Vibration Spectra of Cis and Trans C2H2Cl2 and C2D2Cl2

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Vibration Spectra of *Cis* and *Trans* $C_2H_2Cl_2$ and $C_2D_2Cl_2$

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The infra-red spectra of gaseous and liquid *cis* and *trans* $C_2H_2Cl_2$ and $C_2D_2Cl_2$ have been obtained in the region 3500 to 400 cm^{-1}.

The fine structure of a $\perp$ band in *trans* $C_2H_2Cl_2$ was also resolved and the least moment of inertia obtained.

An assignment of all the fundamentals for the four molecules has been made.

Calculations of potential functions and of the equilibrium constants for the reaction *cis* $\rightleftharpoons$ *trans* support the assignment.

INTRODUCTION

ALTHOUGH *cis* and *trans* dichloroethylene are relatively simple planar molecules with symmetries C_{2v} and C_{2h}, respectively, considerable disagreement exists between the assignments by various authors[1-4] of the twelve fundamental frequencies for each of these molecules. This disagreement is largely caused by the lack of reliable infra-red data, particularly on the contours of the infra-red bands in the vapor. We have therefore re-investigated the infra-red spectra of these molecules and their deuterium analogues. Using these data and the existing Raman data, we have been able to make satisfactory assignments of the twelve frequencies in the *cis* molecule and ten frequencies in the *trans* molecule. The two remaining frequencies in the *trans* molecule are active in the infra-red, but lie beyond the range of a KBr prism. These frequencies have been obtained from combination tones.

Our values for the low frequencies are in agreement with the data of Wood and Stevenson[5] for the equilibrium constants of the *cis* $\rightleftharpoons$ *trans* reaction at different temperatures. These authors deduced from their results that the sum of the two low frequencies must lie between 420 and 450 cm^{-1}.

We have found it necessary, however, to revise the potential function calculation of Pitzer and Freeman[4] for the out-of-plane vibrations of *cis*- and *trans*-dichloroethylene, since these authors used an erroneous value for the *trans* wagging frequency and assumed that the 620 cm^{-1} band reported by Wu[2] for the *cis* molecule was a combination of the Raman frequency at 350 cm^{-1} with the torsion frequency at 270 cm^{-1}. We have shown, however, that the 620 cm^{-1} band was caused by an impurity.

MATERIALS

A mixture of *cis* and *trans* $C_2H_2Cl_2$ was prepared from Eastman Kodak sym $C_2H_4Cl_2$ by reaction with Zn, and the isomers separated by fractional distillation.

$$trans \text{ b.p.} = 48.1 \pm 0.1°C.$$
$$cis \text{ b.p.} = 60.1 \pm 0.1°C.$$

The two samples were judged from their spectra to be about 99 percent pure.

A mixture of *cis* and *trans* $C_2D_2Cl_2$ was prepared in the following manner:

1. $\qquad CaC_2 + D_2O = CaO + C_2D_2,$
2. $\qquad C_2D_2 + 2Cl_2 = C_2D_2Cl_4,$
3. $\qquad C_2D_2Cl_4 + Zn = C_2D_2Cl_2 + ZnCl_2,$

and the isomers were separated by fractional distillation.

The spectra indicated that these samples were about 99 percent deuterated. Owing to the small quantity of material available, it was not possible to obtain as complete a separation as for the "light" isomers. The *cis* $C_2D_2Cl_2$ contained about 2 percent of *trans* $C_2D_2Cl_2$ as impurity and the *trans* $C_2D_2Cl_2$ contained about 10 percent of *cis* $C_2D_2Cl_2$ as impurity.

EXPERIMENTAL

The infra-red spectra of these four molecules were investigated using a Perkin Elmer Model 12B infrared spectrometer with a G-M amplifier and a Brown Pen Recorder. NaCl and KBr prisms were used for the regions 3500–700 cm^{-1} and 700–400 cm^{-1}, respectively. Vapor spectra were investigated using a 10-cm absorption cell, various pressures being used to resolve all the bands observed; liquid spectra were obtained using 0.1-mm and 0.025-mm absorption cells, the more intense bands being resolved using dilute solutions in CS_2 and CCl_4.

The infra-red spectra are reproduced in Figs. 1–4 and the infra-red and Raman frequencies given in Tables I–IV.

[1] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 330.

[2] Ta-You Wu, J. Chem. Phys. **5**, 392 (1937); Phys. Rev. **46**, 465 (1934).

[3] B. Trumpy, Zeits. f. Physik. **98**, 672 (1935).

[4] K. S. Pitzer and N. K. Freeman, J. Chem. Phys. **14**, 586 (1946).

[5] R. E. Wood and D. P. Stevenson, J. Am. Chem. Soc. **63**, 1650 (1941).

ASSIGNMENT OF FREQUENCIES[6]

(a) *Cis* C₂H₂Cl₂

The five strong polarized lines in the Raman spectrum may be assigned to the totally symmetric A_1 vibrations. These frequencies are also active in the infra-red though the 1183-cm⁻¹ band is extremely weak.[7] The two depolarized lines at 406 cm⁻¹ and 876 cm⁻¹ which do not have corresponding infra-red absorptions may be assigned to the two A_2 vibrations since these vibrations are active only in the Raman spectrum. The five remaining vibrations give strong absorptions in the infra-red.
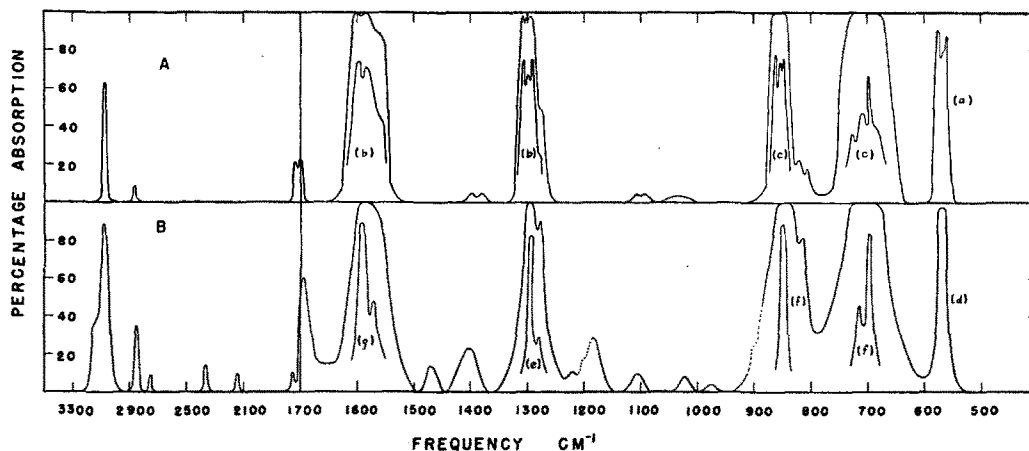
The contours of the infra-red bands may be predicted qualitatively from the curves of Badger and Zumwalt.[8] For vibrations with change of electric moment parallel to the greatest axis of inertia (type B_2) the bands should exhibit a P, Q, R structure with a strong central Q branch. The 697-cm⁻¹ band may be assigned therefore to the lone vibration of this type, ν_{12}. For changes of electric moment parallel to the middle axis of inertia (type A_1) a doublet structure is expected. This is in agreement with the above assignment of frequencies to this type, though for the 714-cm⁻¹ band the doublet structure is overlapped by the rotational contour of the 697-cm⁻¹ band. Finally for changes of electric moment parallel to the least axis of inertia (type B_1),

the bands should exhibit P, Q, and R branches of similar intensity. Such contours are observed for the 571, 857, and 1303 cm⁻¹ bands. The fourth frequency of this type, the C−H stretching frequency, corresponds to the strong 3072-cm⁻¹ absorption. Further confirmation of the assignment is afforded by the fact that all the remaining weak bands have been interpreted as simple combination tones.

