

On the Lattice Frequencies of 1,2Dihalogenoethanes

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Citation: *The Journal of Chemical Physics* **18**, 1420 (1950); doi: 10.1063/1.1747501

View online: <http://dx.doi.org/10.1063/1.1747501>

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Laboratory after a period of four months of almost continuous operation with protons (10 Mev), deuterons (20 Mev), and alpha-particles (40 Mev). The possible transmutation reactions include: $W(d, xn)Re$, $W(p, xn)Re$, $W(\alpha, pxn)Re$, and $W(\alpha, xn)Os$. In the procedure reported here, the long-lived isotopes of rhenium, $Re^{183,184}$, and osmium, Os^{185} , produced by the nuclear reactions $W^{182}(d, n)Re^{183}$, $W^{183}(d, 2n)Re^{183}$, $W^{183}(d, n)Re^{184}$, $W^{184}(d, 2n)Re^{184}$, $W^{182}(\alpha, pn)Re^{184}$, $W^{182}(\alpha, n)Os^{185}$, and $W^{183}(\alpha, 2n)Os^{185}$ were separated from the target element and from other possible long-lived transmutation products by a combination of volatility and solvent extraction methods.

The tungsten strip (approx. 2 g) was fused with 10 g of KOH and 0.5 g of KNO_3 at 500°C for 30 minutes to form the water-soluble tungstate, perrhenate, and osmate. The fused mass was dissolved in a minimum volume of cold water and centrifuged to remove insoluble matter. The solution was acidified with 16N HNO_3 precipitating tungstic acid which was removed by centrifugation. The supernatant containing the carrier-free radio-rhenium and radio-osmium was diluted to 5N and transferred to an all-glass distilling flask. The carrier-free radio-osmium, presumably as the volatile OsO_4 , was distilled into an ice-cooled trap containing 5 N HNO_3 . The rhenium activity remained in the residual solution. The HNO_3 distillate (25 ml) was extracted with two 25-ml aliquots of CCl_4 which removed over 95 percent of the radio-osmium from the aqueous phase. After washing with water to remove HNO_3 , the radio-osmium was quantitatively re-extracted from the CCl_4 phase with 2 ml of 0.1N NaOH which on neutralization gave an isotonic saline solution for biological investigation. The carrier-free radio-rhenium was isolated from the residual HNO_3 solution using the distillation procedure previously² described in the preparation of carrier-free rhenium from tantalum. The Os^{185} was identified by the 97-day half-life and by the 0.75-Mev gamma-ray previously reported.^{3,4} The $Re^{183,184}$ showed the 0.2- and 0.7-Mev beta-particle and the 1.0-Mev gamma-ray reported⁵ for 50-day Re^{184} . Half-life measurements showed an approximately 57-day period which began to lengthen after three weeks due to the approximately 240-day Re^{183} isotope. The activities were further identified by chemical separation using W, Re, and Os carriers.

We wish to thank Professor G. T. Seaborg for helpful suggestions, Mr. T. Putnam and Mr. B. Rossi and the crew of the 60-in. cyclotron for bombardments and Mrs. Alberta Mozley for assistance in counting.

* This document is based on work performed under Contract No. W-7405-eng-48-A for the AEC.

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On the Lattice Frequencies of 1,2-Dihalogenoethanes

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August 16, 1950

THE disappearance of many Raman lines of 1,2-dichloroethane and 1,2-dibromoethane (XH_2C-CH_2X) upon solidification was observed by Mizushima and Morino who explained this phenomenon, considering that these substances are in one molecular form (*trans*-) in the crystalline state and in two molecular forms (*trans*- and *gauche*) in the liquid state.¹ They also found low frequency Raman lines characteristic to the crystalline state which were considered to correspond to lattice vibrations. The assignment of these lattice frequencies can be made by the selection rule for molecular crystals recently developed by Ichishima² which is similar to that proposed by Halford.³

The lattice frequencies of a molecular crystal so far observed in the Raman effect are related closely to the structure of a single molecule. This enables us to adopt an approximate method in which we treat the motions of a molecule moving in a potential field formed by surrounding molecules in their equilibrium positions. According to our view the anharmonicity of the intermolecular forces which would give rise to the observed considerable temperature dependence² of lattice frequencies and the large value of thermal expansion coefficient of molecular crystals may be partly responsible for the characteristic vibrational modes of molecular crystals.

