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Paul C. Cross and Farrington Daniels

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Chemical Aspects of the Infrared Absorption Spectra of the Ethyl Halides

PAUL C. CROSS AND FARRINGTON DANIELS, *University of Wisconsin*

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The infrared absorption spectra of ethyl chloride, ethyl bromide and ethyl iodide have been determined with a prism spectrometer between 1.5μ and 15μ . Eight experimentally observed fundamental frequencies have been selected which, together with their first harmonics and simple combinations, are shown to account for the entire spectrum. A type of vibration between atom pairs believed

to represent the important feature of the motion of the atoms is suggested for each of these fundamentals. The shifts in the absorption maxima produced by the substitution of the different halogens together with absorption and Raman data of related compounds are used in selecting these types of vibration. The bearing of these hypotheses on problems in chemical kinetics is discussed.

IN connection with an extended study of the decomposition of ethyl bromide and related compounds in this laboratory, it was decided to investigate other phenomena connected with the motion of the atoms in the molecule. Remarkable advances in this field have been made through the study of infrared spectra of simple molecules¹ as a result of new mathematical concepts, improved apparatus, and an unexpected wealth of Raman data. Although the more complex molecules such as ethyl bromide cannot yet be subjected to exact mathematical treatment, many useful empirical deductions can be made, and the study of their spectra should not be postponed because of the inability to make a rigorous interpretation in terms of the latest theories. The complicated molecules are often more interesting from a chemical standpoint.

The authors have sought to determine and analyze the infrared absorption spectra of ethyl chloride, ethyl bromide and ethyl iodide from 1.5μ to 15μ . They have endeavored to determine the fundamental frequencies of vibration which combine to form the whole vibrational spectrum, and to associate with each a characteristic type of motion between specific atoms.

The spectrometer used did not permit the observation of the rotational fine structure of the absorption bands (nor was this desirable for the present purpose) but it gave with sufficient precision the positions of the bands and their approximate relative intensities. In the compounds studied, the spectra were quite similar, the bands in general shifting toward lower frequencies with

increasing weight of the halogen. Some of the bands shifted more than others and it is logical to attribute the bands with the larger shifts to atom motions in the molecule which directly involve the halogens.

The first attempt at analysis of a system as complex as the ethyl halides is likely to be incomplete. The solution of certain mathematical problems would be of great help, but it must be remembered that the results of such calculations are no more reliable than the assumptions upon which the mathematical operations are based.

APPARATUS

The spectrometer was constructed by the authors with the help of Mr. Lee Henke, mechanic of the Chemistry Department. It employs the Wadsworth mounting of prism and plane mirror and is equipped with a 60° rocksalt prism having faces 6 cm square. The energy is measured by a Moll thermopile and a Cambridge Paschen-type galvanometer.

The spectrometer was calibrated² for 25° with refractive indices from Paschen³ and temperature coefficients from Liebreich.^{4, 5}

The standard wave-length used for calibration was the 4.26μ band of carbon dioxide in the atmosphere. Although this band is somewhat dif-

¹ Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

² Complete details will be given in another communication.

³ Paschen, *Ann. d. Physik* **26**, 120 (1908).

⁴ Liebreich, *Verh. d. D. Phys. Ges.* **13**, 700 (1911); **13**, 1 (1911).

⁵ Schaefer and Matossi, *Das Ultrarot Spectrum*, page 47, Julius Springer, Berlin, 1930.

fuse, it is very convenient to use and it is located in the region studied. The setting of the spectrometer was checked at frequent intervals during a measurement by reference to this band.

The spectrometer is capable of measuring absolute wave-lengths with an accuracy of $\pm 0.02\mu$ and wave-length differences between ethyl bromide and iodide with an accuracy of $\pm 0.005\mu$, except in the region of the longer wave-lengths.

