J. Phys. Chem. A **1998,** *102,* 6745−6752

A Complete Structure of *trans*-1,2-Dichloroethylene from High-Resolution Infrared Spectroscopy

Norman C. Craig,* Rebecca A. Appleman, Helen E. Barnes, Emilio Morales, and Jason A. Smith

Department of Chemistry, Oberlin College, Oberlin, Ohio 44074

Stefan Klee, Michael Lock, and Georg C. Mellau

Physikalisch-Chemisches-Institut der Justus-Liebig-Universität, D-35392 Giessen, Germany

Received: April 3, 1998; In Final Form: June 15, 1998

The rotational structure in the C-type bands of the high-resolution (0.002 cm^{-1}), gas-phase infrared spectra of four isotopomers of *trans*-1,2-dichloroethylene has been analyzed. The C-type band, which is due to CH or CD out-of-plane flapping, is at 897.949 82 (3) cm^{-1} for the normal species with $^{35}Cl_2$. For the $^{35}Cl_2$ variants, the ground-state rotational constants in cm^{-1} are $A = 1.747\,268$ (3), $B = 0.051\,570\,5$ (3), and $C = 0.050\,080\,7$ (3) for the normal species; $A = 1.677\,033$ (2), $B = 0.051\,501\,0$ (2), and $C = 0.049\,954\,0$ (2) for the $^{13}C_2$ species; and $A = 1.181\,144\,7$ (9), $B = 0.051\,540\,7$ (2), and $C = 0.049\,371\,9$ (2) for the d_2 species. For the d_2-$^{35}Cl^{37}Cl$ isotopomer, $A = 1.180\,765$ (2), $B = 0.050\,164\,9$ (3), and $C = 0.048\,107\,5$ (3) cm^{-1}. A substitution structure (r_s) was fit and found to have $r_{CH} = 1.078$ (4) Å, $r_{CC} = 1.305$ (5) Å, $r_{CCl} = 1.740$ (3) Å, $\alpha_{CCH} = 125.3$ (5) Å, and $\alpha_{CCl} = 119.9$ (4) Å. Structural adjustments in going from the lower energy cis isomer to the higher energy trans isomer are discussed in the context of current qualitative theories of the cis effect.

Introduction

cis-1,2-Dichloroethylene (cDCLE) has a lower electronic energy than its trans isomer (tDCLE).[1,2] This seemingly anomalous energy relationship is an example of what has been called the cis effect. This effect is observed in a diazene and several ethylenes with highly electronegative substituents. It is most pronounced for the 1,2-difluorodiazenes (FN=NF)[2,3] and is also evident for the 1,2-difluoroethylenes, 1-chloro-2-fluoroethylenes, and the 1,2-dimethoxyethylenes.[2,4] A number of ab initio investigations have been made for the isomers of 1,2-difluoroethylene. One recent study is by Muir and Baker;[5] another is by Engkvist, Karlström and Widmark.[6] Earlier investigations have been summarized.[7] In all of the investigations with high-level theory, the cis effect is encompassed because a lower energy is computed for the cis isomer. To our knowledge, no ab initio study has been made of the dichloro system.

Qualitative arguments for the cis effect have been advanced by a number of workers. The most recent examples are the bent-bond interpretation of Wiberg,[7] a four-center interaction proposal of Engkvist et al.,[6] and the valence bond reasoning of Epiotis.[9] All of these workers have applied these arguments to the difluoro species. Similar reasoning should apply to the dichloro species.

Good geometric parameters for both isomers are needed to assess qualitative explanations of the cis effect and to assess future ab initio calculations. Because it has a dipole moment, the cis isomer has been investigated by microwave spectroscopy, resulting in good structural parameters for this isomer.[10,11] Lacking a dipole moment, the trans isomer is not amenable to microwave investigation. Both isomers have been studied by electron diffraction.[12] An electron diffraction study does not, however, give a good definition of the parameters for the C−H bonds due to weak scattering by the hydrogen atoms.

As part of a wider study of nonpolar, small halocarbons that exhibit the cis effect or the related gauche effect, we have now investigated the structure of tDCLE by high-resolution infrared spectroscopy. Recently, this method has been successfully applied to *trans*-1,2-difluoroethylene[13] and to the anti rotamer of 1,2-difluoroethane.[14] Applying this method to tDCLE was, however, more challenging because of the smaller *B* and *C* rotational constants and because of the significant occurrence of the 37 isotope of chlorine, as well as of the 35 isotope, in natural abundance.

Initially we thought it necessary to develop a synthesis of tDCLE with only ^{35}Cl or ^{37}Cl in the molecule. We worked on such a synthesis and developed a low-yield method for it.[15] Before this method was improved to the practical level, we recorded an exploratory spectrum on a natural sample of tDCLE at a resolution of 0.0022 cm^{-1} on the Bruker IFS 120 HR Fourier transform instrument in Giessen and found that this resolution was sufficient to allow assignment of series due to the $^{35}Cl_2$ species (56%) and to the $^{35}Cl^{37}Cl$ species (38%) in natural abundance. Spectral contributions from the $^{37}Cl_2$ species (6%) were unimportant. Use of the computerized Loomis−Wood technique for finding and assigning series was of great help in working with this complex spectrum.[16]

For a good structural analysis, deuterium and ^{13}C isotopomers were needed. For the deuterium species direct exchange with basic D_2O succeeds without accompanying isomerization.[17,18] To make the ^{13}C species, we learned how to control the addition of chlorine to acetylene-$^{13}C_2$ with low-level, flashlight illumination. The resulting 1,1,2,2-tetrachloroethane was dehalogenated with zinc metal to give a mixture of cDCLE and tDCLE.[10]

S1089-5639(98)01740-X CCC: $15.00

cDCLE and tDCLE and their deuterium isotopomers have been well studied by low-resolution vibrational spectroscopy. Ramsay and Bernstein did a comprehensive study that yielded assignments of most of the vibrational fundamentals.[19,20] Hopper and co-workers followed that study with an investigation of infrared intensities of both isomers.[21] Recently, a higher level analysis of the intensities has been contributed by Bruns and co-workers.[22]

From our initial investigation at 0.5 cm^{-1}, we confirmed that a good candidate in the gas-phase infrared spectrum for the structural study of tDCLE was the C-type band at 898 cm^{-1} in the spectrum of the normal species. This band is due to ν_6, the out-of-plane CH flapping mode, of a_u symmetry. The corresponding bands of the $^{13}C_2$ species and the d_2 species at 896 and 663 cm^{-1}, respectively, also showed promising rotational structure.

Experimental Section

Syntheses. Normal tDCLE was a commercial sample (Aldrich) used without purification. tDCLE-d_2 was prepared by exchange of tDCLE with an NaOD solution. The 2 M NaOD was made by slowly adding sodium metal to D_2O (Aldrich, 99.9% D). Five milliliters of the base solution was injected into a 50-mL, breakseal-equipped, borosilicate-glass reaction bulb, which had been rinsed with D_2O. After twice carefully freezing the D_2O solution and pumping away noncondensables, 10 mmol of degassed tDCLE were condensed into the reaction vessel at liquid-nitrogen temperature, and the tube was flame sealed. The mixture was heated and rocked for 41 h at 80 °C. The tDCLE layer was distilled away at room temperature on the vacuum system and dried by passage through a column packed with P_2O_5. The process was repeated a second time for the partially exchanged sample with a 63-h reaction time. After drying the tDCLE-d_2 product, it was judged from its gas-phase infrared spectrum to be about 99% exchanged.[19] The exchange reaction does not cause isomerization. The sample, obtained in high yield, was used for spectroscopy without further purification.