The molecules of 1,2-dihalogenoethanes in the crystalline state being in the *trans*- form with the symmetry C_{2h} , the symmetry of the said potential field would correspond to one of the subgroups of C_{2h} : i.e., C_i , C_2 , C_s , and C_{2h} . The existence of the center of symmetry (C_i) which is very probable in this case allows only the rotatory vibrations in the Raman effect and forbids the translatory vibrations. Of the three Raman active rotatory vibrations one about the molecular axis or the axis joining two halogen atoms would escape detection owing to the small change of polarizability. Therefore, the frequencies 53 and 74 cm^{-1} of 1,2-dichloroethane and 41 and 53 cm^{-1} of 1,2-dibromoethane observed below the transition point should be assigned to the rotatory vibrations about the two axes, both perpendicular to the molecular axis. Since the moments of inertia about these two axes are practically equal to each other, the appearance of two different frequencies for each of these two substances would be due to the difference of the restoring forces for these two motions. This would be seen from the result of the crystal structure analysis made for 1,2-diiodoethane⁴ which would not be much different from that for 1,2-dichloroethane or for 1,2-dibromoethane. The fact that only one lattice frequency (66 cm^{-1} for 1,2-dichloroethane and 49 cm^{-1} for 1,2-dibromoethane) was observed for each of these 1,2-dihalogenoethanes above the transition point can be reconciled with this view, since the free rotation about the molecular axis sets in above the transition point⁵ and the restoring forces tend to become equal to each other.

¹ S. Mizushima and Y. Morino, *Proc. Ind. Acad. Sci.* **8**, 315 (1938), Raman Jubilee Volume. See also Mizushima, Morino, Watanabe, Shimanouchi, and Yamaguchi, *J. Chem. Phys.* **17**, 591 (1949).

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³ R. S. Halford, *J. Chem. Phys.* **14**, 8 (1946).

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⁵ H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.* **18**, 162 (1950).

Directed Valence in IF_6 and IF_7

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August 16, 1950

RECENTLY Lord and co-workers¹ have studied the infra-red and Raman spectra of iodine pentafluoride and iodine heptafluoride and have concluded that the IF_6 molecule is a tetragonal pyramid (C_{4v} symmetry) while the IF_7 molecule is a pentagonal bipyramid (D_{3h} symmetry). By applying group theory to the problem of directed valence, Kimball² showed that the former structure is consistent with sp^2d^2 , sd^4 , p^3d^2 , or pd^4 hybridization, but he did not consider the pentagonal bipyramid for the coordination number seven.³ Duffey⁴ has recently shown that a plausible orthogonal set of pentagonal bipyramidal orbitals can be constructed with the over-all composition sp^3d^3 .

Since atomic iodine has the electronic structure $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}(4s)^2(4p)^6(4d)^{10}(5s)^2(5p)^5$, it is evident that in compounds where iodine has a multiple valency it is necessary to use either the $5d$ or $4f$ orbitals or both. Since it does not appear obvious that the $5d$ orbitals must necessarily be chosen in preference to the $4f$, it seems desirable to extend Kimball's group theoretical treatment to include f electrons for the symmetries C_{4v} and D_{3h} .

Tables I and II give the possible compositions for bonds corresponding to these symmetries. The representations leading to

TABLE I. Five tetragonal pyramidal bonds.

C_{4v}	A_1	A_2	B_1	B_2	E
s	1	0	0	0	0
p	1	0	0	0	1
d	1	0	1	1	1
f	1	0	1	1	2
σ	2	0	0	1	1
π	1	1	1	1	3

TABLE II. Seven pentagonal bipyramidal bonds.*

D_{5h}	A_1'	A_1''	A_2'	A_2''	E_1'	E_1''	E_2'	E_2''
s	1	0	0	0	0	0	0	0
p	0	0	0	1	1	0	0	0
d	1	0	0	0	0	1	1	0
f	0	0	0	1	1	0	1	1
σ	2	0	0	1	1	0	1	0
π	0	0	1	1	2	2	1	1

* The representation A_2'' in this table is labeled A_1'' in Kimball's Table XIII.

π -bonds are included in the tables, although the high electronegativity of fluorine would seem to preclude any significant contribution of bonds of the type I^--F^+ .

For IF_5 there are 21 distinct configurations consistent with C_{4v} symmetry, as well as an infinite number of linear combinations. There are seven valence electrons outside the closed shells of iodine; so we must also account for two non-bonding electrons. Since the energy of electrons in the $5s$ and $5p$ orbitals is appreciably lower than that for $5d$ or $4f$, it seems reasonable to exclude all those configurations which fail to make maximum use of these orbitals, either for bonding or for the non-bonding pair. When this is done, only six remain: sp^3d , fs^2p^3 , sp^2d^2 , fs^2p^2d , and fp^3d .

A particularly inviting explanation for the IF_5 structure is obtained by forming six approximately octahedral orbitals, one of which is occupied by the non-bonding pair, thus minimizing the overlap. For full octahedral symmetry (O_h), the only allowed combinations are sp^3d and f^2sd^2 and the latter does not use the $5p$ orbitals. In addition to these two, $f^2sp^2d^2$ and $fs^2p^2d^2$ satisfy the symmetry (D_{4h}) of a tetragonal bipyramid, but neither uses all the p orbitals. Many combinations give non-planar tetragonal bonds (C_{4v} symmetry) but only three satisfy our additional requirements: sp^3d^2 , sp^3df , and sp^3f^2 .