(b) *Trans* C₂H₂Cl₂

The five strong polarized Raman lines again correspond to the totally symmetric A_g vibrations. The Raman line of medium intensity at 758 cm⁻¹ is probably the B_g wagging frequency, though this line should be depolarized.[9] This assignment, however, is supported by the appearance of a corresponding line at 658 cm⁻¹ in the spectrum of *trans* C₂D₂Cl₂ as expected from the Teller-Redlich[10] product rule.

The strong infra-red bands at 817, 895, 1200, and 3080 cm⁻¹ are presumably infra-red active fundamentals. The 895-cm⁻¹ band which shows a clearly resolved rotational fine structure in the vapor spectrum, may be assigned to type A_u and the 817- and 1200-cm⁻¹ bands which exhibit doublet structures in the vapor spectrum may be assigned to type B_u. The 3080 cm⁻¹ band is obviously the type B_u C−H stretching frequency. This leaves two low frequencies

FIG. 1. Infra-red spectra of *cis*-dichloroethylene.

A. Vapor	Cell length 10 cm	Temperature 20°C
	Pressure (a) 120-mm Hg	(b) 30-mm Hg (c) 10-mm Hg
B. Liquid	(d) Pure liquid 0.1-mm cell	(e) 10 percent solution in CS₂ 0.1-mm cell
	(f) 10 percent solution in CS₂ 0.025-mm cell	(g) 10 percent solution in CCl₄ 0.1-mm cell
------	*trans* impurity	

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[6] The normal modes of vibration of *cis*- and *trans*-dichloroethylene, their symmetry classes and selection rules, have been given by G. Herzberg (see reference 1) and are not reproduced here. The same system of numbering has been used.

[7] It is interesting to note that the first overtone of this band at 2367 cm⁻¹ has approximately the same intensity as the fundamental. A similar phenomenon is found in the *cis* C₂D₂Cl₂ molecule.

[8] R. M. Badger and L. R. Zumwalt, J. Chem. Phys. **6**, 711 (1938). Using the electron diffraction values for the molecular dimensions (see section on product rule) the parameters ρ and S, used by Badger and Zumwalt to express the asymmetry of the molecule, take the values $\rho = 3.89$, $S = -0.91$.

[9] The polarization of this line has been discussed by Herzberg (see reference 1).

[10] E. Teller, quoted in J. Chem. Soc. p. 966 (1936). O. Redlich, Zeits. f. Physik chemie **B28**, 371 (1935).
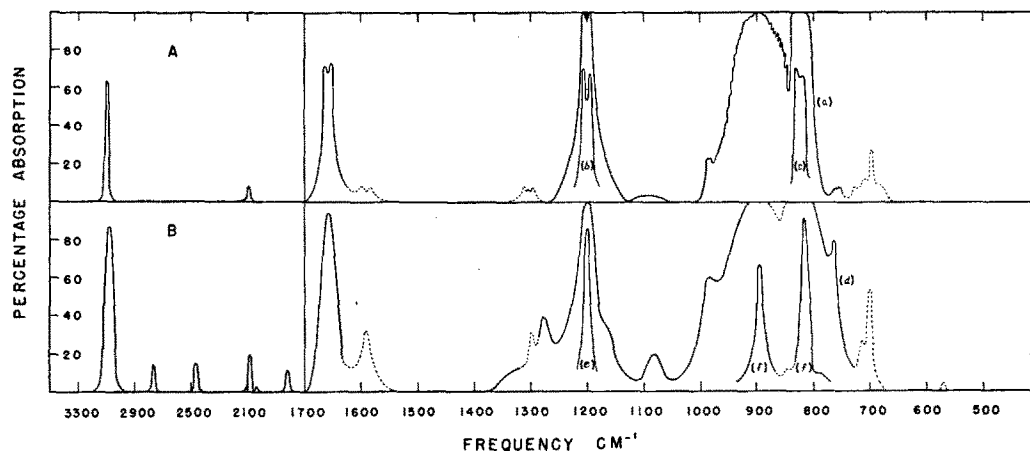
FIG. 2. Infra-red spectra of *trans*-dichloroethylene.

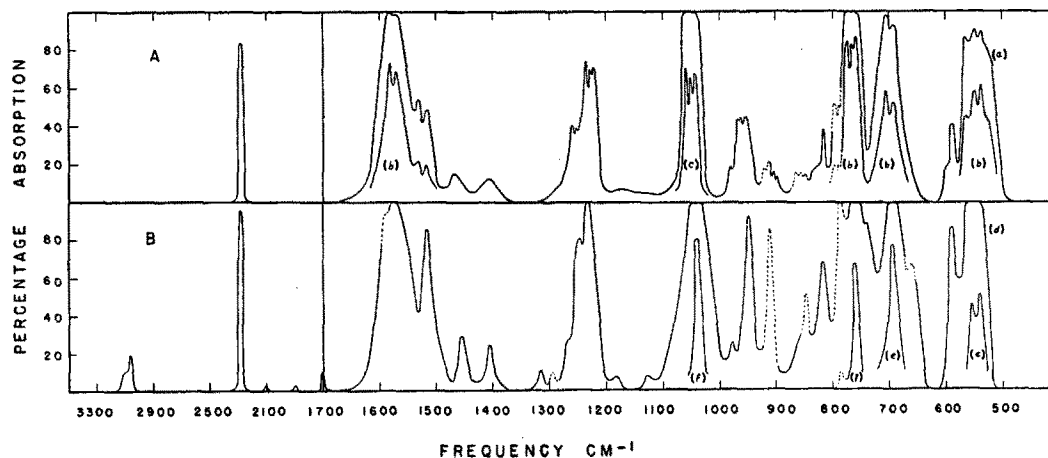| A. Vapor	Cell length 10 cm		Temperature 20°C	
	Pressure	(a) 120-mm Hg	(b) 30-mm Hg	(c) 5-mm Hg
B. Liquid	(d) Pure liquid		(e) 10 percent solution in CS_2	
	0.1-mm cell		0.1-mm cell	
	(f) 10 percent solution in CS_2			
	0.025-mm cell			
------	*cis* impurity			

unassigned, one of type A_u and the other of type B_u. All the remaining weak bands may be interpreted as simple combination tones with the exception of the bands at 763, 983, 1080, 1276, and 1816 cm^{-1}.

The two low frequencies must lie below 400 cm^{-1} since they were not observed using a KBr prism. Moreover, the results of Wood and Stevenson[5] indicated that the sum of these frequencies should lie between 420 and 450 cm^{-1}. Pitzer and Freeman[4] assigned a value of 270 cm^{-1} to the A_u torsion fre-

quency by assuming that the 620-cm^{-1} band reported by Wu[2] was a combination tone, $350 + 270$ cm^{-1}. The 620-cm^{-1} band, however, must have been caused by an impurity, since we have not observed it using even longer absorption paths than Wu.