Exploratory reactions of a 2:1 mixture of gaseous Cl_2 and ordinary acetylene with moderate light levels gave uncontrollable "burn ups." With intermittent flashlight illumination (~2.5 V and 0.35 A) at 70 °C in a darkened room the reaction was, however, controllable. Initial illumination was for 1 min as the flask was rotated vigorously in the warm water bath. The length of illumination was increased by 30-s increments up to 5 min. Then, 15 min of illumination was used, followed by turning on the fluorescent room light. Total reaction time was 1 h.

For the isotope synthesis, 342 Torr (3.1 mmol) of acetylene-$^{13}C_2$ (Cambridge Isotope Laboratories, 99%), which had been dried by distillation through a P_2O_5-packed column, was measured into a 171-mL (nominal 125-mL) flask. Into a 272-mL (nominal 250-mL) flask, 440 Torr (6.3 mmol) of Cl_2 (Matheson), which had been dried by distillation through the P_2O_5 column, was measured and then condensed in the tube on the bottom of the flask. This flask also contained several short lengths of Teflon tubing for use as mixers. The acetylene was then condensed as a separate, higher band. The reaction flask with the reactants still frozen at liquid nitrogen temperature was carried into a darkened room and permitted to warm to room temperature in the dark while being continuously shaken. Then, the flask was put into the warm water bath and illuminated with the flashlight, as described above, while being rotated vigorously by hand. Liquid tetrachloroethane condensed on the walls in this high-yield reaction. The yield of crude tetrachloroethane-$^{13}C_2$ from two reaction batches was 1.15 g. Krytox grease was used on all stopcocks and joints that came in contact with Cl_2 gas. The use of dry reagents as well as low light levels may be important in controlling the chlorine-addition reaction.

The 200-MHz proton NMR spectrum of $HCl_2{}^{13}C-{}^{13}CCl_2H$ was an AA′XX′ multiplet.[23] The very same pattern was observed in the ^{13}C spectrum (without proton decoupling). Chemical shifts were $\delta_H = 5.94$ ppm and $\delta_C = 74.03$ ppm. Coupling constants in Hz were $J_{HH} = 3.14$, $J_{CC} = 43.39$, $J_{HC(local)} = 180.86$, and $J_{HC(distant)} = 0.96$.

Dehalogenation was done by dripping a solution of the tetrachloroethane-$^{13}C_2$ in absolute ethanol through a reflux condenser into boiling ethanol containing a 5-fold molar excess of zinc dust. A very slow flow of helium gas carried the DCLE products into a trap cooled with liquid nitrogen. Although the yield of the dehalogenation reaction in the practice run with commercial tetrachloroethane was 67%, the yield from the corresponding reaction with the ^{13}C material was disappointingly low but adequate for the infrared experiments. After removing most of the ethanol by distillation through a P_2O_5-packed column, tDCLE-$^{13}C_2$ was isolated by preparative gas chromatography at 49 °C on a 4-m silicone oil-on-Chromosorb column. After chromatography, the tDCLE-$^{13}C_2$ was dried by distillation again through the P_2O_5 column.

NMR spectra of the ethylenes were recorded only for the mixture of products. Both *cis*- and *trans*-$HCl^{13}C{=}^{13}CClH$ have AA′XX′ spectra, which were the very same pattern for each isomer in the proton and ^{13}C regions. If slightly larger chemical shifts are associated with the trans isomer as is true for the normal species, then for the trans ^{13}C species $\delta_H = 6.40$ ppm, $\delta_C = 120.41$ ppm, $J_{HH} = 5.20$ Hz, $J_{CC} = 84.74$ ppm, $J_{HC(local)} = 197.58$ Hz, and $J_{HC(distant)} = 15.98$ Hz. For the cis ^{13}C isomer, $\delta_H = 6.33$ ppm, $\delta_C = 119.90$ ppm, $J_{HH} = 12.14$ ppm, $J_{CC} = 91.72$ Hz, $J_{HC(local)} = 198.48$ Hz, and $J_{HC(distant)} = 0.76$ Hz. Because $J_{HH(trans)} < J_{HH(cis)}$, contrary to expectation, it is possible that an isotope effect causes a reversal in the order of chemical shifts and leads to incorrect isomer identifications. In addition to the dichloroethylenes, a smaller amount of $Cl_2{}^{13}C{=}^{13}CClH$ was observed in the NMR spectra. The proton spectrum was a doublet of doublets with $\delta_H = 6.44$ ppm, $J_{HC(local)} = 197.5$ Hz, and $J_{HC(distant)} = 12.5$ Hz. The ^{13}C spectrum consisted of two doublets of doublets with $\delta_C = 116.32$ and 123.74 ppm and $J_{CC} = 103.7$ Hz in addition to the same J_{CH} coupling constants observed in the proton spectrum.

Spectroscopy. High-resolution infrared spectra were recorded at room temperature on a Bruker IFS 120 HR spectrometer in Giessen. Particulars of the instrument setup and calibration were as reported before.[24] The multipass White cell was set for 3.28 m for the spectra of the normal species and the $^{13}C_2$ species. For the spectrum of the normal species the resolution was 0.0022 cm^{-1} (1/MOPD), the number of scans was 250, and the pressure was 0.11 Torr to give a pressure × path length value of 0.37 Torr m. Some HCN got into the sample during spectroscopy but did not interfere with the C-type band of interest. For the spectrum of the $^{13}C_2$ species, the resolution was 0.0021 cm^{-1}, the number of scans was 300, and the sample pressure was 0.66 Torr to give 2.17 Torr m. Some $HCN/H^{13}CN$ and some methanol got into the sample during spectroscopy but did not interfere with the C-type band of interest. For the spectrum of the d_2 species the resolution was 0.0020 cm^{-1}, and the sample was studied in a single-pass 3.02-m cell. The number of scans was 300, and the sample pressure

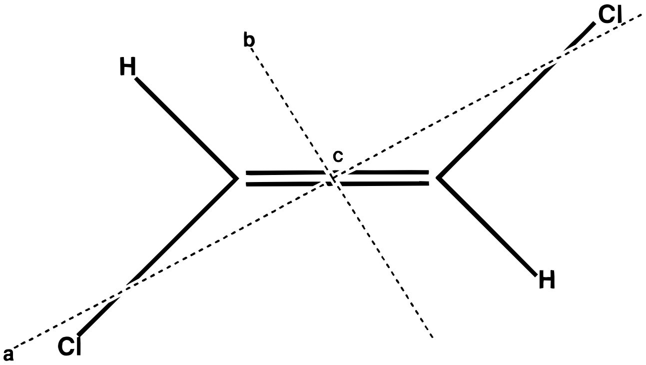


Figure 1. Schematic of the structure of *trans*-1,2-dichloroethylene with locations of principal rotation axes.

was 0.73 Torr to give 2.21 Torr m. Some HCN got into this sample without consequence during spectroscopy.

NMR spectra were recorded on a Bruker AC200 instrument with samples dissolved in $CDCl_3$. Chemical shifts were referenced to external TMS. Infrared spectra at 0.5 cm^{-1} resolution were recorded on a Perkin-Elmer 1760 FT instrument in 10-cm cells with KBr or CsI windows.

A version of Dr. Arthur Maki's ASYMBD program was used to fit ground-state rotational constants to ground-state combination differences (GSCD) and to fit upper state rotational constants to spectral lines. The Giessen Loomis−Wood computer program facilitated assigning $^{R}R_{K}$ and $^{P}P_{K}$ series and processing large data sets when K_c-splitting was not too great.[16]

Results and Discussion

tDCLE-$^{35}Cl_2$ has C_{2h} symmetry. As shown schematically in Figure 1, the *a* axis for the least moment of inertia passes through the center of symmetry and close to the two chlorine atoms. The *b* axis also lies in the plane of the molecule, and the *c* axis is then perpendicular to this plane. This molecule is very nearly a prolate symmetric top with $\kappa = -0.998\ 24$. In the gas-phase infrared spectra, in-plane vibrational modes will lead to hybrid A/B-type bands, and out-of-plane modes will give C-type bands.