For IF_7 , which uses all the valence electrons for bonding, the possibilities are more limited. Of the eight configurations allowed, only two, $d^2p^3d^2$ and $f^2sp^3d^2$, utilize fully the $5s$ and $5p$ orbitals. Both of these are also consistent with the ZrF_7^{3-} and TaF_7^{2-} structures, the only other experimentally observed spatial arrangements with coordination number seven.

It is evident that further study and experiments are required before one can attempt to assess the contributions (if any) of f electrons to these structures.

The author wishes to express his indebtedness to Professor W. G. McMillan, Jr. for many helpful discussions.

¹ Lord, Lynch, Schumb, and Slowinski, J. Am. Chem. Soc. **72**, 522 (1950).

² G. E. Kimball, J. Chem. Phys. **8**, 188 (1940).

³ Kimball discussed pentagonal plane orbitals (p^2d^3) for coordination number five, but excluded them as unstable because of steric interference.

⁴ G. H. Duffey, J. Chem. Phys. **18**, 943 (1950).

On Heat Conductivity in Liquids*

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August 18, 1950

THIS note is not concerned with the more formal and rigorous statistical theories of transport phenomena in liquids such as those of Kirkwood¹ and Born and Green.² Rather, its purpose is to call attention to a simple quasi-empirical relation which per-

TABLE I. The relative variation of heat conductivity in C_2H_5OH as a function of temperature and pressure.

	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Experiment
$K_{30^\circ C}$					
$K_{75^\circ C}$	0.93	1.17	1.08	1.02	1.03
$K_{9000 \text{ kg/cm}^2}$					
$K_{2000 \text{ kg/cm}^2}$	1.00	1.82	2.60	1.49	1.45

TABLE II. Pressure variation of heat conductivity in C_2H_5OH .

Pressure in $\text{kg/cm}^2 \times 10^{-3}$	$\frac{K(P)}{K(0)}$ from Eq. (4)	$\frac{K(P)}{K(0)}$ from experiment
0	1.00	1.00
1	1.16	1.20
2	1.32	1.34
4	1.52	1.55
6	1.76	1.72
9	1.92	1.92
12	2.45	2.09

mits estimates of the temperature and pressure variations of heat conductivities.

Three formulas have been used in the past for the heat conductivity of a liquid; one of these is

$$K \sim C\lambda(mkT)^{1/2}\delta^{-3}, \quad (1)$$

where C is the specific heat per unit mass, λ the mean free path, k Boltzmann's constant, m the molecular weight, and T the absolute temperature. This equation is that used in elementary kinetic theory of gases, in which λ for liquids is usually assumed approximately equal to the interatomic distance δ .

Bridgman³ has suggested the use of

$$K \sim C\delta^{-2}v_s m, \quad (2)$$

where v_s is the velocity of sound. This dimensional equation gave surprisingly good values for the heat conductivity of liquids but failed to predict the pressure variation satisfactorily.

Kittel⁴ and Kincaid and Eyring⁵ have applied the equation

$$K \sim C v_T \delta^{-1} S^{-1} m, \quad (3)$$

where S is the free path in the available volume, which the molecule is assumed to traverse in a gas-like manner in order to execute a collision with a neighbor. This formula also fails to give satisfactory agreement for temperature and pressure variations.

We would like to call attention to the fact that a combination of Eq. (2) and Eq. (3) leads to a more satisfactory model. Thus we propose to write

$$K \sim C\delta^{-1}[(S/v_T) + (\delta/v_s)]^{-1} m. \quad (4)$$

This equation may be interpreted as endowing the available volume with a gas-like resistivity in series with which is the resistivity of the imperfectly rigid but elastic molecule. In other words, a time $t = \delta/v_s$ is required during the actual collision for the momentum of one molecule to be transferred to its neighbor. This t is the order of magnitude of the reciprocal of a low frequency molecular vibration.

We must not expect accurate predictions of the absolute value of heat conductivity, owing to the crude nature of Eqs. (1)–(4) and our inability to estimate the role of vibrational, rotational, and translational degrees of freedom, respectively. We may, however, inquire concerning the temperature and pressure variation of the heat conductivity. A comparison of the various models with experiment is shown in Table I, where to v_s we have arbitrarily assigned the value 2.85×10^6 cm/sec., a not implausible value. Such a value implies that the collision time is comparable to the time required to cross the mean free path at ordinary pressures and is the dominant effect at high pressures. For the available volume V_a of C_2H_5OH at $30^\circ C$ we have used 17 cm^3 . The value of