The in-plane bending frequency of type B_u may be computed from the rotational product rule[11] for *cis-trans* isomers, a value of approximately 280 cm^{-1} being obtained. The torsion frequency of type A_u however, cannot be obtained by this means, as the rule is not applicable to out-of-plane vibrations.

FIG. 3. Infra-red spectra of *cis*-dichloroethylene-d_2.

A. Vapor	Cell length 10 cm		Temperature 20°C	
	Pressure	(a) 120-mm Hg	(b) 30-mm Hg	(c) 10-mm Hg
B. Liquid	(d) Pure liquid		(e) 10 percent solution in CS_2	
	0.1-mm cell		0.1-mm cell	
	(f) 10 percent solution in CS_2			
	0.025-mm cell			
------	*trans-d_2* and *cis* impurities			

[11] H. J. Bernstein, J. Chem. Phys. **17**, 256 (1949).

TABLE I. Infra-red and Raman frequencies for *cis* $C_2H_2Cl_2$.

Infra-red (cm⁻¹) Vapor	Liquid	Raman (cm⁻¹) liquid[a]	Assignment
		173 (s) pol.	$\nu_5(A_1)$
		406 (s) depol.	$\nu_7(A_2)$
P 564, Q 571, R 578	571 (s)	563 (m) depol.	$\nu_{11}(B_1)$
P 688, Q 697, R ?	697 (vs)		$\nu_{12}(B_2)$
?, 727	714 (s)	711 (s) pol.	$\nu_4(A_1)$
808, 823	815 (w)	807 (vw)	$406+406= 812 \ (A_1)$
P 851, Q 857, R 864	848 (vs)		$\nu_{10}(B_1)$
		876 (w) depol.	$\nu_6(A_2)$
	975 (vw)		$406+571= 977 \ (B_2)$
	1022 (vw)		$173+848=1021 \ (B_1)$
	1105 (w)		$406+697=1103 \ (B_1)$
	1183 (w)	1179 (s) pol.	$\nu_3(A_1)$
	1218 (w)		$2\times697-173=1221 \ (A_1)$
	1254 (w)		$406+848=1254 \ (B_2)$
	1279 (m)		$571+714=1285 \ (B_1)$
P 1296, Q 1303, R 1310	1294 (s)		$\nu_9(B_1)$
	1404 (w)		$697+714=1411 \ (B_2)$
	1470 (w)		$173+1294=1467 \ (B_1)$
	1571 (w)		$\{697+876=1573 \ (B_1); \ 714+848=1562 \ (B_1)\}$
1583, 1598	1590 (s)	1587 (s) pol.	$\nu_2(A_1)$
	1695 (w)	1689 (w) depol.?	$\{848+848=1696 \ (A_1); \ 406+1294=1700 \ (B_2)\}$
	1753 (vw)		$\{876+876=1752 \ (A_1); \ 571+1183=1754 \ (B_1); \ 173+1590=1763 \ (A_1)\}$
	2137 (w)		$848+1294=2142 \ (A_1)$
	2367 (w)		$1183+1183=2366 \ (A_1)$
	2753 (w)		$1183+1590=2773 \ (A_1)$
2860	2855 (w)		$1294+1590=2884 \ (B_1)$
3072	3072 (s)		$\nu_8(B_1)$
		3077 (vs) pol.	$\nu_1(A_1)$
	3150 (w)	3160 (w) depol.?	$1590+1590=3180 \ (A_1)$

[a] See reference 1.

Since the sum of the two low frequencies must lie between 420 and 450 cm⁻¹ the torsion frequency may be expected to lie in the region 150 ± 50 cm⁻¹.

Better estimates of these frequencies may be obtained from combination tones. The only simple combinations of the low frequencies which are active in the infra-red are combinations of the Raman frequency at 349 cm⁻¹ with the two low infra-red frequencies. These combination bands should appear in the region 450 to 650 cm⁻¹. The absorption of 1 mm of liquid in this region was investigated using a KBr prism and two weak bands were observed at 541 and 614 cm⁻¹ (see Fig. 5) in addition to the *cis* impurity band at 571 cm⁻¹. If these bands are interpreted in the above manner values of 192 cm⁻¹ and 265 cm⁻¹ are obtained for the two low infra-red frequencies. Using these values, simple interpretations are obtained for the five remaining weak bands hitherto unexplained.

(c) *Cis* $C_2D_2Cl_2$

The five strongest lines in the Raman spectrum, *viz.* 171, 689, 850, 1570, 2325 cm⁻¹, correspond to the five totally symmetric lines for the non-deuterated molecule. Similarly, the 368-cm⁻¹ Raman line corresponds to the A_2 vibration at 406 cm⁻¹ in the light molecule. The other frequency of this species has not been observed but may be estimated from the Teller-Redlich product rule to be in the region of 710 cm⁻¹ (see below).

The lone frequency of type B_2 must correspond to one of the strong infra-red bands at 540 and 558 cm⁻¹. The contours of these bands overlap in the vapor spectrum and are not readily separated, but the isotopic product rule indicates that the band at 558 cm⁻¹ is the B_2 frequency. The band at 540 cm⁻¹ must be assigned then to type B_1 together with the strong infra-red bands at 761, 1040, and 2280 cm⁻¹. The 761 and 1040 cm⁻¹ bands show well defined *PQR* structures in the vapor spectrum.

Most of the remaining bands may be interpreted as simple combination tones corresponding to those found for the non-deuterated molecule. A few weak bands, *viz.* 818, 976, 1179, 1314, however, cannot be explained as simple combination tones and probably represent combinations perturbed by Fermi resonance. This is to be expected since many combinations of the same symmetry have approximately the same frequency in the region 800–1400 cm⁻¹. Tentative assignments have been given in these cases.

TABLE II. Infra-red and Raman frequencies for *trans* $C_2H_2Cl_2$.

Infra-red (cm⁻¹) Vapor	Liquid	Raman (cm⁻¹) liquid[a]	Assignment
		349 (s) pol.	$\nu_5(A_g)$
	541 (vvw)		$349+192= 541 \ (A_u)$
	614 (vvw)		$349+265= 614 \ (B_u)$
		758 (m) pol.	$\nu_8(B_g)$
754, 763	763 (w)		$844+265-349= 760 \ (B_u)$
823, 832	817 (vs)		$\nu_{11}(B_u)$
		844 (s) pol.	$\nu_4(A_g)$
898	895 (vs)		$\nu_6(A_u)$
	985 (w)		$*\{2\times349+265= 963 \ (B_u); \ 265+895-192= 968 \ (B_u)\}$
	1080 (w)		$1270-192=1078 \ (A_u)$
	1166 (w)		$349+817=1166 \ (B_u)$
1195, 1205	1200 (s)		$\nu_{10}(B_u)$
	1276 (w)	1270 (s) pol.	$\nu_3(A_g); \ 192+265+817=1274 \ (A_u)$
		1576 (s) pol.	$\nu_2(A_g)$
		1626 (vw) pol.	$817+817=1634 \ (A_g)$
1654, 1663	1658 (m)		$\{758+895=1653 \ (B_u); \ 817+844=1661 \ (B_u)\}$
		1692 (w) pol.	$844+844=1688 \ (A_g)$
	1816 (w)		$2\times817+192=1826 \ (A_u)$
	2047 (w)		$844+1200=2044 \ (B_u)$
2092	2082 (w)		$817+1270=2087 \ (B_u)$
	2460 (w)		$\{1200+1270=2470 \ (B_u); \ 895+1576=2471 \ (A_u)\}$
	2760 (w)		$1200+1576=2776 \ (B_u)$
		3071 (s) pol.	$\nu_1(A_g)$
3090	3080 (s)		$\nu_9(B_u)$
		3142 (w) depol.?	$1576+1576=3152 \ (A_g)$