C-type bands are a good choice for a structural analysis of tDCLE, because these bands give a good definition of all three rotational constants and are not mixed with an A-type component. Of the six infrared-active fundamentals of tDCLE-$^{35}Cl_2$, two have a_u symmetry. Only one of these modes, ν_6 at 898 cm^{-1}, gives a well-formed C-type band in the gas-phase infrared spectrum. This mode is due to out-of-plane hydrogen flapping. The lower frequency a_u mode near 226 cm^{-1} is involved in very strong Coriolis coupling with ν_{12} (b_u). The outcome for these two modes in the gas phase is a single, distorted band which would be very difficult to analyze. Two other isotopomers, for which ν_6 bands were investigated in this work, tDCLE-$^{13}C_2$-$^{35}Cl_2$ and tDCLE-d_2-$^{35}Cl_2$, also have C_{2h} symmetry. The other three isotopomers investigated here, $^{35}Cl^{37}Cl$ species, have C_s symmetry, but the very small change in isotopic mass has a negligible symmetry consequence for the normal modes.

Along with selection rules, the effect of spin statistics on line intensitites may assist in making assignments of spectral lines. Selection rules for infrared transitions in C-type bands are $\Delta J = 0, \pm 1$; $\Delta K_a = \pm 1$; and $\Delta K_c = 0, \pm 2$. For the centrosymmetric $^{35}Cl_2$ species of the normal form of tDCLE, the intensity ratio due to spin statistics is 28:36 when K_c splitting is apparent.[25] This intensity difference is not, however, large enough to be useful in dense spectra. The ratio is even closer to one in the spectra of the d_2 and $^{13}C_2$ species due to the larger number of nuclear spins being exchanged. The $^{35}Cl^{37}Cl$ species lack a center of symmetry and have no intensity-altering spin statistics. Thus, we made no attempt to use the expected relative intensities in assigning the spectra of tCDLE.

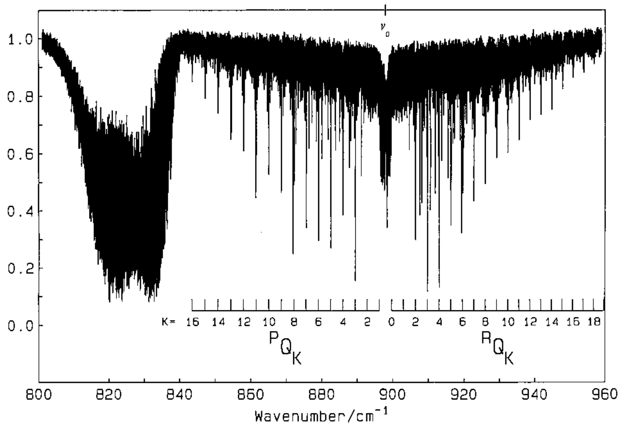


Figure 2. Overall structure of the C-type band of *trans*-1,2-dichloroethylene at 898 cm^{-1} and the intense A/B-band to lower wavenumber. Combs show the K_a'' numbering for the Q branches of the subbands of the C-type band.

The strategy that was used to assign the many subband series in the infrared spectrum of a near-prolate symmetric top molecule has been fully described.[7,13] We give a brief account here. The assignments began in the outer parts of the bands where prolate-symmetric-top theory applies. From GSCDs formed from P-branch ($K_a'' + 2$) and R-branch series (K_a''), ground state (GS) rotational constants were refit as the number of series assigned grew. A Watson-type rotational Hamiltonian was employed in the *A* reduction and the I^r representation as given before.[13] When the splitting of series due to differences in K_c indices became apparent, assignments in the P branch ($K_a'' + 2$) and computed GSCDs helped predict corresponding R-branch series (K_a''), in which the splitting started at lower *J* values. Where feasible, upper state (US) rotational constants were also fit to observed lines and to fixed, but updated GS constants in the growing data set. From the existing GS and US constants, lines in series progressively closer to the center of the band were predicted. These predictions guided assignments in this congested and complicated, band-center region.

Analysis of the C-Type Band near 898 cm^{-1} in the Spectrum of tDCLE-$^{35}Cl_2$. The rotational structure of the C-type band in the gas-phase infrared spectrum of tDCLE-$^{35}Cl_2$ near 898 cm^{-1} was fully analyzed. Figure 2 shows the overall structure of the C-type band and also the intense A/B-band to lower frequency, due largely to the antisymmetric CCl stretching mode. The two combs of the C-type band show the numbering of the Q branches of the subbands in the R and P branches. In the P branch, the $^{P}P_{K}$ series were assigned out to $K_a'' = 16$. Further subband assignments in the P branch were blocked by the wing of the very intense neighboring band. In the R branch, the $^{R}R_{K}$ subband series were assigned from the band center to only $K_a'' = 14$. Higher K_a'' series could have been assigned in the R branch but had no assignable P-branch series with which to form GSCDs. Figure 3 shows, for example, the detailed assignments for the $^{R}R_{11}$ subband. In addition to the full complements of $^{R}R_{K}$ and $^{P}P_{K}$ series, the offside series for subbands with low-K_a values, $^{R}P_2$, $^{R}P_1$, $^{R}P_0$, $^{P}R_1$, $^{P}R_2$, and $^{P}R_3$, were also assigned. Splitting associated with the difference between low-K_c and high-K_c values began at J'' values of about 16 in the $^{R}R_2$ series, of about 41 in the $^{R}R_3$ series, and somewhere above 68 in the $^{R}R_4$ series. Comparable splitting

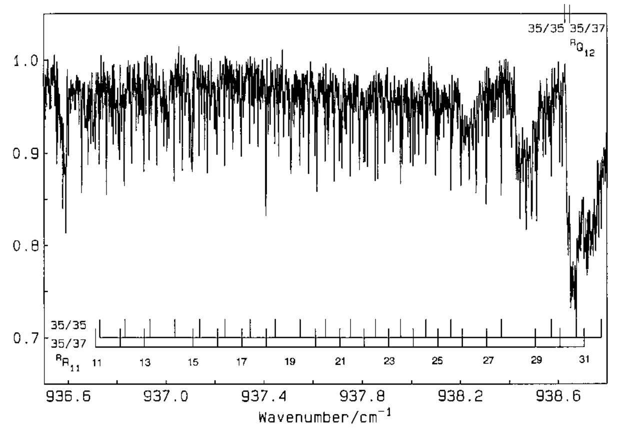


Figure 3. Detail of the assignment of the $^{R}R_{11}$ subband for the $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ species of *trans*-1,2-dichloroethylene.

TABLE 1: Rotational Constants for *trans*-1,2-Dichloroethylene-$^{35}Cl_2$

parameter	ground state[a]	ν_6 vibrational state[a,b]
A	1.747 267 9 (27)	1.737 940 0 (32)
B	0.051 570 46 (28)	0.051 566 215 (49)
C	0.050 080 69 (28)	0.050 110 027 (47)
κ[c]	−0.998 244	−0.998 274
$\Delta_K \times 10^5$	1.9105 (23)	1.8143 (47)
$\Delta_{JK} \times 10^7$	−1.584 (56)	−1.5626 (14)
$\Delta_J \times 10^9$	3.687 (43)	3.7350 (32)
$\delta_K \times 10^7$	−1.28 (45)	0.0
$\delta_J \times 10^{10}$	1.50 (16)	1.547 (47)
$H_K \times 10^{10}$	8.13 (58)	−60.0 (17)
ν_0		897.949 824 (27)
std dev[f]	0.000 485	0.000 492
no. lines fit[d]	1145	1826
max. K_a'	15	4, 10−13[e]

[a] In units of cm^{-1}; uncertainties in last two numbers are given in parentheses. [b] Ground state constants were held fixed while upper state constants were being fitted. [c] Unitless. [d] Number of GSCDs or lines used in the fitting. [e] Perturbed regions from $K_a' = 5-9$ and 14,15 were omitted. [f] std dev = standard deviation.

was found in the respective $^{P}P_3$, $^{P}P_4$, and $^{P}P_5$ series. Six Q branches of subbands were also analyzed, namely, $^{P}Q_3$, $^{P}Q_2$, $^{P}Q_1$, $^{R}Q_0$, $^{R}Q_1$, and $^{R}Q_2$.

