

Internal Rotation I A Product Rule for Cis and Trans Isomers

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TABLE V. Calculated vs. assigned frequencies (cm⁻¹).

Species	Freq. no.	Benzene			sym-benzene-d ₄			Benzene-d ₆		
		Calc.	Assigned	% Diff.	Calc.	Assigned	% Diff.	Calc.	Assigned	% Diff.
A _{1g}	1	996	992	+0.4	948	956	-0.8	939	943	-0.4
	2	3061	3062	0.0	3065	3053	+0.4	2294	2293	0.0
A _{2g}	3	1323	1326	-0.2	1245	1230±2%	—	1034	1037	+0.3
B _{1u}	12	1017	1010	+0.7	1006	1004	+0.2	960	963	-0.3
	13	3058	3060	0.0	2289	2282	+0.3	2291	2290	0.0
B _{2u}	14	1647	1648	0.0	1614	1600	+0.9	1572	1571	+0.1
	15	1112	1110	+0.2	900	920	-2.2	824	825	-0.1
E _{2u}	18	1053	1037	+1.3				815	813	+0.2
	19	1469	1485	-1.1				1320	1333	-1.0
	20	3082	3080	+0.1				2301	2294	+0.3
E _{1g}	6	599	606	-1.2				568	577	-1.6
	7	3050	3047	+0.1				2280	2265	+0.7
	8	1617	1596	+1.3				1561	1552	+0.6
	9	1180	1178	+0.2				869	867	+0.2

Greek constants from which these values are calculated.

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Internal Rotation I

A Product Rule for *Cis*- and *Trans*-Isomers

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The assumption of equal force constants in the potential functions of *cis*- and *trans*-forms leads to a product rule for the planar vibrations of rotational isomers.

The rotational isomers of symmetrical dichloro- and dibromoethane are *trans*- and "gauche."

IF the potential energy of a molecule is expressed as the most general quadratic function of the displacements from the equilibrium configuration, it has been shown¹ that the product of the frequencies of the normal modes of vibration belonging to the same symmetry class can be expressed as the product of two functions. One of these is a function of the force constants only, and the other a function of the masses of the atoms and internuclear distances in the molecule. If some of the atoms of a molecule are replaced by their isotopes the potential energy of the isotopic molecule involves the same force constants as that for the original molecule since isotopic substitution does not change the internal field. Consequently the ratio of the product of the frequencies of a molecule to the product of the frequencies belonging to the same symmetry class of the isotopic molecule is the ratio of the two func-

tions involving masses and internuclear distances only. The Teller-Redlich² product rule expresses this ratio in terms of molecular weights and moments of inertia.

To obtain a product rule for rotational isomers it is necessary as a first approximation to assume that the force constants appearing in the potential function of the two isomers are the same.³ This will be true to a very good approximation for all planar force constants⁴ but need not be true for out-of-plane constants where in general the rotational isomers have different activation energies and thus different curvatures of the potential function at their respective minima. Even for the in-plane vibrations the interaction constants between groups or atoms on neighboring atoms will in general be quite different for *cis*- and *trans*-configurations. However, to a good first approximation, the interaction constants between atoms whose internuclear distance is independent of azimuthal angle will not be very

TABLE I.

<i>Cis</i> -C _{2v}			<i>Trans</i> -C _{2h}		
Type	No. of vib'ns	Non-genuine vib'ns	Type	No. of vib'ns	Non-genuine vib'ns
A ₁	5	T _y	A _g	5	R _z
B ₁	4	T _z R _z	B _u	4	T _z T _y
A ₂	2	R _y	A _u	2	T _z
B ₂	1	T _z R _x	B _g	1	R _z R _y

¹ E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

² E. Teller, quoted in W. R. Angus *et al.*, J. Chem. Soc. (1936), p. 971; O. Redlich, Zeits. f. physik. Chemie B28, 371 (1935).

³ E. L. Pace, J. Chem. Phys. 15, 528 (1947), has obtained a product rule for the E_g and E_u vibrations of an X₂Y₄ molecule by assuming the force constants to be the same and that the interaction constants of the XY₂ groups may be neglected.

⁴ J. A. A. Ketelaar, Rec. Trav. Chim. 58, 266 (1939); J. Sherman and J. A. A. Ketelaar, Physica 6, 572 (1939). Both valence bond and molecular orbital treatments of *cis*- and *trans*-dichloroethylenes gave the same C-Cl bond length. This means that the bond constants are the same.

different for *cis*- and *trans*-forms. When the internuclear distance changes as a function of azimuthal angle the interaction constants will be different but very small since these interactions are between substituents on non-adjacent atoms.

Inspection of the expressions⁵ for the product of the frequencies of vibrations in corresponding symmetry classes for two molecules with *cis*- and *trans*-configurations shows that the ratio of the product of the *trans*-frequencies to that of the *cis*- is given by:

$$\frac{\Pi^T}{\Pi^C} = \left\{ \left(\frac{m_1^C}{m_1^T} \right)^\alpha \left(\frac{m_2^C}{m_2^T} \right)^\beta \cdots \left(\frac{M^T}{M^C} \right)^\alpha \right. \\ \left. \frac{(I_x)^{\delta_x^T} (I_y)^{\delta_y^T} (I_z)^{\delta_z^T}}{(I_x)^{\delta_x^C} (I_y)^{\delta_y^C} (I_z)^{\delta_z^C}} \cdot \left(\frac{4}{d^2} \right)^{\delta_x^T + \delta_y^T + \delta_z^T} \cdot \left(\frac{d^2}{4} \right)^{\delta_x^C + \delta_y^C + \delta_z^C} \right\}^{\frac{1}{2}} \quad (1)$$

