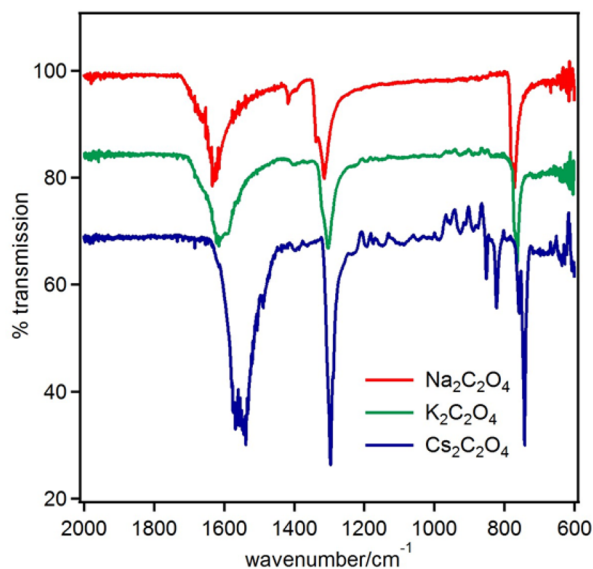
### Gaussian Calculations

Gaussian calculations (geometry optimization followed by IR and Raman simulations) on the two limiting forms of  $C_2O_4^{2-}$  are done using the DFT method with the B3LYP functional and cc-pVDZ basis set.<sup>10</sup> Smaller basis sets may not predict the lowest energy structure correctly. Although the planar form occurs at a maximum in the potential energy curve with respect to the torsional angle about the C–C bond, the geometry is constrained so that it retains  $D_{2h}$  symmetry. The goals of the calculations are to determine which oxalate form has the lowest energy structure and to distinguish the differences in the IR and Raman spectra. In addition, with GaussView,<sup>11</sup> the students are able to visualize the molecular vibrations and see how the motions correlate with the peak positions and to IR and Raman intensities. The positions and intensities of the vibrations are shown in [Figure 1](#), and tables of values with assignments can be found in the [Supporting Information](#). Comparing the two structures, the following significant differences can be observed:

- The C=O asymmetric stretch peaks near 1600  $cm^{-1}$  are about 45  $cm^{-1}$  higher for the planar form and should be observable in the IR and Raman spectra.
- The symmetric stretch peak near 1400  $cm^{-1}$  is about 60  $cm^{-1}$  higher for the nonplanar form. It is IR inactive and strongly Raman active for both forms.
- The C=O stretch near 1300  $cm^{-1}$  is at the same position for both forms; it is Raman inactive in the planar form but of medium strength in the nonplanar form. This characteristic is particularly useful for identifying the nonplanar form with Raman spectroscopy.
- In the IR region between 700 and 900  $cm^{-1}$ , the nonplanar structure has two observed lines, but the planar structure has only one.

### IR Spectra

IR spectra of the solids are taken with a PerkinElmer RX 1 FTIR with an attenuated total reflectance (ATR) element. The ATR sampling is not necessary but is currently available in our lab. Examples of spectra for  $Na_2C_2O_4$ ,  $K_2C_2O_4$ , and  $Cs_2C_2O_4$  are shown in [Figure 2](#) and agree with results found in the literature.<sup>8,12</sup> The  $Na_2C_2O_4$  and  $K_2C_2O_4$  spectra are quite similar to each other, whereas the spectrum for  $Cs_2C_2O_4$  has the peak near 1600  $cm^{-1}$  shifted to a lower wavenumber, and additional small peaks show up near 840  $cm^{-1}$ . Both of these differences are indicative of a nonplanar structure for  $Cs_2C_2O_4$ . (Note: the appearance of two peaks near 840  $cm^{-1}$  may

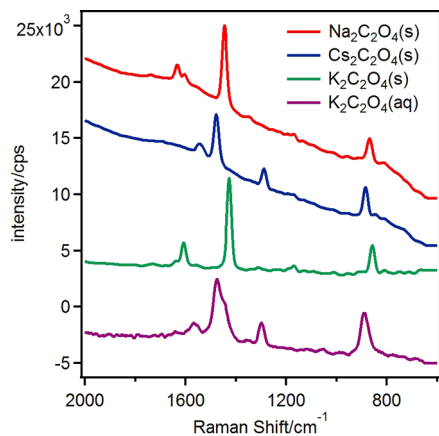


**Figure 2.** Infrared spectra of solid oxalates using a PerkinElmer Spectrum RX 1 FT-IR System with Pike Miracle Omni 1B ATR; resolution = 4  $\text{cm}^{-1}$ .

indicate some lowering of the  $D_{2d}$  symmetry; that is, the dihedral angle may not be exactly  $90^\circ$ .)

