

Applications of Group Theory: Infrared and Raman Spectra of the Isomers of 1,2-Dichloroethylene

A Physical Chemistry Experiment

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Undergraduates may learn some group theory in physical or inorganic chemistry courses. Yet, they rarely encounter applications of group theory in the laboratory and thereby have the opportunity to consolidate what they have learned. A study of the vibrational spectroscopy of the *cis* and *trans* isomers of 1,2-dichloroethylene provides a good opportunity to do so. An investigation of this pair of molecules permits assigning all of the vibrational fundamentals and thereby lets students see that there is much more to vibrational spectroscopy than the few group frequencies encountered in a typical organic chemistry course. The necessity of using Raman spectroscopy as well as infrared (IR) spectroscopy in making full vibrational assignments is illustrated. Results of the assignments are compared with frequencies of fundamentals and intensities of infrared bands as computed with density functional theory (DFT). Thus, current practice of comparing quantum chemical calculations with observations is illustrated. This experiment shows, however, that a full command of the standard theory still leaves room for the application of the experimenter's judgment. We developed this experiment for an advanced analytical and physical chemistry laboratory. The experiment is also suitable for a physical chemistry laboratory.

We have described the essentials of Raman spectroscopy in a recent article in this *Journal* and refer the reader to this source (1).

Symmetry and Selection Rules

The different symmetries of the two isomers of 1,2-dichloroethylene (DCIE) illustrate the impact of molecular symmetry on vibrational spectra, and the simple symmetries of these molecules make the analysis of their spectra tractable for undergraduates. The DCIE isomers, which consist of 6 atoms, are shown in Figure 1. Each has $3 \times 6 - 6 = 12$ normal modes of vibration. Three degrees of translational freedom and 3 degrees of rotational freedom have been subtracted from 18 overall degrees of freedom. The *cis* isomer belongs

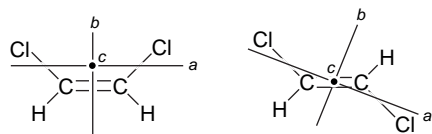


Figure 1. Structures of *cis* and *trans* isomers of 1,2-dichloroethylene and approximate relationships of the principal axes (*a*, *b*, and *c*) of rotation to these structures. The *c* axis is perpendicular to the plane of the molecule.

to the C_{2v} point group, which consists of four symmetry operations: identity (E), 2-fold rotation axis (C_2), reflection through the plane of the molecule (σ), and reflection through the plane that includes the C_2 axis but lies perpendicular to the plane of the molecule (σ'). The *trans* isomer belongs to the C_{2h} symmetry group, which consists of four symmetry operations: identity (E), 2-fold rotation (C_2), reflection through the plane of the molecule (σ_h), and inversion through the center of symmetry (i).

Texts on chemical applications of group theory, such as Cotton's book (2), show how to use symmetry theory and character tables to derive the selection rules for vibrational spectroscopy. In addition, these texts explain the naming of symmetry species. An earlier publication in this *Journal* describes useful models and a good strategy for introducing students to point groups in relation to molecular structure (3). This reference also shows how to help students distinguish symmetry operations from symmetry elements.

The selection rules for *cis*-DCIE, organized by the four symmetry species, a_1 , a_2 , b_1 , and b_2 are given in Table 1. The results for *trans*-DCIE, organized by the four symmetry species, a_g , a_u , b_g , and b_u given in Table 2. The last two columns of these tables give, respectively, approximate descriptions of the various normal modes and rough estimates of frequencies.

In the next few paragraphs we develop the various aspects of the selection rules given in Tables 1 and 2. However, we see already that the two sets of selection rule specifications differ uniquely for the suite of symmetry species for each isomer and thus provide a basis for assigning all 12 vibrational fundamental frequencies to spectral features for each isomer. In particular, we observe that some symmetry species are active in only one of the two types of vibrational spectroscopy. For the *trans* isomer, which has a center of symmetry, there is mutual exclusion between the IR and Raman spectra. Thus, those modes that are active in the IR spectrum are inactive in the Raman spectrum and vice versa.