[a] See reference 1.
* Fermi resonance gives 985 cm⁻¹ and 945 cm⁻¹ the latter being obscured by the intense 895 cm⁻¹ band.
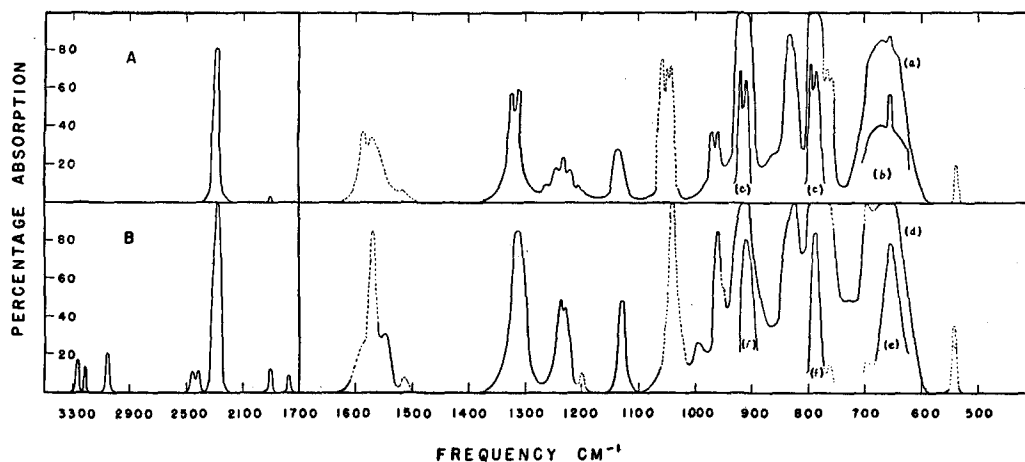
FIG. 4. Infra-red spectra of *trans*-dichloroethylene-d_2.

A. Vapor   Cell length 10 cm
              Pressure   (a) 120-mm Hg   Temperature 20°C
                                                (b) 30-mm Hg   (c) 10-mm Hg

B. Liquid   (d) Pure liquid
                   0.1-mm cell   (e) 10 percent solution in CS₂
                   (f) 10 percent solution in CS₂   0.1-mm cell
                        0.025-mm cell

       ------   *cis-d₂* impurity

(d) Trans $C_2D_2Cl_2$

By comparison with the assignment for *trans* $C_2H_2Cl_2$, the Raman frequencies at 346, 765, 992, 1570, and 2325 cm^{-1} may be assigned unambiguously to type A_g and the 657-cm^{-1} Raman line to type B_g. The infra-red band at 658 cm^{-1} which exhibits a P, Q, R structure in the vapor spectrum corresponds to the 895 cm^{-1} band for the light molecule though the resolving power proved insufficient to resolve the rotational fine structure for the heavy molecule. The strong infra-red bands at 784, 912, and 2285 cm^{-1} may be assigned to type B_u, the doublet structures for the 784- and 912-cm^{-1} bands being resolved in the vapor spectrum. If it is assumed that the two low frequencies in the light molecule, *viz.* 192 and 265 cm^{-1} are not appreciably

affected by substitution of deuterium, a complete assignment is obtained and all the remaining weak bands may be satisfactorily interpreted as simple combination tones.

PRODUCT RULE RATIOS FOR *CIS* AND *TRANS* $C_2H_2Cl_2$ AND $C_2D_2Cl_2$

Using the dimensions for the *cis* and *trans* molecules obtained by the electron diffraction method[12] *viz.*

	cis	*trans*
$r_{C=C}$	1.38A (assumed)	1.38A (assumed)
r_{C-Cl}	1.67±0.03A	1.69±0.02A
Cl—C=C	123.5 ±1°	122.5 ±1°

and further assuming $r_{C-H} = 1.07$A, H—C=C $= 120°$ as in ethylene[13] the principal moments of inertia for the light and heavy molecules are evaluated as follows:

	cis $C_2H_2Cl_2$	*cis* $C_2D_2Cl_2$	*trans* $C_2H_2Cl_2$	*trans* $C_2D_2Cl_2$
I_A	70.3	82.4	15.8	23.2
I_B	329.8	334.8	548.2	548.6
I_C	400.1	417.2	564.0	571.8

units of 10^{-40} g cm²

The theoretical product rule ratios for the various symmetry types of the *cis* and *trans* molecules may now be calculated and compared with the observed ratios (Tables V and VI). The agreement, in general, is good though the observed ratio for the *cis* B_1
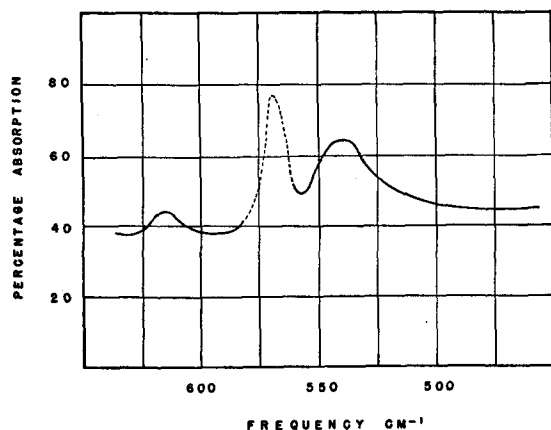

FIG. 5. Infra-red absorption of *trans* dichloroethylene from 450 to 650 cm^{-1} using 1-mm path length of liquid. Dotted band at 571 cm^{-1} caused by *cis*-dichloroethylene impurity.

[12] L. O. Brockway, J. Y. Beach, and L. Pauling, J. Am. Chem. Soc. **57**, 2693 (1935).
[13] W. S. Gallaway and E. F. Barker, J. Chem. Phys. **10**, 88 (1942).

vibration is slightly high. Liquid frequencies have been used throughout.

ANALYSIS OF THE FINE STRUCTURE OF THE 898-CM^{-1} BAND OF *TRANS* $C_2H_2Cl_2$

The frequencies of the individual rotation lines were obtained from the ammonia data given by Oetjen, Kao and Randall[14] (see Fig. 6) and are listed in Table VII. The frequencies have been corrected to vacuum and are probably accurate to ±0.1 cm^{-1}. The *trans* $C_2H_2Cl_2$ molecule approximates very closely to a symmetric top whose figure axis passes approximately through the two chlorine atoms. Since the 898-cm^{-1} band corresponds to an out-of-plane wagging motion of the CHCl groups, the change in electric moment is perpendicular to this

TABLE III. Infra-red and Raman frequencies for *cis* $C_2D_2Cl_2$.