DETERMINATION OF SPECTRA

The results are shown in Figs. 1 and 2 in which transmissions in percent are plotted as ordinates and wave numbers (cm^{-1}) as abscissas. Curves *A* represent the transmission of 1.5 mm thicknesses of liquid ethyl bromide and ethyl iodide. These were run simultaneously with the aid of a device which permitted putting each liquid cell and a blank cell successively into the beam of radiation at each position of the spectrometer table. Curves *B* are for liquid layers 0.05 mm in thickness. Curves *C* are for the vapors at their respective vapor pressures at 25° , in a gas cell 16 cm long. Curves *D* were taken at undetermined reduced

pressures to show more accurately the positions of maximum absorption. Curve *E* for ethyl chloride was taken at atmospheric pressure. Curve *F* on ethyl bromide shows the transmission of a 0.5 mm layer of the liquid. The cells were made of glass tubes or mica sheets to which rocksalt windows were attached with LePage's fish glue.

Any differences in positions of the bands observed here and those obtained from Raman data are probably due to the differences in the intensities of the fine structure components, causing a difference in the point of maximum intensity of the envelope as measured by the two methods. The positions of the fundamentals in absorption measurements may, in some cases, be affected by the proximity of other absorption bands.

INTERPRETATION OF SPECTRA

The intensities of absorption at the different bands is indicated roughly by the percent transmission plotted as ordinates in Figs. 1 and 2. The intense absorption in certain bands, even for very small quantities of absorbing material, leads to the conclusion that these bands are fundamentals, involving displacements of the atoms only to the first excited quantum state. The displacements to higher quantum states and the combination between two sets of quantum states are less probable; and, consequently, the harmonics and the combination frequencies show less intense absorption.

In the region investigated there are six intense absorption bands for each compound corresponding to fundamental frequencies. Two additional fundamentals of lower frequency, fully established from Raman spectra, give a total of eight experimentally observed fundamentals out of a possible eighteen if the system is non-degenerate.

The harmonics and combinations of these fundamentals which play the most important part in the determination of the whole spectrum may be assumed to be of the types $2F_i$ and $F_i + F_j$. The following table gives the values of the wave numbers of the fundamentals and the combinations of these types for each of the three compounds studied. The values for the fundamentals are arbitrary values between those obtained in the present investigation by absorption measurements and those given by Raman data.

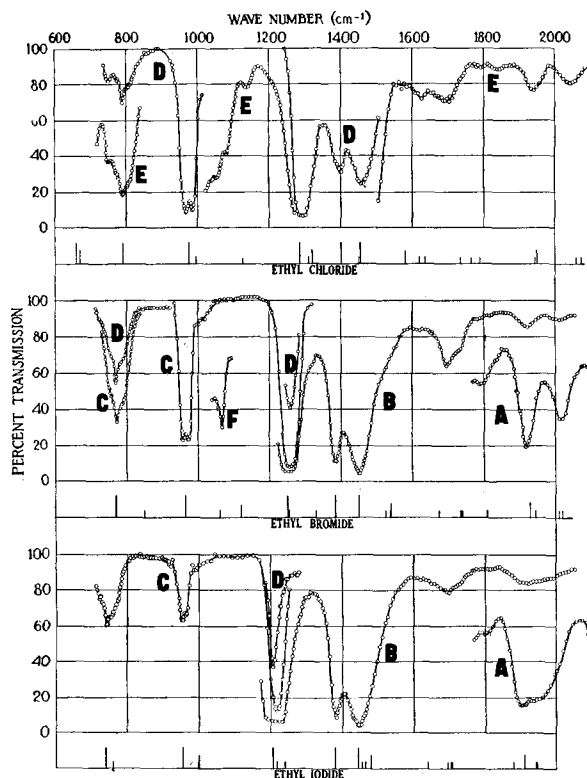


FIG. 1. Absorption spectra of ethyl halides 600 to 2000 cm^{-1} .

In Figs. 1 and 2 these calculated positions are indicated below each spectrum by 3-unit lines for fundamentals, by shorter 2-unit lines for first harmonics and by lines of 1-unit length for combinations. It will be observed that a region of intense absorption in the experimental curve is