Polarization in Raman Spectra

One aspect of the selection rules in Tables 1 and 2 is the polarized (pol), depolarized (dpol) specification with respect to bands in Raman spectra observed for the liquid phase. Lasers produce polarized light, typically polarized in the vertical plane.² When light scattered by a sample is observed at 90° to the direction of the laser beam with a polarization analyzer, two outcomes are observed. If the sense of the polarization analyzer is parallel to the polarization of the laser beam, a spectrum ($I_{||}$) is observed with maximum intensity in its bands. If the sense of the polarization analyzer is per-

Table 1. Selection Rules for Vibrational Fundamentals of *cis*-1,2-Dichloroethylene

Sym Species	Raman ^a Activity	IR ^b Activity	Approx. Normal Coord. ^c	Frequency ^d /cm ⁻¹
a_1	pol	B-type	ν_1 sym CH str	3100
			ν_2 C=C str	1600
			ν_3 sym CH bend	1400
			ν_4 sym CCl str	600
			ν_5 sym CCl bend	200
a_2	dpol	ia	ν_6 sym (C_2) CH flap ^e	900
			ν_7 ClC=CCl torsion	400
b_1	dpol	A-type	ν_8 asym CH str	3100
			ν_9 asym CH bend	1400
			ν_{10} asym CCl str	600
			ν_{11} asym CCl bend	400
b_2	dpol	C-type	ν_{12} asym (C_2) CH flap ^e	600

^aPol is polarized and dpol is depolarized.

^bA, B, C refer to band shapes in gas-phase infrared spectra and ia is inactive.

^cApproximate normal coordinates expressed in terms of the principal symmetry coordinate: sym is symmetric and asym is antisymmetric.

^dFrequency is an estimate.

^eSym (C_2) and asym (C_2) are symmetric or antisymmetric with respect to C_2 rotation.

pendicular to the polarization of the laser, a spectrum (I_{\perp}) is observed with reduced intensities. The ratio of intensities, I_{\perp}/I_{\parallel} , for individual bands is called the depolarization ratio, ρ . For bands associated with totally symmetric (TS) vibrational modes, ones in which the vibrating molecule retains the full symmetry of the undistorted molecule, $\rho \leq 0.75$. For all the other, nontotally symmetric modes (NTS), $\rho = 0.75$.

In principle, from depolarization ratios of Raman bands, we have a way to distinguish TS modes from NTS modes. The experimental distinction is, however, not so certain. An NTS mode must have $\rho = 0.75$, but a TS mode can also have a ρ close to 0.75. Because the measurement of depolarization ratios is typically not precise owing to optical imperfections, a ρ of about 0.75 is not definitive for distinguishing between TS and NTS modes. A $\rho \leq 0.65$ is, however, strong evidence for a TS mode, and NTS modes must have an experimental ρ of about 0.75. In the selection rules in Tables 1 and 2, TS modes are labeled as polarized (pol) for bands with $\rho \leq 0.75$. NTS modes are labeled as depolarized (dpol) for bands with $\rho = 0.75$. Not only are most bands due to TS modes expected to be polarized to an observable extent, but most bands due to TS modes generally have good intensities for parallel polarization.

Shapes of Gas-Phase IR Bands

Like depolarization ratios in liquid-phase Raman spectra, shapes of gas-phase IR bands are useful guides to vibrational assignments. The shapes of bands are a consequence of the blending together of a vast manifold of quantized rotational transitions accompanying a vibrational transition at

Table 2. Selection Rules for Vibrational Fundamentals of *trans*-1,2-Dichloroethylene

Sym Species	Raman ^a Activity	IR ^b Activity	Approx. Normal Coord. ^c	Frequency ^d /cm ⁻¹
a_g	pol	ia	ν_1 sym CH str	3100
			ν_2 C=C str	1600
			ν_3 sym CH bend	1400
			ν_4 sym CCl str	600
			ν_5 sym CCl bend	300
a_u	ia	C-type	ν_6 sym (C_2) CH flap ^e	900
			ν_7 ClC=CCl torsion	200
b_g	dpol	ia	ν_8 asym (C_2) CH flap ^e	600
b_u	ia	A/B-type	ν_9 asym CH str	3100
			ν_{10} asym CH bend	1400
			ν_{11} asym CCl str	600
			ν_{12} asym CCl bend	200

^aPol is polarized and dpol is depolarized.

^bA, B, C refer to band shapes in gas-phase infrared spectra and ia is inactive.

^cApproximate normal coordinates expressed in terms of the principal symmetry coordinate: sym is symmetric and asym is antisymmetric.

^dFrequency is an estimate.

^eSym (C_2) and asym (C_2) are symmetric or antisymmetric with respect to C_2 rotation.

room temperature. For the most part detailed rotational structure is not distinguished unless the resolution is at least 0.5 cm^{-1} and the molecule has at least one rather small moment of inertia. Thus, the band shapes refer to the blended structure of the band. Bands may have A-type, B-type, or C-type shapes, depending on the relationship between the direction of change of the dipole moment and the direction of the principal axes of rotation of the molecule (4).