Table 1 gives the rotational constants that were fit to 1145 nonredundant GSCDs obtained from the assignment of the entire C-type band. Table 1 also gives the rotational constants that were fit to the US of the ν_6 vibrational mode. Perturbations in the band structure required selective use of the assigned lines. Lines with the K_a' values in the range 5−9 and 14, 15 were omitted from the fitting of US constants. A total of 1826 lines was used in the US fitting. The band center is at 897.94982 cm^{-1}. Table IS (Supporting Information) gives all of the GSCDs used in the GS fitting and the details of this fitting. Table IIS (Supporting Information) gives all of the lines used in the US fitting and the details of this fitting. Table IIIS (Supporting Information) gives the remaining 890 lines that were not used in the US fitting but were used in computing GSCDs.

Partial Assignment of Subbands of the tDCLE-$^{35}Cl^{37}Cl$ Species. Considerable effort was expended in assigning subbands of the $^{35}Cl^{37}Cl$ species. The assignment was, however, left incomplete. Values of $\bar{B}$ for the $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ species differ by 2.6%. For the P- and R-branch subband series, this difference in $\bar{B}$ values is large enough to give decidedly different slopes for series of the two isotopomers in the Loomis−Wood display on the computer screen. This characteristic difference in the series for $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ isotopomers, valid for both normal and d$_2$ species, is depicted, for example, in Figure 4 for the d$_2$ species.

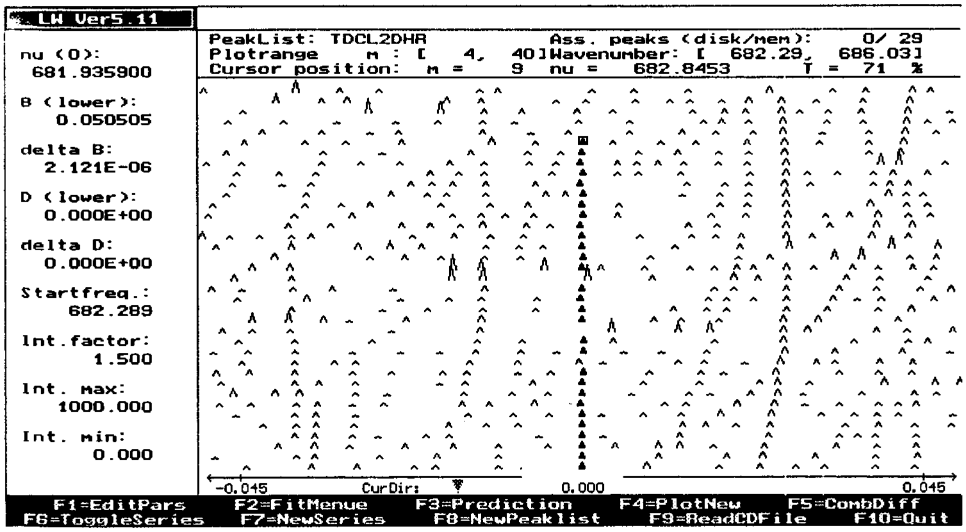
The spacing between Q branches of the subbands is also affected by the ^{37}Cl substitution. The principal term in the spacing of the Q branches is $2(A - \bar{B})$. For the $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ isotopomers, the A values differ by only 0.00066 cm^{-1}. The 2.6% smaller $\bar{B}$ value for the heavier isotopomer means that $2(A - \bar{B})$ is larger for the heavier isotopomer. Thus, the locations of the subband Q branches of the $^{35}Cl^{37}Cl$ species spread out faster with increasing K_a than do the subband Q branches for the $^{35}Cl_2$ species. Even though the isotope shift on the frequency of the vibrational transition is only 0.0129 cm^{-1}, most of the Q branches for the $^{35}Cl^{37}Cl$ species in the P branch can be distinguished because the weaker Q-branch cluster due to the $^{35}Cl^{37}Cl$ species lies at a frequency lower than that of the sharp falloff of the stronger cluster due to the $^{35}Cl_2$ species. In contrast, in the R branch the weaker Q-branch subband clusters due to the $^{35}Cl^{37}Cl$ species are obscurred by the gradual falloff to higher frequency of the stronger subband clusters due to the $^{35}Cl_2$ species.

We were able to make subband assignments from $^{R}R_3$ to $^{R}R_{14}$ and from $^{P}P_5$ to $^{P}P_{16}$, but we were unable to go further into the congested band center. K_c splitting information from the region of the band center is, however, crucial to a good definition of the difference between B and C rotational constants. Fortunately, as described below, the $^{35}Cl^{37}Cl$ subbands were fully assignable in the spectrum of the d$_2$ species.

As obtained from fitting 427 GSCDs and then 641 lines, the approximate band center for the C-type band of the $^{35}Cl^{37}Cl$ isotopomer is 897.963 cm^{-1}. This wavenumber is 0.013 cm^{-1} higher than for the lighter $^{35}Cl_2$ species, an unexpected result based on the Rayleigh rule, which predicts a frequency decrease for this mode with substitution of a heavier isotope.

Analysis of the C-Type Band near 896 cm^{-1} in the Spectrum of tDCLE-$^{13}C_2$-$^{35}Cl_2$. Figure 5 shows the overall structure of the C-type band centered at 896 cm^{-1} in the gas-phase infrared spectrum of the $^{13}C_2{}^{35}Cl_2$ isotopomer of tDCLE. Also seen in this part of the spectrum to lower frequency is the very intense A/B-type band at 805 cm^{-1} due largely to the antisymmetric C−Cl stretching mode. For the C-type band, combs are shown with the K_a'' numbering of the subband Q branches in the overall P and R branches. Because the intense neighboring band in the $^{13}C_2$ species is shifted down 20 cm^{-1} from the value for the normal species, the extent of subband assignments in the P branch is much larger for the $^{13}C_2$ species than for the normal species. $^{P}P_K$ series were assigned from $K_a'' = 1$ to 19. $^{R}R_K$ subband series were assigned from $K_a'' = 0$ to 19. In addition, the offside series $^{R}P_1$, $^{R}P_0$, $^{P}R_1$, and $^{P}R_2$ were assigned. K_c splitting began at J'' of about 15 for $^{R}R_2$, of about 40 for $^{R}R_3$, and of about 70 for $^{R}R_4$ for the $^{13}C_2$ isotopomer which has $\kappa = -0.99810$. These results are consistent with the observations for the normal species, in which K_c splitting starts at lower J values. The $^{13}C_2$ species is slightly closer to being a symmetric top with $\kappa = -0.99824$. Q-branch assignments were made for $^{P}Q_3$, $^{P}Q_2$, $^{P}Q_1$, $^{R}Q_0$, $^{R}Q_1$, and $^{R}Q_2$.