Infra-red (cm^{-1}) Vapor	Liquid	Raman (cm^{-1}) liquid[a]	Assignment
		171 (s)	$\nu_6(A_1)$
		368 (m)	$\nu_7(A_2)$
		515 (w)	$689-171= 518$ (A_1)
	540 (s)		$\nu_{11}(B_1)$
	558 (s)		$\nu_{12}(B_2)$
	590 (m)		$761-171= 590$ (B_1)
693⎫ 706⎭	695 (s)	689 (s)	$\nu_4(A_1)$
	741 (w)		$368+368= 736$ (A_1)*
P 759⎫ Q 766⎬ R 773⎭	761 (vs)		$\nu_{10}(B_1)$
818	818 (w)		†
		850 (m)	$\nu_3(A_1)$
P 899⎫ Q 905⎬ R 912⎭	912 (m)#		$368+558= 926$ (B_1)* Fermi Resonance
P 955⎫ Q 962⎬ R 967⎭	949 (m)		$171+761= 932$ (B_1)*
	976 (w)		†
P 1045⎫ Q 1051⎬ R 1058⎭	1040 (vs)		$\nu_9(B_1)$
	1129 (w)		$368+ 761=1129$ (B_2)* ††
	1179 (w)		
P 1222⎫ Q 1228⎬ R 1235⎭	1228 (m)		$540+ 695 =1235$ (B_1)*
	1247 (w)		$558+ 695 =1253$ (B_2)*
	1263 (w)		$558+ 710 =1268$ (B_1)*
	1314 (w)		††
	1405 (w)		$368+1040 =1408$ (B_2)*
	1455 (w)		$695+ 761 =1456$ (B_1)*
1518⎫ 1532⎭	1515 (m)	1507 (w)	$761+ 761 =1522$ (A_1)*
1569⎫ 1582⎭	1572 (s)	1570 (s)	$\nu_2(A_1)$
	1702 (w)		$850+ 850 =1700$ (A_1)*
	1885 (vw)		$850+1040 =1890$ (B_1)
	2107 (vw)		$540+1572 =2112$ (B_1)
2280	2280 (s)		$\nu_8(B_1)$
		2325 (s)	$\nu_1(A_1)$
	3060 (w)		$2325+ 761 =3086$ (B_1)
	3110 (w)		$2280+ 850 =3130$ (B_1)
		3150 ? (vw)	$1572+1572 =3144$ (A_1)*

[a] See reference 3.
* The corresponding combination tone was observed for *cis* $C_2H_2Cl_2$.
# *Trans* $C_2D_2Cl_2$ impurity contributes partly to the intensity of this band.
† Fermi resonance between $2\times171+558=900$ (B_2); $368+540=908$ (B_2).
†† Fermi resonance between two of the following; $171+368+710$ $=1249$ (A_1); $2\times710-171=1249$ (A_1); $2\times540+171=1251$ (A_1).

14 R. A. Oetjen, C. L. Kao, and H. M. Randall, Rev. Sci. Inst. 13, 515 (1942).

TABLE IV. Infra-red and Raman frequencies for *trans* $C_2D_2Cl_2$.

Infra-red (cm^{-1}) Vapor	Liquid	Raman (cm^{-1}) liquid[a]	Assignment
		346 (s)	$\nu_6(A_g)$
		657 (m)	$\nu_8(B_g)$
P ?⎫ Q 660⎬ R ?⎭	658 (s)		$\nu_6(A_u)$
	729 (vw)		$265+658-192= 731$ (B_u)*
		765 (m)	$\nu_4(A_g)$
786⎫ 796⎭	784 (vs)		$\nu_{11}(B_u)$
	826 (m)#		†
	836 (w)		$657+192= 849$ (B_u)
911⎫ 921⎭	912 (vs)		$\nu_{10}(B_u)$
960⎫ 969⎭	960 (m)		$265+2\times346= 957$ (B_u)*
		992 (s)	$\nu_3(A_g)$
	995 (w)		992 cm^{-1} Raman line
	1130 (w)		$346+784=1130$ (B_u)*
	1230 (w)		$765+657-192=1230$ (B_u)
	1238 (w)		$192+265+784=1241$ (A_u)
1314⎫ 1324⎭	1314 (m)		$657+658 =1315$ (B_u)*
		1312 (w) ?	$658+658 =1316$ (A_g)
		1545 (m)	$765+765 =1530$ (A_g)*
	1549 (w)		$765+784 =1549$ (B_u)*
		1570 (s)	$\nu_2(A_g)$
	1780 (w)		$784+992 =1776$ (B_u)*
	1900 (w)		$912+992 =1904$ (B_u)*
2290	2285 (s)		$\nu_9(B_u)$
		2325 (s)	$\nu_1(A_g)$
	2417 (w)		$2\times765+ 912 =2442$ (B_u)
	2462 (w)		$912+1570 =2482$ (B_u)
	3054 (w)		$765+2285 =3050$ (B_u)
		3154 (w)	$1570+1570 =3140$ (A_g)*
	3226 (w)		$912+2325 =3237$ (B_u)
	3265 (w)		$992+2285 =3277$ (B_u)

[a] See reference 3.
* The corresponding combination tone was observed for *trans* $C_2H_2Cl_2$.
# Part of the intensity of this band is contributed by *trans* $C_2H_2Cl_2$ impurity.
† Probably Fermi resonance between; $346+657-192=811$ (B_u); 3×265 $=795$ (B_u); to give 826 cm^{-1} and a component which is masked by the intense 784 cm^{-1} band.

axis, hence we should expect a perpendicular type band. Moreover since $I_A \ll I_B$ or I_C the band will consist mainly of a series of Q branches of the various sub-bands present, the PR separations in the individual sub-bands being considerably smaller than the separations between the various Q branches.

The fact that a strong "Q branch" is found in the region of the band origin gives the band the appearance of a $\parallel$ band. This is altogether out of the question however due to the magnitude of the spacing. The appearance of this Q branch is probably due to the slight deviation of the molecule from a perfect symmetric top, c.f., the type C band at 949 cm^{-1} for ethylene.[15] The spacing of the Q branches is given by the equation[16]

$$\nu = \nu_0 + (A'-B') \pm 2(A'-B')K + [(A'-B')-(A''-B'')]K^2, \quad (1)$$

where A', B', are the rotational constants for the upper state, A'', B'', are the rotational constants for the lower state, the positive sign applies to the ^RQ

15 See reference 1, p. 483.
16 See reference 1, p. 424.

TABLE V. Frequency assignments and product rule ratios for *cis* $C_2H_2Cl_2$ and *cis* $C_2D_2Cl_2$.

Type		Cis $C_2H_2Cl_2$	Cis $C_2D_2Cl_2$	Theor. ratio	Obs. ratio
A_1	ν_1	3077 R	2325 R		
	ν_2	1587 R	1570 R		
	ν_3	1179 R	850 R	1.98	1.94
	ν_4	711 R	689 R		
	ν_5	173 R	171 R		
A_2	ν_6	876 R	710*	1.40	(1.36)
	ν_7	406 R	368 R		
B_1	ν_8	3072 I.R.	2280 I.R.		
	ν_9	1294 I.R.	1040 I.R.		
	ν_{10}	848 I.R.	761 I.R.	1.94	1.97
	ν_{11}	571 I.R.	540 I.R.		
B_2	ν_{12}	697 I.R.	558 I.R.	1.29	1.25

* Calculated from the theoretical ratio after correction for anharmonicity.

