

## Lab Documentation

### **Applications of Group Theory: Infrared and Raman Spectra of the Isomers of 1,2-Dichloroethylene. A Physical Chemistry Experiment**

**Norman C. Craig and Nanette N. Lacuesta**, Department of Chemistry, Oberlin College, Oberlin, OH 44074

In our use of this experiment in upper-level laboratories, we do not give the students detailed instructions. We provide classroom instruction in the use of character tables to find selection rules for vibrational spectroscopy. We give each student a copy of the description of the experiment as it appears in print. We assist pairs of students with sample preparation and with use of the instrument.

#### **Sample Handling for Infrared Spectroscopy**

Reasonably pure samples of *cis* and *trans* 1,2-dichloroethylene [*156-59-2* and *156-60-5*] are available from Aldrich Chemical Company, Milwaukee, WI. (The sample of the *cis* isomer used for the spectra in the paper was from Eastman Kodak Chemical. It contained about 10% of the *trans* isomer.) The *cis* isomer boils at 60°C; the *trans* isomer boils at 48°C.

The gas-phase infrared spectra were obtained in a Wilmad (Buena, NJ) Mini Gas Cell 117A of 10-cm length and 2.5 cm diameter. Larger cells of 5-cm diameter may also be used. The glass Wilmad cells are supplied with two side tubes and fittings for attaching crystal windows with O-ring seals. The cells are also supplied with a metal support for use in mounting the cell in the sample compartment of an infrared spectrometer. A stopcock and ball joint were sealed to one arm of the Wilmad cell, and the other arm was sealed off. Polished potassium bromide windows were attached with O-rings lightly lubricated with Silicone grease.

Measured samples of gases were put into the gas cell on a vacuum system. The cell was attached to the vacuum manifold, and air was pumped out. A few tenths of a milliliter of one of the liquids was put into a small glass tube equipped with a ground joint. The joint was greased with Silicone grease and then joined to a mating joint which was attached to a stopcock and another joint for mating to a joint on the vacuum system. The dichloroethylene sample in the very tip of the tube was frozen with liquid nitrogen, and the air pumped away quickly before much water had condensed out of the air enclosed in the tube. To free the frozen liquid of entrapped air, the stopcock on the sample tube was closed, and the liquid allowed to melt. Then, liquid nitrogen was used again to freeze the sample, and the residual gas was pumped away. Monitored with a mercury manometer, gas from the room-temperature liquid was expanded into the gas cell to give a pressure of about 15 torr.

For the far-infrared spectrum of the *trans* isomer, a Wilmad mini cell equipped with cesium iodide windows was used. The pressure of the *trans* sample was about 130 torr, as is needed for the typically weaker bands in the far-infrared region. Near saturation vapor pressure the chloroethylenes tend to dissolve in stopcock grease. Silicone grease is a relatively poor solvent for organics. That is the reason for using Silicone grease for this experiment. For the *cis* isomer

the far-infrared spectrum was run in a Wilmad cell equipped with polyethylene windows in an attempt to observe the band at about  $170\text{ cm}^{-1}$ , which lies below the cutoff of cesium iodide.

If a vacuum system is not available, the gas samples can be handled in another way. Wilmad mini cells come equipped with serum bottle caps on the two side arms. With potassium bromide windows in place on the cell, a small amount of one of the liquids can be injected through one of the serum bottle caps with a syringe. About  $1.6\ \mu\text{L}$  of dichloroethylene should give 15 torr in the 30-mL volume of the Wilmad cell. To clear the cell for the next sample the two serum bottle caps are removed, and the cell is purged with a stream of dry nitrogen. For best performance the cell should be purged with dry nitrogen before the first sample is introduced. Getting the right amount of liquid injected into the cell will require experimenting. With a gas-tight syringe the amount gas can be adjusted to give intensities comparable to those shown in the spectra in the paper.

To simplify the experiment, air was not purged from the spectrometer with dry nitrogen for the mid-range IR spectra. The IR spectra shown in Figures 2 and 3 were obtained by placing the evacuated cell in the beam during the recording of the background spectrum. As a consequence, the compensation for bands due to atmospheric water and carbon dioxide is reasonably good. For spectra run in the far-IR region, as in Figure 5, it is essential to purge the instrument very well. This requirement is an added complication when running the far-IR spectrum as part of the laboratory experiment.

### **Sample Handling for Raman Spectroscopy**

With a Pasteur pipet samples were injected into cut-off, standard 5-mm Pyrex NMR tubes to a depth of about 2 cm. These NMR sample tubes were mounted in the sample tube holder supplied by Nicolet. The plastic caps of these sample tubes can be sealed with paraffin wax for reuse of the samples or the contents can be returned to storage bottles. Standard Pyrex melting point capillaries of 1.6-1.8-mm diameter may also be used for samples in an appropriate mount if polarization studies are not to be made.