The directions of the principal rotation axes of *cis* and *trans* DCIE are shown in Figure 1. The axes, which are labelled a , b , and c , pass through the center of mass and give cross-products of inertia equal to zero, that is, $\sum m_i a_i b_i = 0$, et cetera. For both molecules under consideration, the c axis is perpendicular to the plane of the molecule. By convention, the rotational constants, which are inversely proportional to the moments of inertia, have the relationship $A \geq B \geq C$. An A-type band is a consequence of the dipole moment change occurring along the a rotation axis. A B-type band is a consequence of the dipole moment change occurring along the b axis. A C-type band is a consequence of the dipole moment change occurring along the c axis. The corresponding band shapes are shown in Figure 2. From high frequency to low frequency, an IR band has features labelled as R, Q, and P branches. The Q branch lies at the band center. An A-type band has comparable intensities for the R, Q, and P branches. A B-type band has a gap in the center and thus appears to have no Q branch.³ A C-type band has a dominant Q branch. For more discussion of band shapes, which depend on different selection rules for rotational transitions for oscillating dipole vectors pointing along the a , b , or c axes, see Herzberg (4) or Hollas (5).

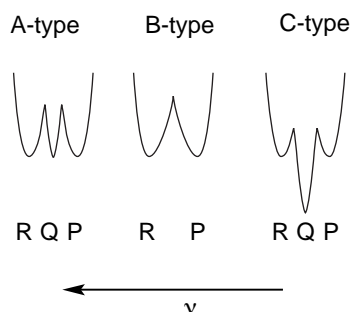


Figure 2. Sketches of A-type, B-type, and C-type band shapes for the gas-phase infrared spectrum.

The predictions of the band shapes of IR gas-phase bands for *cis*- and *trans*-DCIE are considered. Because of its favorable symmetry, normal vibrations of *cis*-DCIE have dipole moment changes occurring exclusively along the *a*, *b*, or *c* axis. The *b* dipole moment vector is totally symmetric in the C_{2v} group and thus belongs to the a_1 symmetry species. The *a* dipole moment vector is antisymmetric with respect to the C_2 and σ' operations and thus belongs to b_1 symmetry species. The *c* dipole moment vector is antisymmetric with respect to the C_2 and σ operations and thus belongs to the b_2 symmetry species. Thus, the band shapes for *cis*-DCIE are expected to be cleanly B-type for modes of the a_1 species, A-type for modes of the b_1 symmetry species, and C-type for the mode of the b_2 symmetry species, as specified in Table 1 and depicted in Figure 2.

The predictions for the *trans* isomer, which has C_{2h} symmetry, are less definitive. For the modes of the a_u symmetry species, which are antisymmetric with respect to the σ_h and *i* operations and for which the dipole moment change occurs along the *c* axis, the bands are expected to be simply C-type in shape. Bands for the modes of the b_u symmetry species will, in principle, have dipole components along both the *a* and *b* axes and thus be hybrid sums of A-type and B-type bands. These hybrids may range from nearly A-type to nearly B-type bands.

If one of the moments of inertia is not too large, another indicator of band type appears in spectra with moderate resolution of 0.5 to 0.1 cm^{-1} . This additional indicator is a series of equally-spaced spines, which are the separate *Q* branches of subbands that make up the overall band. Such structure is expected at moderate resolution for B-type and C-type bands but not for A-type bands. This structure is especially evident in the bands of the *trans* isomer because its I_a moment of inertia is quite small. The expected band shapes for the gas-phase IR spectrum of the *trans* isomer are summarized in Table 2.

Normal Modes

The entries in Tables 1 and 2 remaining to be discussed are the approximate descriptions of normal modes, which are given in the next-to-last column, and the estimates of frequencies, which are given in the last column. The descriptions are in terms of the symmetry coordinate that is the

largest contributor to a particular normal mode.⁴ These descriptions are listed within each symmetry species in descending order of the expected “group” frequency within each symmetry species. In considering the various descriptions and frequencies, we keep in mind several relationships. For diatomic molecules the relationship between the force constant *k*, roughly speaking the bond strength, and the mass of the vibrating atoms is given by,

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where $\tilde{\nu}$ is the wavenumber value in cm^{-1} , often loosely called frequency, *c* is the speed of light, and μ is the reduced mass, $m_1 m_2 / (m_1 + m_2)$. Thus, a vibration frequency for a given bond type increases with an increase in bond strength and increases with a decrease in the reduced mass, for which the lightest mass makes the more important contribution. The expression for vibration frequency can be generalized to a dependence on geometric factors as well as masses and force constants with the use of **F** and **G** matrices of Wilson (2, 6).