TABLE VI. Frequency assignments and product rule ratios for *trans* $C_2H_2Cl_2$ and *trans* $C_2D_2Cl_2$.

Type		Trans $C_2H_2Cl_2$	Trans $C_2D_2Cl_2$	Theor. ratio	Obs. ratio
A_g	ν_1	3071 R	2325 R		
	ν_2	1576 R	1570 R		
	ν_3	1270 R	992 R	1.98	1.89
	ν_4	844 R	765 R		
	ν_5	349 R	346 R		
A_u	ν_6	895 I.R.	658 I.R.	1.40	1.36
	ν_7	192 I.R.*	192 I.R.*		
B_g	ν_8	758 R	657 R	1.17	1.15
B_u	ν_9	3080 I.R.	2285 I.R.		
	ν_{10}	1200 I.R.	912 I.R.		
	ν_{11}	817 I.R.	784 I.R.*	1.96	1.85
	ν_{12}	265 I.R.*	265 I.R.*		

* From combination tones.

branch ($K=0, 1, 2, \cdots$) the negative sign applies to the ^PQ branch ($K=1, 2, \cdots$).

The band center may be determined from the relation

$$^RQ_K + {}^PQ_{K+1} = 2\nu_0 \\ + [(A'-B') - (A''-B'')][K^2 + (K+1)^2]$$

by plotting $^RQ_K + {}^PQ_{K+1}$ against $K^2 + (K+1)^2$ and extrapolating to zero (see Fig. 7). From this graph it is found that $\nu_0 = 898.1$ cm^{-1} and $(A'-B') - (A''-B'') = -0.0084$ cm^{-1}.

Individual values for $(A'-B')$ and $(A''-B'')$ may be obtained from the combination relations

$$^RQ_K - {}^PQ_K = 4(A'-B')K, \\ ^RQ_{K-1} - {}^PQ_{K+1} = 4(A''-B'')K.$$

Since the band positions were determined with an accuracy of ± 0.1 cm^{-1}, the probable errors in the values of $(A'-B')$ and $(A''-B'')$ will depend on the K value but will be of the order of $\pm(0.2/4 \times 15) \sim 0.004$ cm^{-1}. Hence from Table VII we see that

$$A'-B' = 1.674 \pm 0.004 \text{ cm}^{-1}, \\ A''-B'' = 1.682 \pm 0.004 \text{ cm}^{-1},$$

these values being consistent with the difference found above. Substituting into Eq. (1) the frequencies of the rotation lines were calculated and found to agree with the observed values in most cases to ± 0.1 cm^{-1}, though occasional differences of ± 0.2 cm^{-1} were found.

If we take $I_{B'} = I_{B''} =$ mean of I_B and I_C (obtained from electron diffraction data),
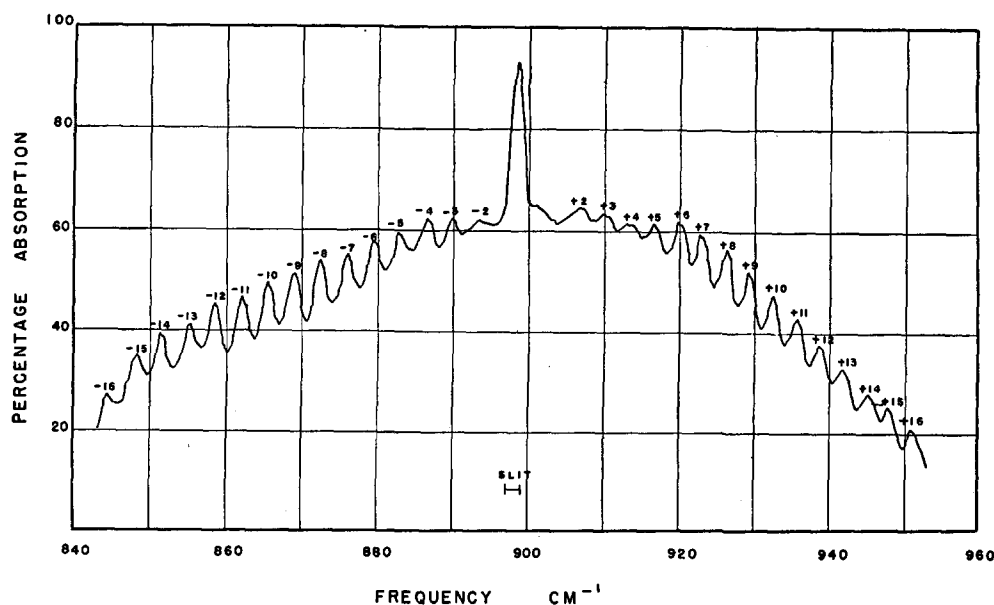
$$B' = B'' = 0.050 \pm 0.001 \text{ cm}^{-1}.$$

FIG. 6. Rotational fine structure of the 898.1-cm^{-1} band of *trans*-dichloroethylene. Absorption path 10-cm, pressure 30-mm Hg, Temperature 20°C.

Hence,

$$A' = 1.724 \pm 0.005 \text{ cm}^{-1}; \quad A'' = 1.733 \pm 0.005 \text{ cm}^{-1},$$

and

$$I_{A'} = 16.23 \pm 0.05 \times 10^{-40} \text{ g cm}^2;$$
$$I_{A''} = 16.15 \pm 0.05 \times 10^{-40} \text{ g cm}^2.$$

These values are considerably more accurate than the value obtained from the electron diffraction results *viz.* 15.8×10^{-40} g cm².

A slight refinement of the molecular dimensions for the *trans* molecule may be made in the following manner. For small changes in the C−Cl and C=C bond lengths and the $\overset{\frown}{\text{Cl−C=C}}$ bond angle, the contribution from the hydrogen atoms to the least moment of inertia is approximately constant. Hence by taking the C−H bond length to be 1.07A and the $\overset{\frown}{\text{H−C=C}}$ bond angle to be 120°, the hydrogen contribution may be evaluated and subtracted from the moment of inertia. The remaining contributions from the carbon and chlorine atoms depend on three variables, the C−Cl and C=C bond lengths and the $\overset{\frown}{\text{Cl−C=C}}$ bond angle. By using the electron diffraction result for the distance between the two chlorine atoms *viz.* 4.27±0.02A, the number of independent variables is reduced to two. Moments of inertia are then calculated for reasonable ranges of values of the C=C and C−Cl bond lengths and the values compared with the spectroscopic figure. The ranges used were $r_{C=C} = 1.34$ to 1.40A and $r_{C-Cl} = 1.65$ to 1.75A and it was found that the moments of inertia were consistent with the spectroscopic data only when

$$r_{C=C} + r_{C-Cl} = 3.08 \pm 0.01A.$$

TABLE VII. Rotational fine structure for 898 cm⁻¹ *trans* C₂H₂Cl₂ band.