### **Optional Polarization Studies for the Raman spectra**

To do the polarization studies shown in the Raman spectra in the paper, the spectrometer must be equipped with a polarization analyzer and a sample module for  $90^\circ$  optics. This configuration has much less light-gathering capacity in the Nicolet instrument than the standard  $180^\circ$  optical configuration. Because of diminished light gathering in the  $90^\circ$  optical configuration, we used a liquid-nitrogen-cooled germanium detector. The experiment could be profitably done in the  $180^\circ$  configuration without the polarization measurements, which can be read from the figures in the paper.

### **Computer Files for Spectra**

Computer files are available for the spectra reported in this experiment. They are PC files in two formats: the .SPA format for use with Nicolet OMNIC software and .CSV format, which can be opened with Excel or with spectral analysis software such as Igor. Included in these files are IR

spectra recorded at the higher resolution of 0.1 cm<sup>-1</sup>. Because of the higher resolution, sharp lines are much stronger and more numerous for H<sub>2</sub>O and CO<sub>2</sub> due to incomplete compensation of the background. For this reason the higher resolution IR spectra are not given in the Lab Summary section. However, these spectra are useful in revealing greater detail in the rotational structure. For the IR spectral files, it may be necessary to convert from absorbance mode to transmittance mode and to set the transmittance range from 0 to 100. For the Raman files, the low-frequency limit of the spectrum should be set to 100 cm<sup>-1</sup>. When comparing the scan for perpendicular polarization with the scan for parallel polarization, the vertical axis of the perpendicular polarization must be reset to the same value as for the parallel polarization.

## Hazards

The dichloroethylenes used in this experiment are members of a class of substances that are suspected carcinogens. Thus, the dichloroethylenes should be handled carefully with the protection of rubber gloves, and transfers should be made in a fume hood. Excess material should be disposed of in special waste containers for halogen-containing organics. The amounts of the dichloroethylenes used in the experiment are small, which gives an added measure of safety.

All instruments that use lasers must be handled with care. FT-infrared spectrometers use helium-neon lasers to track the moving mirror in the interferometer. These very low power red lasers are not dangerous unless viewed directly down the beam, an unlikely event given the optical arrangement. On the other hand, the near-infrared laser used to excite the Raman spectrum is very dangerous, because of its power level and the invisibility of the light to the human eye. The Nicolet instrument is set up with a special interlock to insure that the laser beam is blocked off whenever the sample compartment for the Raman module is open. Thus, infrared laser light is never falling on the sample when the sample tube is being inserted or removed. However, the red laser light from the infrared module falls on the sample tube and is very useful in aligning the sample in the path of the scattered light collected for analysis in the infrared module.

## Spectral Files Supplied in Electronic Format

### cDCIE Folder

cDCIE\_IR.SPA IR spectrum at 0.5 cm<sup>-1</sup> resolution as in Fig. 4. Nicolet OMNIC.  
cDCIE\_IR.CSV " " " " " " " " " " Excel readable.  
cDCIE\_hiresIR.SPA IR spectrum at 0.1 cm<sup>-1</sup> resolution. Nicolet OMNIC.  
cDCIE\_hiresIR.CSV " " " " " " " " " " Excel readable.  
cDCIE\_parR.SPA Raman spectrum with parallel polarization. Nicolet OMNIC.  
cDCIE\_parR.CSV " " " " " " " " " " Excel readable.  
cDCIE\_perpR.SPA Raman spectrum with perpendicular polarization. Nicolet OMNIC.  
cDCIE\_perpR.CSV " " " " " " " " " " Excel readable.

### tDCIE Folder

tDCIE\_IR.SPA IR spectrum at 0.5 cm<sup>-1</sup> resolution as in Fig. 5. Nicolet OMNIC.  
tDCIE\_IR.CSV " " " " " " " " " " Excel readable.  
tDCIE\_hiresIR.SPA IR spectrum at 0.1 cm<sup>-1</sup> resolution. Nicolet OMNIC.  
tDCIE\_hiresIR.CSV " " " " " " " " " " Excel readable.

tDCIE\_parR.SPA Raman spectrum with parallel polarization. Nicolet OMNIC.  
tDCIE\_parR.CSV " " " " " . Excel readable.  
tDCIE\_perpR.SPA Raman spectrum with perpendicular polarization. Nicolet OMNIC.  
tDCIE\_perpR.CSV " " " " " . Excel readable.  
tDCIEfarIR.SPA Far-IR spectrum at 1 cm<sup>-1</sup> resolution, Fig. 5. Nicolet OMNIC.  
tDCIEfarIR.CSV Far-IR spectrum at 1 cm<sup>-1</sup> resolution, Fig. 5. Excel readable.