The rotational constants and related parameters for the $^{13}C_2$ isotopomer are given in Table 2. To fit the GS constants, 1307 nonredundant GSCDs were used. These GSCDs ranged from the band center to values computed from $^{R}R_{17}$−$^{P}P_{19}$ lines. Due to perturbations in the band, US state constants were fit to 1678 lines from the center of the band up to only $K_a' = 6$ with the exception of $K_a' = 5$. An additional 1916 lines were assigned with $K_a' = 5$ and $K_a' \geq 7$ values. The band center is at 895.55779 cm^{-1}. Table IVS (Supporting Information) contains



nu (0): 681.935900
B (lower): 0.050505
delta B: 2.121E-06
D (lower): 0.000E+00
delta D: 0.000E+00
Startfreq.: 682.289
Int.factor: 1.500
Int. max: 1000.000
Int. min: 0.000

PeakList: TDCL2DHR Ass. peaks (disk/mem): 0/ 29
Plotrange m : [4, 40]Wavenumber: [682.29, 686.03]
Cursor position: m = 9 nu = 682.8453 T = 71 %

Figure 4. Loomis-Wood computer display for *trans*-1,2-dichloroethylene-d_2 with the $^{R}R_8$ series for the $^{35}Cl_2$ species assigned in the middle of the screen. The two strong series to the right are $^{R}R_7$ and $^{R}R_6$ subbands, respectively. Series with distinctly shallower slopes are from the $^{35}Cl^{37}Cl$ species.

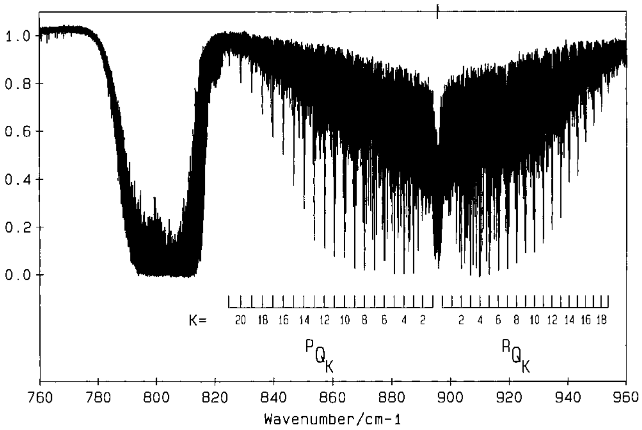


Figure 5. Overall structure of the C-type band of *trans*-1,2-dichloroethylene-$^{13}C_2$ at 896 cm^{-1} and the neighboring A/B-type band. Combs show the K_a'' numbering of the Q branches of the subbands of the C-type band.

TABLE 2: Rotational Constants for *trans*-1,2-Dichloroethylene-$^{13}C_2$-$^{35}Cl_2$

parameter	ground state[a]	ν_6 vibrational state[a,b]
A	1.677 033 2 (16)	1.667 90 (10)
B	0.051 501 00 (20)	0.051 496 103 (34)
C	0.049 953 96 (22)	0.049 983 167 (36)
κ^c	−0.998 098	−0.998 130
$\Delta_K \times 10^5$	1.821 15 (82)	7.569 (90)
$\Delta_{JK} \times 10^7$	−1.5416 (22)	−1.4925 (41)
$\Delta_J \times 10^9$	3.743 (21)	3.7403 (21)
$\delta_K \times 10^8$	8.7 (20)	0.0
$\delta_J \times 10^{10}$	1.770 (68)	1.627 (27)
$H_K \times 10^{10}$	5.48 (13)	16 351 (180)
ν_0		895.557 788 (27)
std dev[f]	0.000 371	0.000 410
no lines fit[d]	1307	1678
max K_a'	19	4, 6[e]

[a] In units of cm^{-1}; uncertainties in last two numbers are given in parentheses. [b] Ground state constants were held fixed while upper state constants were being fitted. [c] Unitless. [d] Number of GSCDs or lines used in the fitting. [e] Perturbation for $K_a' = 5$. [f] std dev = standard deviation.

the GSCDs and the details of fitting the GS constants. Table VS (Supporting Information) has the lines used in fitting the US constants. Table VIS (Supporting Information) has the additional lines that were not used in the upper state fitting but which were used in computing GSCDs.

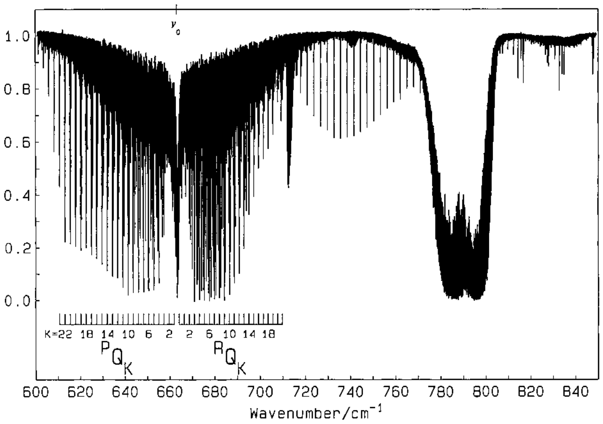


Figure 6. Overall structure of the C-type band of *trans*-1,2-dichloroethylene-d_2 at 663 cm^{-1}. Combs show the K_a'' numbering of the Q branches of the subbands. Also shown to higher wavenumber is the very intense A/B-type band. A band due to impurity HCN is centered at 712 cm^{-1}.

Assignments of subbands in the C-type band due to the $^{35}Cl^{37}Cl$ variant of the $^{13}C_2$ species were also investigated. These assignments were carried from $K_a'' = 2$ to $K_a'' = 15$ in the R branch and from $K_a'' = 3$ to $K_a'' = 17$ in the P branch. $^{R}R_0$ was also assigned. It is likely that the assignment into the band center could be completed, but we settled for the analysis of the lines of the $^{35}Cl^{37}Cl$ variant of the d_2 species as described below. The band center for the $^{35}Cl^{37}Cl$ variant of the $^{13}C_2$ species is 895.5656 cm^{-1}. The change in wavenumber for the heavy isotope substitution is 0.0079 cm^{-1}, which, as for the normal species, is small and in the unexpected direction.

Analysis of the C-Type Band near 663 cm^{-1} in the Spectrum of tDCLE-d_2-$^{35}Cl_2$. Figure 6 shows the overall structure of the C-type band centered at 663 cm^{-1} in the gas-phase infrared spectrum of the d_2 species. Deuterium substitution has caused a significant shift of this band to lower frequency. For the deuterated species the very intense A/B-type band due largely to the antisymmetric C−Cl stretching mode is to higher frequency of the C-type band. In Figure 6, combs display the assignment of K_a'' values to Q branches of subbands in both the P and R branches for the C-type band. In

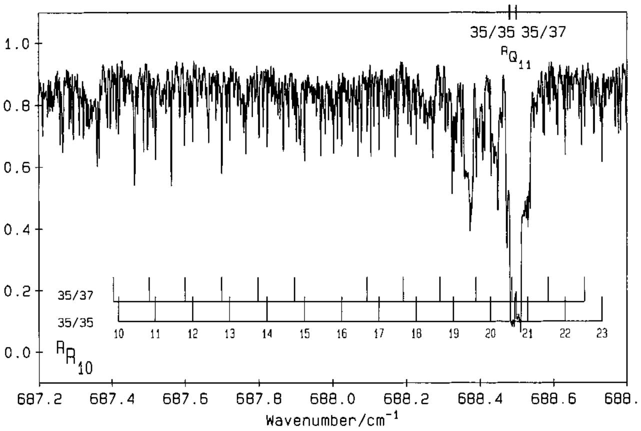


Figure 7. Detail of the assignment of the $^{R}R_{10}$ subband of the C-type band of *trans*-1,2-dichloroethylene-d_2. Series are indexed for both the $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ species.