The considerations about group frequencies are applied to the DCIE isomers. The stretching modes involving light hydrogen atoms will have the highest frequencies. Because the CH bonds in ethylenes involve sp^2 hybridization for the carbon atoms, the CH bonds are stronger than in saturated hydrocarbons and thus have higher frequencies, typically well above 3000 cm^{-1} . The strength of CC double bonds gives C=C stretching modes relatively high frequencies despite the heavier atoms involved in their vibration. As with macroscopic springs, the bending of bonds is easier than their stretching. Bending frequencies are therefore lower and typically about 1/2 the value of corresponding stretching frequencies. Thus, the bending modes for CH bonds come next in the descending order. Out-of-plane bending of bonds is typically easier than in-plane bending because atoms do not bump in out-of-plane modes. Thus, out-of-plane CH bending for a planar molecule is at a somewhat lower frequency than in-plane CH bending. Because of the relatively weak CCl bond and the added mass of chlorine atoms, frequencies for CCl stretching are low. In-plane and out-of-plane CCl bending modes have yet lower frequencies. Much accumulated experience with vibrational spectra supports the rough ordering of frequencies for the normal modes and gives the estimates for the frequencies, which are in the last column of Tables 1 and 2 (7).

Vibrational Spectra

The gas-phase IR spectrum and the liquid-phase Raman spectrum of the *trans* isomer are shown in Figure 3. The corresponding spectra for the *cis* isomer, which contained about 10% of the *trans* isomer as an impurity, are shown in Figure 4. The IR spectra, which are in transmittance mode, were recorded on a Nicolet 760 Magna FT spectrometer at 0.5- cm^{-1} resolution. The gaseous samples were 15 torr in a 10-cm cell equipped with potassium bromide windows. For the background and for the sample, 64 scans were accumulated. Sharp lines in the spectra are due to incompletely compensated atmospheric lines from water vapor in the 1900–1300-

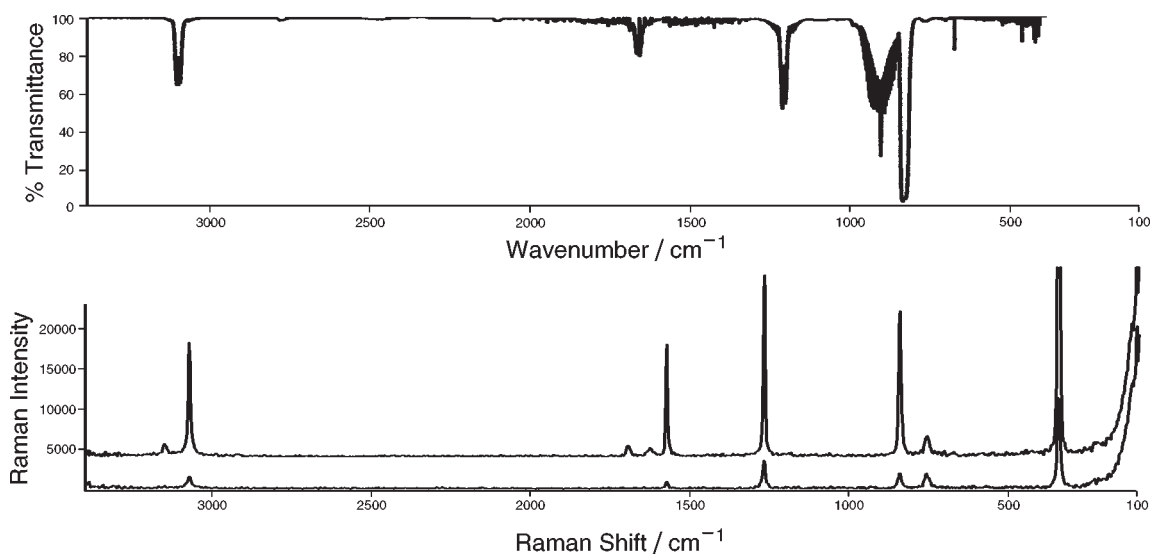


Figure 3. Infrared and Raman spectra of *trans*-1,2-dichloroethylene: (top) gas-phase infrared spectrum at 15 torr and (bottom) stronger polarized and weaker depolarized Raman spectra of the liquid phase.