K	ν obs.	ν calc.	Diff.	K	$^RQ_K - ^PQ_K$	$4K(A'-B')$	$(A'-B')$
−16	844.3	844.1	0.2	2	906.7−893.1	13.6	(1.700)
−15	847.8	847.7	0.1	3	909.7−889.6	20.1	1.675
−14	851.4	851.3	0.1	4	913.0−886.3	26.7	1.669
−13	854.9	854.8	0.1	5	916.4−882.8	33.6	1.680
−12	858.3	858.4	−0.1	6	919.7−879.3	40.4	1.683
−11	861.9	861.9	0.0	7	922.9−875.9	47.0	1.679
−10	865.4	865.5	−0.1	8	926.0−872.4	53.6	1.675
−9	868.9	869.0	−0.1	9	929.2−868.9	60.3	1.675
−8	872.4	872.5	−0.1	10	932.4−865.4	67.0	1.675
−7	875.9	875.9	0.0	11	935.6−861.9	73.7	1.675
−6	879.3	879.4	−0.1	12	938.7−858.3	80.4	1.675
−5	882.8	882.8	0.0	13	941.7−854.9	86.8	1.669
−4	886.3	886.3	0.0	14	945.0−851.4	93.6	1.671
−3	889.6	889.7	−0.1	15	947.9−847.8	100.1	1.668
−2	893.1	893.1	0.0	16	951.0−844.3	106.7	1.667
−1		896.4					
0		899.8				Mean =1.674	
1		903.1					
2	906.7	906.5	0.2	K	$^RQ_{K-1} - ^PQ_{K+1}$	$4K(A''-B'')$	$(A''-B'')$
3	909.7	909.8	−0.1	3	906.7−886.3	20.4	(1.700)
4	913.0	913.0	0.0	4	909.7−882.8	26.9	1.681
5	916.4	916.3	0.1	5	913.0−879.4	33.6	1.680
6	919.7	919.6	0.1	6	916.4−875.9	40.5	1.687
7	922.9	922.8	0.1	7	919.7−872.5	47.2	1.686
8	926.0	926.0	0.0	8	922.9−869.0	53.9	1.684
9	929.2	929.2	0.0	9	926.0−865.5	60.5	1.681
10	932.4	932.4	0.0	10	929.2−861.9	67.3	1.683
11	935.6	935.6	0.0	11	932.4−858.4	74.0	1.682
12	938.7	938.8	−0.1	12	935.6−854.8	80.8	1.683
13	941.7	941.9	−0.2	13	938.7−851.3	87.4	1.681
14	945.0	945.0	0.0	14	941.7−847.7	94.0	1.679
15	947.9	948.1	−0.2	15	945.0−844.1	100.9	1.682
16	951.0	951.2	−0.2			Mean =1.682	

POTENTIAL FUNCTION FOR OUT-OF-PLANE FREQUENCIES

Type A_2 (*Cis*)

A general quadratic potential function was used (Fig. 8) *viz.*

$$V = k_\theta \theta^2 + k_\phi \phi^2 + k'\theta\phi,$$

where θ = angle of wag between the CHCl group and the extended C=C axis, ϕ = angle of twist about the extended C=C referred to the equilibrium plane, k_θ, k_ϕ, k' are the appropriate force constants.

The equations for the frequencies were derived by

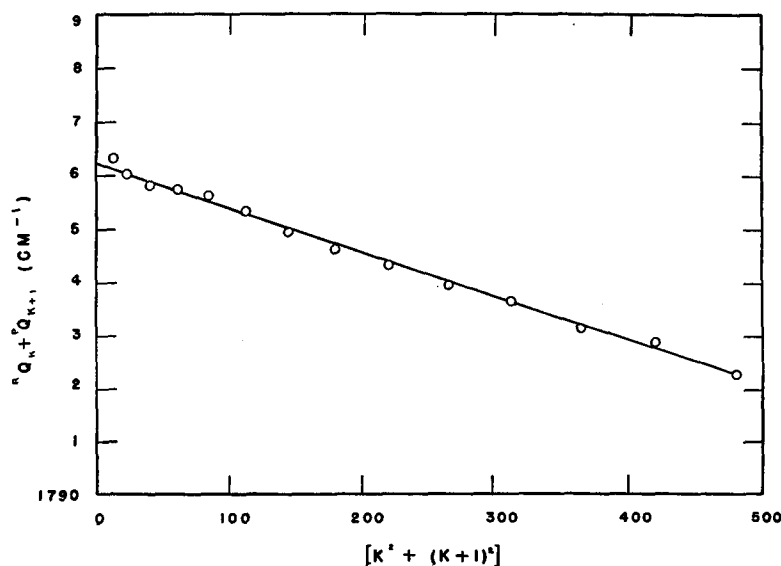FIG. 7. Determination of the band center for the 898-cm⁻¹ band of *trans* dichloroethylene.
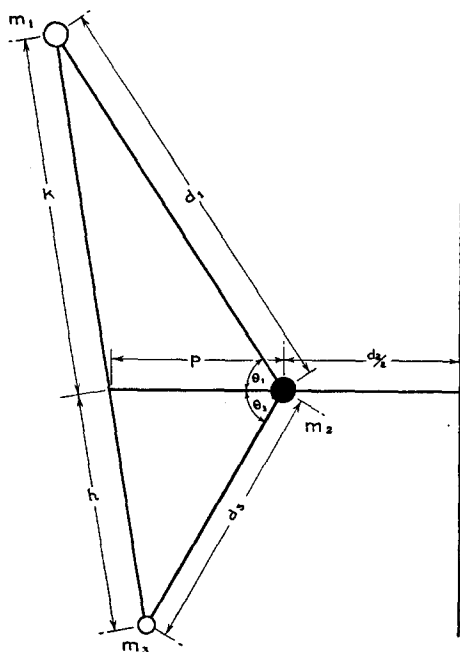
FIG. 8. ●=C, ○=Cl, ○=H. Structural parameters for one half of the dichloroethylene molecule.

the method of Eliashevich[17] and may be expressed as follows:

$$\lambda_1{}^2 + \lambda_2{}^2 = 2(ak_\theta + ck_\phi - bk'),$$
$$\lambda_1{}^2\lambda_2{}^2 = (4k_\theta k_\phi - k'^2)(ac - b^2),$$

where

$$\lambda = 2\pi c\nu,$$

$$a = \left(\frac{h'^2}{m_1} + \frac{f^2}{m_2} + \frac{k'^2}{m_3}\right),$$

$$b = \left(-\frac{h'}{m_1 d_1 \sin\theta_1} + \frac{fg}{m_2} + \frac{k'}{m_3 d_3 \sin\theta_3}\right),$$

$$c = \left(\frac{1}{m_1 d_1{}^2 \sin^2\theta_1} + \frac{g^2}{m_2} + \frac{1}{m_3 d_3{}^2 \sin^2\theta_3}\right);$$

$$h' = \frac{h}{p(h+k)}, \quad k' = \frac{k}{p(h+k)}, \quad f = \frac{1}{p} + \frac{2}{d_2},$$

$$g = -\frac{1}{d_1 \sin\theta_1} + \frac{1}{d_3 \sin\theta_3}.$$

The equations for the other out-of-plane vibrations for the *cis* and *trans* molecules may be obtained from the above as follows:

type B_2 (*cis*) : let $d_2 = \infty$, $\quad k_\phi = 0$, $\quad k' = 0$,
type A_u (*trans*) : let $d_2 = \infty$,
type B_g (*trans*) : let $k_\phi = 0$, $\quad k' = 0$.

[17] M. A. Eliashevich, Comptes. Rendus. U.R.S.S. **28**, 604 (1940).