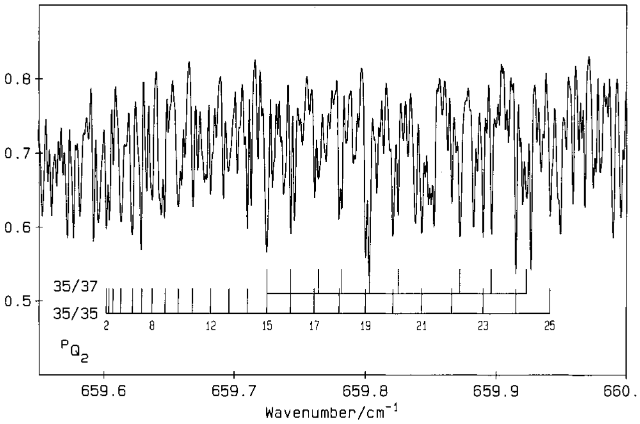


Figure 8. Detail of the assignment of $^{P}Q_2$ lines of the C-type band of *trans*-1,2-dichloroethylene-d_2. High-K_c series are designated for both the $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ species. The lines for the $^{35}Cl^{37}Cl$ species begin with $J'' = 17$, which is blended with $J'' = 15$ for the $^{35}Cl_2$ species.

the R branch, subband series were assigned from $K_a'' = 0$ to $K_a'' = 21$. In the P branch, subband series were assigned from $K_a'' = 1$ to $K_a'' = 23$. Offside series were assigned for $^{P}R_0$ and $^{R}P_1$. K_c splitting began at J'' values of about 10 for $^{R}R_2$, of about 27 for $^{R}R_3$, of about 50 for $^{R}R_4$ and of about 74 for $^{R}R_5$. Comparable onsets of K_c splitting were observed in series in the P branch. The smaller J values for the onset of K_c splitting for the d_2 species compared with the normal species are consistent with the d_2 species being farther from a symmetric top. Q-branch series were assigned for $^{P}Q_3$, $^{P}Q_2$, $^{P}Q_1$, $^{R}Q_0$, $^{R}Q_1$, and $^{R}Q_2$.

Figures 7 and 8 provide examples of the details of the assignments in the spectrum of the d_2 species. Figure 7 displays the beginning of the $^{R}R_{10}$ subband series in the region of the $^{R}Q_{11}$ feature. Series are indexed for both the $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ species. Figure 8 shows the assignment of the early part of the $^{P}Q_2$ subband for both chlorine isotopic species for the high-K_c values only. The lines for the $^{35}Cl^{37}Cl$ species begin with $J'' = 17$, which is blended with $J'' = 15$ for the $^{35}Cl_2$ species.

Table 3 contains the rotational constants fit to the GS and the US for the ν_6 vibrational mode. For fitting the GS rotational constants, 1229 GSCDs were used, including ones as high as $^{R}R_{21}-^{P}P_{23}$. For fitting the US rotational constants, assignments from the middle of the band out to $K_a' = 4$ were used. A perturbation prevented using series with higher K_a'' values. A total of 992 lines was used in this fitting. The band center is 662.99113 cm^{-1}. Table VIIS (Supporting Information) gives the GSCDs and the fitting of the GS rotational constants. Table VIIIS (Supporting Information) gives the lines used in the US fitting and the details of the fitting. Table IXS (Supporting Information) gives the 2320 additional lines that were not used in the US fitting due to the onset of a perturbation at $K_a' = 5$.

TABLE 3: Rotational Constants for *trans*-1,2-Dichloroethylene-d_2-$^{35}Cl_2$

parameter	ground state[a]	ν_6 vibrational state[a,b]
A	1.181 144 74 (93)	1.180 436 (26)
B	0.051 540 67 (15)	0.051 520 215 (54)
C	0.049 371 87 (17)	0.049 401 985 (42)
κ[c]	−0.996 167	−0.996 254
$\Delta_K \times 10^6$	6.2765 (32)	121.7 (41)
$\Delta_{JK} \times 10^8$	−6.546 (15)	−4.24 (19)
$\Delta_J \times 10^9$	3.735 (14)	3.7564 (50)
$\delta_K \times 10^8$	6.8 (14)	0.0
$\delta_J \times 10^{10}$	1.963 (64)	0.230 (42)
$H_K \times 10^{10}$	0.958 (34)	15 600 (1600)
ν_0		662.991 131 (38)
std dev[e]	0.000 254	0.000 384
no. lines fit[d]	1229	992
max K_a'	23	4

[a] In units of cm^{-1}; uncertainties in last two numbers are given in parentheses. [b] Ground state constants were held fixed while upper state constants were being fitted. [c] Unitless. [d] Number of GSCDs or lines used in the fitting. [e] std dev = standard deviation.

Assignment of Subbands due to tDCLE-d_2-$^{35}Cl^{37}Cl$ in the C-Type Band near 663 cm^{-1}. Subband series due to the tDCLE-d_2-$^{35}Cl^{37}Cl$ isotopomer were fully assigned in the C-type band of the d_2 species, which is shown overall in Figure 6. As described above in the discussion of the incomplete assignment of subband series for the $^{35}Cl^{37}Cl$ isotopomer of the normal species, the difference in $\bar{B}$ values for $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ species distinguishes the series due to the less abundant, heavier isotopomer in the Loomis−Wood computer display. For the d_2 species, the difference in the $\bar{B}$ values is 2.6%. This difference in the slopes of subband series due to $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ species is shown convincingly in Figure 4 in the vicinity of the $^{R}R_8$ subband. Series due to the $^{35}Cl^{37}Cl$ species have obviously shallower slopes in the Loomis−Wood display.

Figure 7 is an example of assigning subband series for the two chlorine isotopomers of the d_2 species. The J'' values are shown for both isotopic species. The smaller 2 $\bar{B}$ spacing for the $^{35}Cl^{37}Cl$ series is apparent. Figure 8 shows some of the analysis of the $^{P}Q_2$ band of the d_2 species. Only the high-K_c lines are shown. J'' values are for the $^{35}Cl_2$ species. Lines for the $^{35}Cl^{37}Cl$ species, which are not labeled with J'' values, begin with $J'' = 17$ of this species coincident with $J'' = 15$ of the $^{35}Cl_2$ species. $^{P}P_K$ subband series were assigned from $K_a'' = 0$ to $K_a'' = 20$. $^{R}R_K$ subband series were assigned from $K_a'' = 1$ to $K_a'' = 18$. In addition, the Q-branch series $^{P}Q_3$, $^{P}Q_2$, $^{P}Q_1$, $^{R}Q_0$, $^{R}Q_1$, and $^{R}Q_2$ and the offside series $^{R}P_0$ and $^{P}R_1$ were analyzed. A total of 2108 lines was assigned and used to find 692 GSCDs. The number of GSCDs is reduced for the $^{35}Cl^{37}Cl$ species due to more frequent breaks in the assignments caused by the lower intensities of this less abundant species. Different breaks in R-branch and P-branch series lead to fewer GSCDs.

Table 4 contains the rotational constants fit to the GS and the ν_{10} US (ν_6 equivalent for C_s the symmetry) for the tDCLE-d_2-$^{35}Cl^{37}Cl$. Table XS (Supporting Information) gives the GSCDs used and the details of fitting of the GS rotational constants. Table XIS (Supporting Information) gives the US rotational constants fit to 808 lines with $K_a' = 5$. A perturbation prevented extending the lines being fit to higher K_a' values.