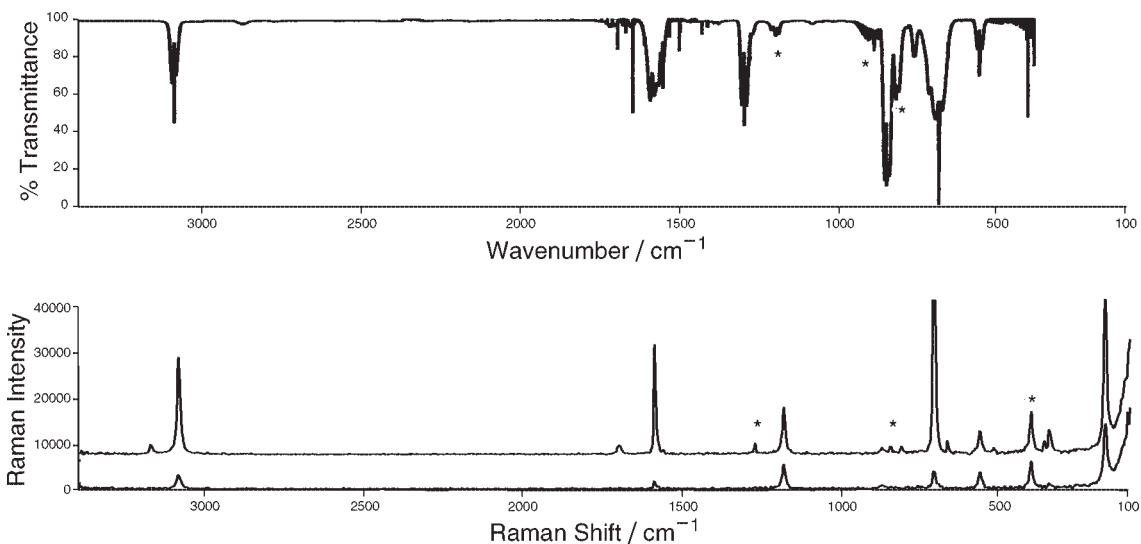


Figure 4. Infrared and Raman spectra of *cis*-1,2-dichloroethylene: (top) gas-phase infrared spectrum at 15 torr above and (bottom) stronger polarized and weaker depolarized Raman spectra of the liquid phase. Asterisks designate bands due to the *trans* impurity. The narrow band at 775 cm^{-1} in the IR spectrum is due to an unknown impurity.

cm^{-1} region, from CO_2 at 667 cm^{-1} , and from water vapor and spectrometer end effects below 600 cm^{-1} . Two recordings of the Raman spectrum are shown in the same figures. The higher intensity trace is for the parallel setting of the polarization analyzer; the lower intensity trace is for the perpendicular setting of the polarization analyzer. These FT-Raman spectra were recorded with a Nicolet Raman accessory associated with the 760 Magna spectrometer. The exciting light was from a Nd:YVO₄ laser at 1064 nm in the near IR, and the sample geometry was 90° optics. 1000 scans were accumulated at 4- cm^{-1} resolution with a liquid-nitrogen-cooled germanium detector for each setting of the polarization analyzer.⁵ A white light correction was applied.⁶ Liquid

samples of commercial material held in 5-mm Pyrex NMR tubes were used for the Raman spectra. The Raman effect is too weak to permit routine recording of gas-phase spectra. The far-IR spectrum of the *trans* isomer at a pressure of about 130 torr is shown in Figure 5. This spectrum was recorded in 10-cm cell equipped with cesium iodide windows on a Perkin-Elmer 1700X FT spectrometer at a resolution of 1.0 cm^{-1} . The far-IR spectrum of the *cis* isomer was also examined at 91 torr in a 10-cm cell equipped with polyethylene windows. A hint of a band was seen at 169 cm^{-1} . See the Supplemental Material^W for more details on sample handling.

It should be possible for students to record the mid-IR spectra of gas-phase samples. The two isomers of dichloro-

Table 3. Assignment of Vibrational Fundamentals for *trans*-1,2-Dichloroethylene and Comparison with Calculated Frequencies

Sym	Vib	Raman ^a Liquid	IR ^b Gas	Obs ^c Freq/ cm ⁻¹	Calc Freq/ cm ⁻¹	Calc IR Intens/ (km mol ⁻¹)
a _g	ν ₁	pol, s	ia	3072	3240	0
	ν ₂	pol, s	ia	1578	1645	0
	ν ₃	pol, vs	ia	1272	1303	0
	ν ₄	pol, s	ia	847	842	0
	ν ₅	pol, vs	ia	350	348	0
a _u	ν ₆	ia	C, s	898 ^d	937	51
	ν ₇	ia	?, w	247 ^d	241	0.21
b _g	ν ₈	dpol, m	ia	763	808	0
b _u	ν ₉	ia	A, m	3096	3238	14.3
	ν ₁₀	ia	B, m	1200 ^d	1225	16.8
	ν ₁₁	ia	A, vs	829	804	136.2
	ν ₁₂	ia	?, m	226	222	3.1

^aPol is polarized and dpol is depolarized. Intensities: vs is very strong, s is strong, m is medium, w is weak, vw is very weak, and ia is inactive.