### Raman Spectra

Raman spectra are taken using a student spectrometer by Raman Systems (Model R-3000QE-532). Sample spectra for solid  $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{K}_2\text{C}_2\text{O}_4$ , and  $\text{Cs}_2\text{C}_2\text{O}_4$  and a nearly saturated aqueous solution of  $\text{K}_2\text{C}_2\text{O}_4$  are shown in Figure 3. A water



**Figure 3.** Raman spectra of solid oxalates and potassium oxalate in aqueous solution ( $\sim 2$  M) measured with a Raman Systems spectrometer with 532 nm laser excitation; resolution  $\cong 10$   $\text{cm}^{-1}$ .

spectrum is also taken so that it can be subtracted from the aqueous potassium oxalate spectrum; the subtracted spectrum is shown in the figure. Again, the spectra agree with results found in the literature.<sup>8,12,13</sup> The differences between the oxalate structures are readily apparent; the spectra for  $\text{Na}_2\text{C}_2\text{O}_4$  and  $\text{K}_2\text{C}_2\text{O}_4$  indicate planar oxalate structures, whereas those for  $\text{Cs}_2\text{C}_2\text{O}_4$  and aqueous  $\text{K}_2\text{C}_2\text{O}_4$  indicate nonplanar structures. This conclusion is suggested most obviously by the appearance of the peak near  $1300$   $\text{cm}^{-1}$  in the nonplanar spectra, but the shifts in the peaks in the  $1400$ – $1600$   $\text{cm}^{-1}$  region in the nonplanar form are also well-predicted by the

calculations. The broad underlying intensity observed in the  $\text{Na}_2\text{C}_2\text{O}_4$  and  $\text{Cs}_2\text{C}_2\text{O}_4$  spectra is presumably due to fluorescence. Spectra taken with a research grade Raman microscope gave much higher signal-to-noise and reduced fluorescence (see Supporting Information), but the student model is sufficient for the purposes of this lab. There is a noteworthy feature of the solid  $\text{Na}_2\text{C}_2\text{O}_4$  and  $\text{K}_2\text{C}_2\text{O}_4$  spectra that may confuse the students. Although the oxalate anion is planar in these compounds, the IR and Raman spectra do not appear to be entirely complementary because both have a peak near  $1640$   $\text{cm}^{-1}$ . Here, the Gaussian calculations are helpful because they show that there are two nearby vibrations in this region, one Raman active and the other IR active.

### HAZARDS

Oxalate compounds are toxic, and ingestion leads to renal failure. It is estimated that as little as 5 g of sodium oxalate can be fatal if swallowed.<sup>14</sup> The compounds are strongly irritating to the skin, respiratory tract, and eyes, and care should be taken to prevent atmospheric dispersion of the powder.

### DISCUSSION

The students' task is to evaluate the experimental and computational data to determine the structural form of oxalate in each sample. We encourage them to develop their own approaches. Although the constructions of the above figures make the structural determination seem fairly simple, few students think of presenting the data in this way. Nonetheless, many develop creative strategies. The structures of the alkali oxalates have been determined by X-ray crystallography,<sup>8</sup> so the students may find them in the literature, but in their reports, they are required to give convincing arguments supporting their conclusions. Simple arguments in which some of the observed peaks are matched with theoretical peaks, without any regard for peak intensities, will be inadequate. With regard to this last point, we have found that the  $\text{Na}_2\text{C}_2\text{O}_4$  peaks can be matched to either the nonplanar or planar structures if one ignores the lack of a Raman peak near  $1300$   $\text{cm}^{-1}$  and an IR peak around  $800$ – $850$   $\text{cm}^{-1}$ . Only when all peaks are considered will the correct structure be identified. Students should notice that the Raman spectrum of  $\text{K}_2\text{C}_2\text{O}_4$  changes from that of a planar structure to a nonplanar structure when dissolved in water. This agrees with the theoretical result that the unperturbed nonplanar form is lower in energy, and planarity arises as the electrostatic forces between the cations and anions increase.

An interesting computational extension to this project is to calculate the structure of  $\text{Na}_2\text{C}_2\text{O}_4$  with the oxalate initially in its nonplanar form. If the input structure is constructed with the sodium ions lined up along the C–C bond and on opposite sides of the oxalate, the minimum-energy form is nonplanar, but if the sodium ions are lined up along an axis bisecting the C–C bond, the oxalate ion minimizes to the planar form. This exercise gives some qualitative insight into the effect of ions in the crystal lattice and helps to explain why the planar form is so often found in oxalate compounds.