TABLE 4: Rotational Constants for *trans*-1,2-Dichloroethylene-d_2-$^{35}Cl^{37}Cl$

parameter	ground state[a]	ν_{10} vibrational state[a,b]
A	1.180 764 6 (20)	1.182 507 (20)
B	0.050 164 94 (30)	0.050 142 85 (11)
C	0.048 107 53 (32)	0.048 142 09 (11)
κ^c	−0.996 367	−0.996 472
$\Delta_K \times 10^6$	6.2569 (96)	213.7 (20)
$\Delta_{JK} \times 10^8$	−6.451 (40)	−1.24 (15)
$\Delta_J \times 10^9$	3.573 (43)	3.7380 (88)
$\delta_K \times 10^8$	0.0	0.0
$\delta_J \times 10^{10}$	2.00 (11)	−6.46 (15)
$H_K \times 10^{11}$	7.8 (14)	1240 (150)
ν_0		662.964 494 (58)
std dev[e]	0.000 363	0.000 493
no lines fit[d]	692	808
max K_a'	20	5

[a] In units of cm^{-1}; uncertainties in last two numbers are given in parentheses. [b] Ground state constants were held fixed while upper state constants were being fitted. [c] Unitless. [d] Number of GSCDs or lines used in the fitting. [e] std dev = standard deviation.

TABLE 5: Principal Moments of Inertia of *trans*-1,2-Dichloroethylene and Its Isotopomers in the Ground State (I's in u Å^2)

	I_a	I_b	I_c	Δ^a
$H^{35}ClC{=}C^{35}ClH$	9.647 994	326.8854	336.6094	0.0760
$H^{35}Cl^{13}C{=}^{13}C^{35}ClH$	10.052 056	327.3263	337.4633	0.0849
$D^{35}ClC{=}C^{35}ClD$	14.272 283	327.0743	341.4421	0.0955
$D^{35}ClC{=}C^{37}ClD$	14.276 877	336.0441	350.4157	0.0947

[a] Inertial defect, $I_c - (I_a + I_b)$.

TABLE 6: Cartesian Coordinates of the Atoms of *trans*-1,2-Dichloroethylene[a]

	a/Å	b/Å	c/Å
Carbon (r_s)	±0.4708	±0.4515	0.0
Carbon (r_0)[b]	±0.4735	±0.4525	0.0
	±0.4727	±0.4516	0.0
Hydrogen (r_s)	±0.3119	±1.5179	0.0
Hydrogen (r_0)[b]	±0.3034	±1.5176	0.0
	±0.2991	±1.5167	0.0
Chlorine (r_s)[c]	±2.1411	∓0.0363	0.0
Chlorine (r_0)[b]	±2.1435	∓0.0405	0.0
	±2.1435	∓0.0403	0.0

[a] All coordinates in d_0 axis system. The Cl coordinates were fit in the d_2 axis system and then transformed into the d_0 axis system. [b] First entries are from the global fitting to I_a, I_b, and I_c for all isotopomers ($\Delta I_{rms} = 0.0290$). Second entries are from the global fitting to I_a and I_b only for all isotopomers $\Delta I_{rms} = 0.00557$). [c] From second moment condition, $\Sigma m_i a_i b_i = 0$, $b = -0.040$ Å.

These 1300 additional lines are given in Table XIIS (Supporting Information).

Structure Fitting for tDCLE. A substitution structure was fit to tDCLE since moments of inertia were found for species in which each atom type has been substituted. Table 5 gives the moments of inertia for all four species. Relative to the normal $^{35}Cl_2$ species, double substitution was available for the carbon atoms and the hydrogen atoms. Because the fully assignable spectrum for a $^{35}Cl^{37}Cl$ species was for the d_2 modification, the chlorine coordinates were determined from this substitution of the d_2 species and then transformed into the d_0 coordinate system. Table 6 gives the Cartesian coordinates obtained with Kraitchman-type relationships,[26,27] and Figure 1 shows the relationship of the principal rotation axes to the molecule. These coordinates are labeled r_s. Table 6 also gives the Cartesian coordinates as found by global fitting in two ways by means of the University of Michigan adaptation of Professor Richard Schwendeman's STRFIT program. One fitting was done to the I_a, I_b, and I_c set; the other was done with only the I_a and I_b set. The two sets sets of coordinates from the two global fittings are in good agreement. These coordinates are labeled r_0. In addition, the agreement between the r_s and r_0 coordinate sets is good, thereby providing us with a high level of confidence in the structure determination from the infrared data.

Because the chlorine atoms are very close to the *a* axis, the *b* coordinate of the chlorine atom was also fit using the second moment condition, $\Sigma m_i a_i b_i = 0$, and the other r_s coordinates. This value of $b = -0.040$ Å is reassuringly close to the r_s value.

Table 7 contains a summary of the structural parameters reported from two published studies of the isomers of DCLE, as well as the results of the present investigation. Schäfer and co-workers derived structures of both isomers from their electron diffraction investigation.[12] These results are labeled ED in the table. The r_s structure of the cis isomer obtained from the microwave investigation of Takeo and co-workers is labeled MW in the table.[10] In the last three lines, labeled IR and differentiated as r_0 and r_s, are the results of the present study. In general, good agreement exists between the geometric parameters found in these two ways from the rotational constants for the trans isomer. The uncertainties given with the r_0 values are the Costain values. These same uncertainties have been given with the r_s values, even though smaller uncertainties come from propagating the uncertainties in the rotational constants through the structure fitting. With one small exception these uncertainties encompass the difference between the r_s and r_0 values. The different CCl parameters found with the *b* value of −0.040 Å from the second moment condition are also within the error range. We regard the r_s values as the preferred geometric parameters for tDCLE. We also regard these parameters as the best ones for comparison with those derived for the cis isomer by the same methodology.[10]

Significant differences exist between the geometric parameters for *cis*- and *trans*-DCLE as derived from the spectroscopic and electron diffraction studies. These differences are particularly large for ClC=CCl backbone of the trans isomer. Compared to the spectroscopic results, the C=C bond length is too large and the C−Cl bond length is too small for the trans isomer in the electron diffraction study. A similar discrepancy was found

TABLE 7: Geometric Parameters for *cis*- and *trans*-1,2-Dichloroethylene

	r_{CH}/Å	r_{CC}/Å	r_{CCl}/Å	α_{CCH}/deg	α_{CCCl}/deg	ref
MW, cis isomer	1.100(1)	1.319(2)	1.717(2)	123.2(2)	124.1(1)	*a*
ED, cis isomer	1.096(16)	1.337(4)	1.717(2)	120.3(24)	124.0(2)	*b*
ED, trans isomer	1.092(26)	1.332(8)	1.725(2)	124.0(26)	120.8(6)	*b*
IR, trans isomer, r_0[c]	1.079(4)	1.310(5)	1.741(3)	124.6(5)	119.8(4)	*d*
	1.079	1.308	1.742	124.4	119.9	*d*
IR, trans isomer, r_s	1.078(4)	1.305(5)	1.740(3)[e]	125.3(5)	119.9(4)[e]	*d*

[a] MW = microwave. Reference 10. [b] ED = electron diffraction. Reference 12. [c] First row of entries from fitting to I_a, I_b and I_c; second row of entries from fitting to I_a and I_b only. [d] Present work. [e] With $b = -0.040$ Å from the second moment condition, $r_{CCl} = 1.741$ Å and $\alpha_{CCl} = 119.8°$.

in comparing the electron diffraction and spectroscopic results for *trans*-1,2-difluoroethylene.[13] Thus, it would appear that the C═C and C−Cl bond length differences must have been correlated in the fitting of the radial distribution curves in the electron diffraction study. The sizable uncertainties in fitting the CH parameters in the electron diffraction study are as expected because of weak electron scattering by hydrogen atoms. In the following discussion of differences in geometric parameters between the two isomers, we focus on the results of the microwave and infrared investigations.