^bBand shapes: A, B, C. For intensities see footnote a.

^cObserved frequencies are gas-phase values where available.

^dQ-branch rotational spacing seen.

Table 4. Assignment of Vibrational Fundamentals for *cis*-1,2-Dichloroethylene and Comparison with Calculated Frequencies

Sym	Vib	Raman ^a Liquid	IR ^b Gas	Obs ^c Freq/ cm ⁻¹	Calc Freq/ cm ⁻¹	Calc IR Intens/ (km mol ⁻¹)
a ₁	ν ₁	pol, s	—	3080	3228	0.41
	ν ₂	pol, s	B, s	1593 ^d	1652	36.5
	ν ₃	pol, m	—	1182	1207	0.04
	ν ₄	pol, vs	B?, m	721 ^d	709	22.9
	ν ₅	pol, s	—	175	170	0.32
a ₂	ν ₆	dpol, w	ia	875	914	0
	ν ₇	dpol, m	ia	407	426	0
b ₁	ν ₈	—	A, m	3088	3207	15.2
	ν ₉	—	A, s	1305	1315	27.1
	ν ₁₀	dpol, vw	A, vs	858	847	82.1
	ν ₁₁	dpol, w	A, m	571	570	7.4
b ₂	ν ₁₂	—	C, s	696 ^d	726	48.3

^aPol is polarized and dpol is depolarized. Intensities: vs is very strong, s is strong, m is medium, w is weak, vw is very weak, and ia is inactive.

^bBand shapes: A, B, C. For intensities see footnote a.

^cObserved frequencies are gas-phase values where available.

^dQ-branch rotational spacing seen.

ethylene are commercially available. Most physical chemistry laboratories will have access to an IR spectrometer with reasonable resolution of at least 0.5 cm⁻¹ in the mid-IR range and a vacuum system for handling the samples. Spectrometers equipped with far-IR optics are rarer. If a Raman spectrometer is available, the Raman spectra are readily recorded with liquid samples. Optics for making polarization measurements are desirable. Various Raman spectrometers are useful for this experiment. In the initial version of the experiment, we used a Spex Ramalog 5 system with a dispersive double monochromator and excitation with the green 514.5-nm line of a Coherent Innova 70 argon-ion laser. Of course, the Raman spectra and the far-IR spectra reported here may be used as needed. See the Supplemental Material¹⁰ for computer files of all the spectra, including IR spectra recorded with 0.1-cm⁻¹ resolution.

Applying the Selection Rules to the Spectra

The selection rules summarized in Tables 1 and 2 are applied to the infrared and Raman spectra of the two isomers of DCIE. Some immediate characteristics of the selection rules in Tables 1 and 2 are observed in the spectra in Figures 3 and 4. Examples of A-, B-, and C-type bands are found in the gas-phase IR spectra. Examples of polarized bands ($\rho \leq 0.65$) are present in the Raman spectra as well as examples of seemingly depolarized bands ($\rho = 0.75$). In the spectra for the *trans* isomer, we find evidence of mutual exclusion between bands in the IR and Raman spectra. Interactions between neighboring molecules in the liquid phase affect frequencies. Thus, there are differences in frequency, usually small, between bands observed in the gas phase and

in the liquid phase. In addition to observable bands due to transitions of vibrational fundamentals, which are single quantum changes from the ground state, the spectra contain generally weaker bands due to combination tones, that is, transitions in which two quantum numbers change. We will disregard such bands in this experiment.

Results of the assignment of vibrational fundamentals are summarized in Tables 3 and 4. Where available, gas-phase frequencies are chosen because they are characteristic of individual molecules. The observed frequencies and intensities are compared with frequencies and infrared intensities calculated by the hybrid DFT method with a CC-PVTZ(-F) (triple zeta) basis set. The calculations were done with Titan software.⁷ Calculations with simpler basis sets would also be useful for this experiment. In making comparisons of the ob-

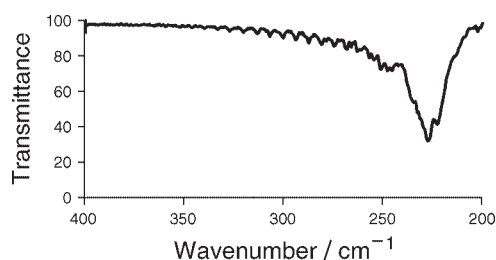


Figure 5. Far-IR spectrum of *trans*-1,2-dichloroethylene in the gas phase; pressure of ~130 torr. The extensive Q-branch structure is consistent with B-type and C-type bands.

served and calculated frequencies, one expects most of the calculated frequencies to be larger than the observed ones and corrections of the calculated frequencies to be approximately proportional to the magnitude of the frequency. Scaling factors that adjust for this deficiency can be found, for example, in the study of Scott and Radom (8).