where the superscripts *C*, *T* indicate *cis*- and *trans*- respectively and $m_1 m_2 \cdots \alpha, \beta, \cdots M, I_x, I_y, I_z$ have the same significance as in the Teller-Redlich product rule (see G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand and Company, New York, 1945), p. 232); a, b are the number of translations of the symmetry type considered; $\delta_x^T, \delta_y^T, \delta_z^T, \delta_x^C, \delta_y^C, \delta_z^C$, are 1 or 0 depending on whether or not the rotation about the x, y, z axis is a non-genuine vibration of the symmetry type considered; d is the internuclear distance in Å° between the two atoms lying on the rotation axis (x axis) about which *cis*- and *trans*-configurations may be obtained by rotation; the moments of inertia and molecular weights are expressed in atomic units and the xy plane is the plane of the molecule.

As an example one may consider *cis*- and *trans*-dichloroethylene. The symmetry types and non-genuine vibrations are given in Table I.

It is readily seen for the totally symmetric classes of *trans*- and *cis*- since R_z and T_y are the only non-genuine vibrations that appear, that $a=0$ and $b=1$, and $\delta_x^T = \delta_y^T = \delta_z^C = \delta_y^C = \delta_z^C = 0$ and $\delta_x^T = 1$.

If there is no isotopic substitution $m_1^T = m_1^C$ etc. so that relation (1) becomes

$$\Pi_{A_g}/\Pi_{A_1} = \left\{ \frac{I_z^T}{M} \cdot \frac{4}{d^2} \right\}^{\frac{1}{2}}$$

Table II lists various product ratios for *cis*- and *trans*-dichloroethylene, dibromoethylene, and butene-2.

The agreement over a wide range of product ratios is quite satisfactory and indicates that this

⁵ F. Lechner, S. B. Akad. Wiss. Wien (IIA) **141**, 633 (1932); A. Verleysen, Ann. Bruxelles **59**, 267 (1939).

TABLE II.

Product ratio	Molecule	Ratio calc. from (1)	Observed ratio	Percent diff.
Π_{A_g}/Π_{A_1}	$C_2H_2Cl_2^a$	2.70	2.57	5.1
$\Pi_{A_g}/\Pi_{A_1}^{(i)*}$		5.35	5.03	6.3
$\Pi_{A_g}^{(i)}/\Pi_{A_1}$		1.36	1.36	—
$\Pi_{A_g}^{(i)}/\Pi_{A_1}^{(i)}$		2.69	2.66	1.1
Π_{B_u}/Π_{B_1}		0.436	0.422	3.3
$\Pi_{B_u}/\Pi_{B_1}^{(i)}$		0.861	0.822	4.5
$\Pi_{B_u}^{(i)}/\Pi_{B_1}$		0.224	0.227	-1.3
$\Pi_{B_u}^{(i)}/\Pi_{B_1}^{(i)}$		0.435	0.442	-1.6
Π_{A_g}/Π_{A_1}	$C_2H_2Br_2^b$	3.1	2.8	10.0
Π_{A_g}/Π_{A_1}	$CH_3CH=CHCH_3^c$	2.3	2.1	11.0

* The superscript (i) designates the completely deuterated molecule.

^a Bond distances from L. R. Maxwell (reference 7). B_u and B_1 frequencies from H. J. Bernstein and D. A. Ramsay (to be published); A_g and A_u frequencies from T. Wu (reference 8).

^b Bond distances from L. R. Maxwell (reference 7); frequencies are those of A. Dadiou, A. Pongratz, and K. W. F. Kohlrausch, Monats. f. Chem. **60**, 221 (1932).

^c Bond distances from L. R. Maxwell (reference 7); frequencies are those given by Kohlrausch, *Ramanspektren* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1945).

ratio may be used to an accuracy of within 10 percent.

Structure of the Rotational Isomers of 1,2-Dichloro- and 1,2-Dibromoethane

Equation (1) may be applied to the rotational isomers of substituted ethanes which have a plane of symmetry. Because of the lack of free rotation about the C—C bond in dihalogen substituted ethanes two rotational isomers are present.⁶ It is known definitely that the more stable isomer has a *trans*-(C_{2h}) configuration⁶ but whether the other isomer is *cis*- or "gauche" has not been established. The "gauche" form is one in which the halogens are at an intermediate position, between *cis*- and *trans*-. If the other isomer has C_{2v} symmetry then the computed product ratio from Eq. (1) should agree to within 10 percent with the observed ratio. From the known bond distances⁷ and angles, the value computed for Π_{A_g}/Π_{A_1} for 1,2-dichloroethane and 1,2-dibromoethane are 2.36 and 2.76 respectively. The observed ratios⁸ are 1.46 and 1.90 respectively. These large differences between observed and computed ratios are strong evidence that the configuration of the less stable rotational isomer in these halogenated ethanes is "gauche."

It is unsafe to extend the use of this rule to calculate the azimuthal angle that the "gauche" forms make with the *trans*-configuration since out-of-plane vibrations are involved and the approximation of equality of force constants would not be valid.

⁶ S. Mizushima and Y. Morino, Proc. Ind. Acad. Sci. **8A**, 315 (1938).

⁷ L. R. Maxwell, J. Opt. Soc. Am. **30**, 374 (1940).

⁸ The frequencies used to compute the observed ratios are taken from T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1946).