In general, the adjustment in geometric parameters in going from cDCLE to tDCLE are similar to those found for the isomers of 1,2-difluoroethylene.[13] Both isomer pairs display the cis effect. The biggest change is the decrease in the C═C−X bond angle. That change is 2.9° for the difluoroethylenes and 4.2° for the DCLEs. The C═C−H bond angle increases by 2.4° in the difluoroethylenes and increases by 2.1° in the DCLEs. The C═C bond length decreases about 0.01 Å in each case. The CX bond lengths increase by 0.015 and 0.026 Å, respectively, for the difluoroethylenes and the DCLEs. The CH bond length decreases in both cases. The decrease in the C═C−Cl bond angle is consistent with greater repulsion between the C−X bond dipoles in the cis isomers. The larger decrease in the DCLE case probably reflects some additional steric repulsion of the larger chlorine atoms in the cis configuration. The increase in the C═C−H angle is consistent with the CH bond rotating sympathetically with the CCl bond. According to the Wiberg theory of bent bonds which predicts a destabilization of the trans configuration relative to the cis configuration,[8] one would expect the weakened C═C bond to be longer in the trans isomer, the opposite of what is observed. One might also expect longer CX bonds in the cis isomer due to replusion of partly negative halogen atoms, the opposite of what is observed. By a qualitative valence bond analysis, Epiotis has predicted the C═C bond shortening and the C−X bond lengthening that is observed.[9]

Engkvist et al. investigated the origin of the cis effect by computing the energy and electron distribution in the singly occupied σ and π orbitals of the CFH fragment. Two of these fragments bind to give the two isomers of 1,2-difluoroethylene.[6] Both orbitals suggests a significant contribution of four-center interaction in the F−C−C−F framework that favors the cis isomer. This conclusion is opposite to the Wiberg interpretation that explains the cis effect in terms of *de*stabilization of the trans isomer due to unfavorable orbital matching in the bent CC σ bond of this isomer.[8] Flow of electron probability into an F···F interaction in the Engkvist interpretation should weaken and thereby lengthen the CC bond in the cis isomer in accord with the differences found experimentally.

Summary. From the analysis of the rotational structure in C-type bands recorded at high resolution (0.002 cm^{-1}) in the infrared spectrum, rotational constants have been obtained for the normal form of *trans*-1,2-dichloroethylene and three isotopomers. Lines for a $^{35}\mathrm{Cl}^{37}\mathrm{Cl}$ species, as well as for the more abundant $^{35}\mathrm{Cl}_2$ species, have been assigned in the naturally occurring isotopic mixtures. From the rotational constants for substitution of all three atom types, a substitution (r_s) structure has been fit for this nonpolar molecule. The microwave-based and infrared-based structures for the two isomers are compared with the structures derived from an electron diffraction investigation, which are regarded as more approximate. Changes in geometric parameters in going from the cis to the trans isomer are similar to those found for the 1,2-difluoroethylene isomer pair, the largest changes being a decrease in the C═C−X bond angle and an increase in the C═C−H bond angle in going from the cis to the trans isomer. Both isomer pairs exhibit the cis effect in which the cis isomer has the lower electronic energy.

Acknowledgment. We thank Qing-Tian Shang and Laura Sonnichsen for the exploration of the synthesis of isotopically pure tDCLE. We thank Joshua Ellison for his work on the assignment of the $^{13}\mathrm{C}_2$-$^{35}\mathrm{Cl}^{37}\mathrm{Cl}$ species. His work was supported by a grant from the Dow Chemical Foundation. Some of J.A.S.'s work was supported by a grant from the ACS Petroleum Research Fund. Most of this research was supported by a grant from the National Science Foundation, Grant CHE-9207156.

Supporting Information Available: Tables IS−XIIS contain the assignments for all of the lines and for the GSCDs reported in this paper (94 pages). These tables include details of fitting rotational constants. Ordering information is given on any current masthead page.

References and Notes

(1) Pitzer, K. S.; Hollenberg, L. J. *J. Am. Chem. Soc.* **1954**, *76*, 1493.

(2) Craig, N. C.; Piper, L. G.; Wheeler, V. L. *J. Phys. Chem.* **1971**, *75*, 1453.

(3) Armstrong, G. T.; Marantz, S. *J. Chem. Phys.* **1963**, *38*, 169.

(4) Connor, T. M.; McLauchlan, K. A. *J. Phys. Chem.* **1965**, *69*, 1888.

(5) Muir, M.; Baker, J. *Mol. Phys.* **1996**, *89*, 211.

(6) Engkvist, O.; Karlström, G.; Widmark, P.-O. *Chem. Phys. Lett.* **1997**, *265*, 19.

(7) Craig, N. C.; Brandon, D. W.; Stone, S. C.; Lafferty, W. J. *J. Phys. Chem.* **1992**, *96*, 1598.

(8) Wiberg, K. B. *Acc. Chem. Res.* **1996**, *29*, 229.

(9) Epiotis, N. D. *Deciphering the Chemical Code. Bonding across the Periodic Table*; VCH Publishers: New York, 1996; Chapter 11.

(10) Takeo, H.; Sugie, M.; Matsumura, C. *J. Mol. Struct.* **1988**, *190*, 205.

(11) Leal, L. A.; Alonso, J. L.; Lesarri, A. G. *J. Mol. Spectrosc.* **1994**, *165*, 368.

(12) Schäfer, L.; Ewbank, J. D.; Siam, K.; Paul, D. W.; Monts, D. L. *J. Mol. Struct.* **1986**, *145*, 135.

(13) Craig, N. C.; Abiog, O. P.; Hu, B.; Stone, S. C.; Lafferty, W. J.; Xu, L.-H. *J. Phys. Chem.* **1996**, *100*, 5310.

(14) Craig, N. C.; Chen, A.; Suh, K. H.; Klee, S.; Mellau, G. C.; Winnewisser, B. P.; Winnewisser, M. *J. Phys. Chem.* **1997**, *101*, 9302.

(15) Reaction of Cl_2 with 1,2-dibromoethylene in CS_2 to give 1,2-dibromo-1,2-dichloroethane followed by dehalogenation with zinc dust in refluxing ethanol. The problem with this method is that elementary Br_2 is produced by oxidative replacement of bromine with chlorine in the ethlyene, and the Br_2 formed adds to the ethylene. A complex mixture of bromochloroethanes forms. As a consequence, the yield of the desired 1,2-dichloroethylenes is reduced, and some of the isotopically pure Cl_2 is wasted in side reactions. A better method would be to add isotopically pure Cl_2 to acetylene in the "flashlight" reaction, which was explored subsequently in our laboratory.

(16) Winnewisser, B. P.; Reinstädler, J.; Yamada, K. M. T.; Behrend, J. *J. Mol. Spectrosc.* **1989**, *136*, 12.

(17) Craig, N. C.; Overend, J. *J. Chem. Phys.* **1969**, 51, 1127.

(18) Hopper, M. J. Ph.D. Dissertation, University of Minnesota, Minneapolis, MN, 1967.

(19) Bernstein, H. J.; Ramsay, D. A. *J. Chem. Phys.* **1949**, *17*, 556.

(20) Bernstein, H. J.; Pullin, A. D. E. *Can. J. Chem.* **1952**, *30*, 963.

(21) Kagel, R. O.; Powell, D. L.; Overend, J.; Hopper, M.; Ramos, M. N.; Bassi, A. B.; Bruns, R. E. *J. Chem. Phys.* **1984**, *88*, 521.

(22) da Silva, J. B. P.; Ramos, M. N.; Suto, E.; Bruns, R. E. *J. Phys. Chem. A* **1997**, *101*, 6293.

(23) Becker, E. D. *High-Resolution NMR theory and Chemical Applications*, 2nd ed.; Academic Press: New York, 1980; pp 167−171.

(24) Craig, N. C.; Klee, S.; Mellau, G. C.; Winnewisser, B. P.; Winnewisser, M. *J. Phys. Chem.* **1996**, *100*, 15049.

(25) Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; Dover: New York, 1975; p 104.

(26) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*, 3rd ed.; Wiley-Interscience: New York, 1984.

(27) Chutjian, A. *J. Mol. Spectrosc.* **1964**, *14*, 361.