Because some allowed bands have low intensities and because strong bands may overlap weaker bands, some expected features are missing. In addition, although the selection rules tell what bands are allowed, the rules do not give magnitudes of the intensities. Thus, we shall find that some allowed bands are too weak to observe in the IR or Raman spectrum. These omissions are indicated in Table 4 with dashes. Observed intensities are designated qualitatively with the abbreviations w, weak; m, medium; s, strong; and vs, very strong. Calculated absolute intensities for IR transitions are in units of km mol^{-1} and are proportional to absorbance. IR spectra in Figures 3, 4, and 5 are in percent transmittance, $100I/I_0$, whereas absorbance is $A = -\log(I/I_0)$. Observed intensities in absorbance should be comparable relatively to the calculated intensities.

Some bands in the IR spectra have Q-branch splittings of $1\text{--}2\text{ cm}^{-1}$ caused by chlorine isotope effects. The samples contain $(3/4)^2 = 9/16$ parts of $^{35}\text{Cl}_2$, $2(3/4)(1/4) = 6/16$ parts of $^{35}\text{Cl}^{37}\text{Cl}$, and $(1/4)^2 = 1/16$ parts of $^{37}\text{Cl}_2$. The highest frequency and intensity in the Q-branches is for the $^{35}\text{Cl}_2$ species.

Trans Isomer

The spectra of the trans isomer are considered first because it is a contaminant in the commercial sample used for the spectra of the cis isomer. The assignment for the trans isomer is given in Table 3. Mutual exclusion of vibrational bands between the Raman and IR spectra is generally helpful in making this assignment. Bands for the six Raman-active fundamentals are easily found in the spectrum, and only one band, the weaker one, is depolarized. In contrast, only five bands of good intensity are found in the combined IR spectra of Figures 3 and 5. The band of reasonable intensity at about 1600 cm^{-1} in the IR spectrum cannot be due to the C=C stretching mode because absorption by this fundamental is not allowed in the IR spectrum. This band is due to a combination tone.

The challenge in completing the assignment for the trans isomer is deciding on the sixth IR-active fundamental. In Figure 5 only one band is found for certain in the low-frequency, far-IR region. Yet, two bands were predicted in this region, as summarized in Table 2. The band in Figure 5 does not have the predicted A, B, or C shape shown in Figure 2, but the band does have spines of subband Q branches on the high-frequency side. There is little choice but to assign two fundamentals as largely overlapped in the 230-cm^{-1} region.⁸ Consideration of the predicted intensities in Table 3 shows that the band for the b_u mode is about 15 times stronger than the band for the a_u mode and thus the intensity for the b_u mode dominates the band. The weaker feature at 247 cm^{-1} is chosen for the a_u mode. Not only are the various predicted frequencies in overall agreement with the observed frequencies but so are the predicted and observed intensities.

Cis Isomer

In assigning vibrational fundamentals of the cis isomer, we must keep in mind bands due to the trans impurity, which are designated with asterisks in Figure 4. Trans impurity bands at 1200 , 898 and 829 cm^{-1} are evident in the IR spectrum; another narrow band due an impurity is at 775 cm^{-1} . Trans impurity bands at 1272 , 847 , and 350 cm^{-1} are seen in the Raman spectrum. Although bands for most of the fundamentals of the cis isomer are allowed in the two types of spectroscopy, three of the ten expected bands, including the one at about 170 cm^{-1} , are missing in the IR spectrum and three of the expected twelve bands are missing in the Raman spectrum. The Raman spectrum is expected to be the better guide for the more intense TS a_1 modes, and the IR spectrum is the better guide for the more intense b_1 modes. The bands for the a_1 modes, which are missing in the IR spectrum, are predicted to have very low intensities. Together the two spectroscopies yield a good assignment for all twelve fundamentals, as summarized in Table 4. Agreement of the predicted frequencies and IR intensities is generally good.