The condition that $d_2 = \infty$ eliminates the contribution to the potential energy from the relative motion of the carbon atoms.

Force constants may be evaluated as follows. Using $\nu_8(B_g) = 758$ cm^{-1} for the *trans* molecule,

$$k_\theta = 1.12 \times 10^{-12} \text{ dyne cm/radian}.$$

Assuming that this force constant may be taken over for type A_2 (*cis*) as has been done by Pitzer and Freeman[4] and using $\nu_6 = 876$ cm^{-1}, $\nu_7 = 406$ cm^{-1} in the above equations,

$$k_\phi = 1.46 \times 10^{-12} \text{ dyne cm/radian},$$
$$k' = 0.62 \times 10^{-12} \text{ dyne cm/radian}.$$

Using these force constants to calculate the two frequencies for *cis* $C_2D_2Cl_2$ we obtain

$$\nu_6 = 678 \text{ cm}^{-1}, \quad \nu_7 = 374 \text{ cm}^{-1}.$$

The low frequency agrees well with the Raman frequency observed at 368 cm^{-1} while the other frequency is in tolerable agreement with the value deduced from the product rule *viz.* 710 cm^{-1}.

In a similar manner the wagging force constant for type B_2 (*cis*) may be used in type A_u (*trans*). Using $\nu_{12}(B_2) = 697$ cm^{-1} for the *cis* molecule, we obtain

$$k_\theta = 1.51 \times 10^{-12} \text{ dyne cm/radian}.$$

Only one of the A_u frequencies for the *trans* molecule, however, has been observed, *viz.* at 895 cm^{-1} for $C_2H_2Cl_2$ and 658 cm^{-1} for $C_2D_2Cl_2$. Since the unobserved frequency is expected to be low, it will change very little from $C_2H_2Cl_2$ to $C_2D_2Cl_2$ and may be assumed to be unchanged to a very good approximation. The three unknowns for type A_u, *viz.* k_ϕ, k', and ν_7 may then be evaluated from the three equations, for the sums of the frequencies in $C_2H_2Cl_2$ and $C_2D_2Cl_2$ and the product of the frequencies in either $C_2H_2Cl_2$ or $C_2D_2Cl_2$. Solution of these equations gives

$$k_\phi = 1.00 \times 10^{-12} \text{ dyne cm/radian},$$
$$k' = 0.20 \times 10^{-12} \text{ dyne cm/radian},$$
$$\nu_7 = 196 \text{ cm}^{-1}.$$

This value for the low frequency is in good agreement with the value 192 cm^{-1} deduced from combination tones.
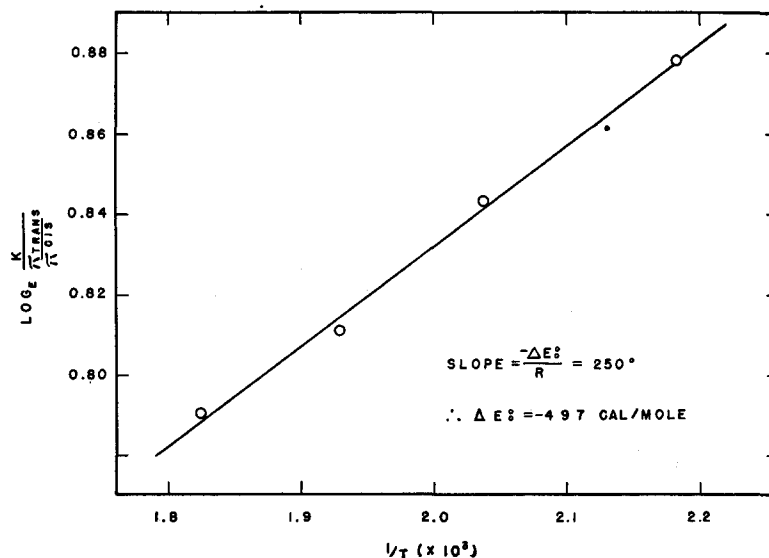
THE ENERGY DIFFERENCE BETWEEN *CIS* AND *TRANS* DICHLOROETHYLENE

For an equilibrium of the type *cis*⇌*trans* the equilibrium constant[18]

$$K = \frac{\text{Number of } cis \text{ molecules}}{\text{Number of } trans \text{ molecules}}$$

$$= \frac{f_{cis}}{f_{trans}} \cdot \exp(-\Delta E_0{}^0/RT), \quad (2)$$

[18] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The Macmillan Company, New York, 1939), p. 157.

FIG. 9. Plot of $\log_e K/(\Pi\ trans/ \Pi\ cis)$ against $1/T$.

where f_{cis}, f_{trans} are the partition functions of *cis*- and *trans*-dichloroethylene, respectively, R is the gas constant, and ΔE_0^0 is the energy difference between the two forms at $0°K$.

Assuming the rigid rotator and harmonic oscillator approximations[19]

$$\frac{f_{cis}}{f_{trans}} = \left[\frac{(I_A I_B I_C)_{cis}}{(I_A I_B I_C)_{trans}}\right]^{\frac{1}{2}} \frac{\prod_{i=1}^{12}(1-e^{-h\nu i/kT})_{trans}}{\prod_{i=1}^{12}(1-e^{-h\nu i/kT})_{cis}}. \quad (3)$$

Substituting in Eq. (2) and taking logarithms, we get

$$\log_e\frac{K}{\Pi_{trans}/\Pi_{cis}}$$
$$= \frac{1}{2}\log_e\left[\frac{(I_A I_B I_C)_{cis}}{(I_A I_B I_C)_{trans}}\right] - \Delta E_0^0/RT. \quad (4)$$

Hence by plotting $\log_e K/(\Pi_{trans}/\Pi_{cis})$ against $1/T$ a straight line is obtained whose slope is $-\Delta E_0^0/R$ and intercept $\frac{1}{2}\log_e(I_A I_B I_C)_{cis}/(I_A I_B I_C)_{trans}$. In this way the value of ΔE_0^0 is not dependent on experimental errors in the determination of the principal moments of inertia of the two molecules.

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[19] See reference 1, p. 503, *et. seq.*

Wood and Stevenson[5] have obtained equilibrium data for the isomerization of *cis* and *trans* dichloroethylene at $185°C$, $215°C$, $245°C$, and $275°C$. Using their values of K and our values of Π_{trans}/Π_{cis} and plotting $\log_e K/(\Pi_{trans}/\Pi_{cis})$ against $1/T$ (see Fig. 9) the best straight line obtained by the method of least squares gives

$$\Delta E_0^0 = -497 \text{ cal./mole.}$$

The principal source of inaccuracy in this determination lies in the assignment to the *trans* molecule of the two low frequencies obtained from combination tones. If we assume that these frequencies *viz.* 192 and 265 cm^{-1}, are accurate to ± 5 cm^{-1}, the error introduced into ΔE_0^0 is ± 30 cal./mole. Hence for dichloroethylene the *cis* isomer is more stable than the *trans* isomer by 500 ± 30 cal./mole.

The moment of inertia ratio $[(I_A I_B I_C)_{cis}/ (I_A I_B I_C)_{trans}]^{\frac{1}{2}}$ may also be evaluated from Eq. (4) a range of values of 1.39 ± 0.04 being obtained. This is consistent with the value calculated from electron diffraction results *viz.* 1.38.

ACKNOWLEDGMENT