For the last eight years, we have included a project with Raman and IR spectroscopy combined with Gaussian calculations in our physical chemistry lab course. It is a critical component of the course, because students have a lot of trouble understanding the difference between the two spectroscopies. Also, we have found that they do not have a practical appreciation of the usefulness of computational methods in

interpreting experimental results. This lab addresses both of those issues. Initially, the lab focused on the hexyne system; 1-hexyne and 3-hexyne were compared to explore how the symmetry affects the vibrational spectra (3-hexyne has an inversion center). With the more open-ended character of the oxalate system, the students are obliged to be more creative, and through that creative process, they learn more about vibrational spectroscopy. We feel that this adds a new dimension to the experiment. The written reports that have been submitted by the students have shown that many of them have developed a good understanding of the subject by creatively analyzing their data. Some students have struggled to understand the connections, but the exposure that they have received through doing such an in-depth project will surely help them in their future understanding of the subject.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00118.

Gaussian results; high-resolution Raman spectra of solid alkali oxalates; student handout; general instructions for Gaussian computations with the GaussView interface. (PDF)

Gaussian results; high-resolution Raman spectra of solid alkali oxalates; student handout; general instructions for Gaussian computations with the GaussView interface. (DOCX)

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### Notes

The authors declare no competing financial interest.

## ■ REFERENCES

- (1) Baran, E. J. Review: Natural Oxalates and their Analogous Synthetic Complexes. *J. Coord. Chem.* **2014**, *67* (23–24), 3734–1368.
- (2) Smith, L. H. The Many Roles of Oxalates in Nature. *Trans. Am. Clin. Climatol. Assoc.* **2002**, *113*, 1–20.
- (3) Frost, R. L. Raman Spectroscopy of Natural Oxalates. *Anal. Chim. Acta* **2004**, *517*, 207–214.
- (4) Franceschi, V. R.; Nakata, P. A. Calcium oxalate in plants: Formation and function. *Annu. Rev. Plant Biol.* **2005**, *56*, 41–71.
- (5) Monico, L.; Rosi, F.; Miliani, C.; Daveri, A.; Brunetti, B. G. Non-invasive Identification of Metal-Oxalate Complexes on Polychrome Artwork Surfaces by Reflection Mid-infrared Spectroscopy. *Spectrochim. Acta, Part A* **2013**, *116*, 270–280.
- (6) Kuroda, D. G.; Hochstrasser, R. M. Dynamic Structures of Aqueous Oxalate and the Effects of Counterions Seen by 2D IR. *Phys. Chem. Chem. Phys.* **2012**, *14*, 6219–6224.
- (7) McClain, B. L.; Clark, S. M.; Gabriel, R. L.; Ben-Amotz, D. Educational Applications of IR and Raman Spectroscopy: A Comparison of Experiment and Theory. *J. Chem. Educ.* **2000**, *77* (5), 654–660.
- (8) Dinnebier, R. E.; Vensky, S.; Panthöfer, M.; Jansen, M. Crystal and Molecular Structures of Alkali Oxalates: First Proof of a Staggered Oxalate Anion in the Solid State. *Inorg. Chem.* **2003**, *42* (5), 1499–1507.
- (9) Dean, P. A. W. The Oxalate Dianion,  $C_2O_4^{2-}$ : Planar on Nonplanar? *J. Chem. Educ.* **2012**, *89* (3), 417–418.
- (10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Hatzakos, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision D.01; Gaussian, Inc.: Wallingford CT, 2013.
- (11) Dennington, R.; Keith, T.; Millam, J. *GaussView*, Version 4; Semichem Inc.: Shawnee Mission, KS, 2009.
- (12) Clark, R. J. H.; Firth, S. Raman, Infrared and Force Field Studies of  $K_2^{12}C_2O_4 \cdot H_2O$  and  $K_2^{13}C_2O_4 \cdot H_2O$  in the Solid State and in Aqueous Solution, and of  $(NH_4)_2^{12}C_2O_4 \cdot H_2O$  and  $(NH_4)_2^{13}C_2O_4 \cdot H_2O$  in the Solid State. *Spectrochim. Acta, Part A* **2002**, *58*, 1731–1746.
- (13) Hind, A. R.; Bhargava, S. K.; Van Bronswijk, W.; Grocott, S. C.; Eyer, S. L. On the Aqueous Vibrational Spectra of Alkali Metal Oxalates. *Appl. Spectrosc.* **1998**, *52* (5), 683–691 Note: The solid cesium oxalate Raman spectrum in this paper does not agree with our results or those in ref 6.
- (14) Hamilton, S. E.; Pielage, P. J.; Fassett, R. G. Acute Renal Failure Following Sodium Oxalate Ingestion. *Emergen. Med.* **1999**, *11*, 35–37.