In sum, we see that complete assignments of the vibrational fundamentals for cis and trans DCIE can be made but only with the availability of Raman as well as IR spectra. The application of selection rules derived with the aid of symmetry theory, band shapes in the gas-phase IR spectrum, and polarizations in the liquid-phase Raman spectrum are crucial in making these assignments. Calculated frequencies and intensities from the DFT method, as given in Tables 3 and 4, are in good agreement with the observations.

Related Studies

Convincing experimental evidence for the characterizations of the normal modes with symmetry coordinates comes from studies of isotopomers. Normal modes rich in CH motion will shift down in frequency by a factor about $1/\sqrt{2}$ when deuterium is substituted. Bernstein and Ramsay investigated the d_2 species of the cis and trans isomers of DCIE (9), and Bernstein and Pullin investigated the d_1 species (10). Their data can be analyzed with theory similar to that used in the present discussion with the proviso that the two d_1 isotopic species have lower, C_s , symmetry and thus all of the normal modes are, in principle, active in the two types of vibrational spectroscopy. In his critical evaluation of the vibrational assignments of a large number of small molecules, Shimanouchi has summarized the assignments for the two isomers of DCIE and the two deuterium isotopomers (11). However, we note that the frequencies quoted in the present paper for the d_0 species differ some from those in Shimanouchi's table and are more accurate owing to use of modern instrumentation.

An investigation of the vibrational spectra of the cis and trans isomers of 1,2-difluoroethylene and their d_1 and d_2 isotopomers has been reported (12). The analysis of the vibrational spectra for these two species is similar to that for the isomers of DCIE and in some ways simpler because of less ambiguous spectra. Rotational structure for a C-type band in the gas-phase IR spectrum of *trans*-1,2-difluoroethylene, similar to that seen in the 898-cm^{-1} band of *trans*-DCIE, has been analyzed to give $A - (B + C)/2$ (12). A similar exercise

could be done for the C-type band in *trans*-DCIE. Because the difluoroethylenes are gases at room temperature and not commercially available, they are not suited to an experiment for an undergraduate laboratory. Consideration of the literature data for the difluoroethylenes, including the recently reported spectra for the $^{13}\text{C}_2$ species (13), makes a good extension of the experiment described here.

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 and properly disposed of. The quantities 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. The low-power, helium–neon lasers used to track the moving mirror in the interferometer are commonplace and relatively safe. On the other hand, the near-IR laser used to excite the Raman spectrum is dangerous, because of its power level and because it is not visible to the human eye. The Nicolet instrument has a safety interlock to block the laser beam whenever the sample compartment is open.

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^WSupplemental Material

Details on sample handling and spectra used in the experiment are available in this issue of *JCE Online*.

Notes

1. Two conventions are used for defining the b_1 and b_2 symmetry species of the C_{2v} group. We follow the convention in Cotton (2) in which b_1 is chosen for the symmetry species that are symmetric in the molecular plane.

2. To obtain nearly 100% transmission, the windows of a laser are set at the Brewster angle. As a consequence, the accompanying laser beam is polarized in the plane that includes the long axis of the windows.

3. A B-type band has a Q branch. However, the Q branch has two halves that degrade into the R and P branches and thus are often not discerned in low-resolution spectra.

4. Symmetry coordinates are synchronous motions of bonds that have the symmetry characteristic of a particular symmetry spe-

cies. As such, they are linear combinations of internal bond length change or bond angle change coordinates. Symmetry coordinates are as close as we can get to normal coordinates without major numerical analysis. Normal coordinates are linear combinations of symmetry coordinates. Some normal coordinates are principally one symmetry coordinate; others are significant linear combinations of several symmetry coordinates.

5. The liquid-nitrogen-cooled germanium detector gives about three times as much signal as the standard InGaAs detector operated at room temperature.

6. To obtain a Raman spectrum with comparable intensities throughout the spectral range, a white light correction is applied. Thus, a spectrum of a white light source is recorded and used to correct the relative intensities.

7. Titan software is a combination of a Spartan (Wavefunction) graphical user interface (GUI) and a Jaguar (Schrodinger) 3.5 computing engine. Neither the frequencies nor the force constants have been scaled. To obtain infrared intensities in DFT calculations with Titan the numerical derivative option is required. In duplicate calculations of frequencies, frequencies differ by up to 10 cm^{-1} . Tighter convergence limits for the energy minimization improve reproducibility but greatly increase the length of time for the calculations.

8. The distorted band shape and the wide spacing of the Q-branch structure (≈ 2 times that for the C-type band at 898 cm^{-1}) imply a strong Coriolis coupling between ν_7 and ν_{12} (12). The coupling probably transfers some intensity from ν_{12} to ν_7 . A high-resolution investigation of this band is yet to be done.

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