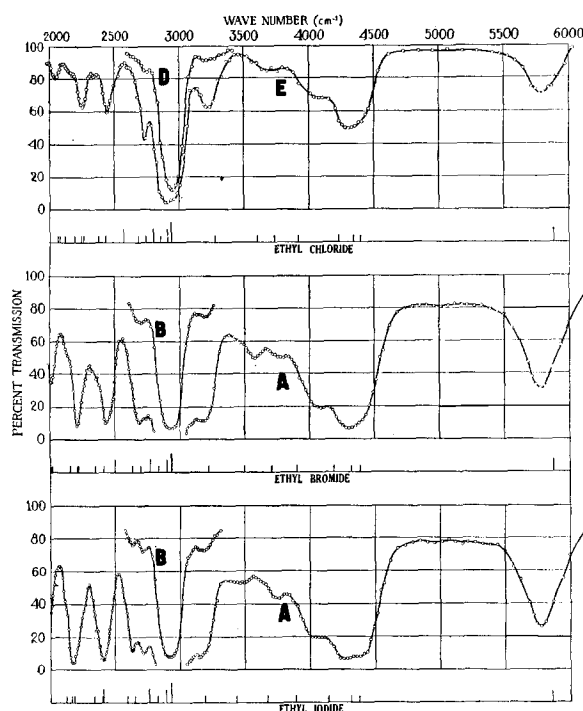


FIG. 2. Absorption spectra of ethyl halides 2000 to 6000 cm^{-1} .

indicated by the grouping of a number of calculated values, and that regions of high transmission are accompanied by a scarcity of calculated values. In fact the whole complex spectrum, experimentally determined, can be reconstructed with fair accuracy from these fundamentals and their first harmonics and combinations. The agreement cannot be exact because it is impossible to include all the factors involved. It is known, for example, that harmonics are not exact multiples of the fundamentals but that there are small correction terms.

Another cause for difference in calculated and observed spectra may be found in the fact that certain of the listed combinations may be very strong while others may be immeasurably weak, but it is not as yet possible to predict which are strong and which are weak.

The calculated positions do not represent all the possible absorption bands. There may be second or even higher harmonics, combinations of harmonics with fundamentals, etc., which are sufficiently strong to be factors in the observed spectra. Also there may be combinations of the type $F_i - F_j$ which are fairly strong. This will be particularly true when F_j is a low frequency fundamental, since a large fraction of these may be excited at room temperature.

Still another cause for the difference between the calculated and observed absorptions is the existence of weaker fundamentals. As an example of this, the Raman line at about 1065 cm^{-1} may be cited. Although this band did not appear in the transmission of the vapor cell, the curve *F* for 0.5 mm liquid ethyl bromide clearly shows a band in this region, perhaps a fundamental.

APPROXIMATE MOTIONS ASSOCIATED WITH THE FREQUENCIES

After selecting the most important fundamental frequencies from which the infrared spectrum is built, it becomes of interest to attribute to each a definite bond or type of vibration. Although such relations are quite speculative, there is now sufficient evidence to establish some of them with a fair degree of confidence.

The problem has been attacked by several investigators⁶⁻¹¹ using infrared and Raman measurements on a large number of organic compounds. In general, at least two different types of vibration seem to be well established: one a *stretching* vibration in which two atoms move back and forth essentially along a line joining their centers, and another, a *bending* vibration in which two atoms swing back and forth laterally with respect to a third atom or group of atoms. This previous work has been freely drawn upon in choosing some of the types of vibration given

⁶ Coblenz, *Investigations of Infrared Spectra*, Carnegie Inst. Pubs. 35 (1905).

⁷ Ellis, *Phys. Rev.* 27, 298 (1926); 28, 25 (1926).

⁸ The work previous to 1931 is splendidly summarized by Kohlrausch, *Der Smekal-Raman Effekt*, Julius Springer, Berlin, 1931.

⁹ *Trans. Faraday Soc.* 103 (1929). Symposium on Molecular Structure and Molecular Spectra Part III.

¹⁰ Harkins and Bowers, *Phys. Rev.* [2], 38, 1845 (1931).

¹¹ Harkins and Haun, *J. Am. Chem. Soc.* 54, 3920 (1932).

TABLE I. *Calculated wave numbers of absorption bands.*

	Ethylchloride	Ethyl bromide	Ethyl iodide
F_1	2940	2935	2930
F_2	1455	1450	1445
F_3	1400	1385	1380
F_4	1285	1250	1205
F_5	975	965	955
F_6	790	770	740
F_7	660	560	500
F_8	335	290	260
$2F_1$	5880	5870	5860
$2F_2$	2910	2900	2890
$2F_3$	2800	2770	2760
$2F_4$	2570	2500	2410
$2F_5$	1950	1930	1910
$2F_6$	1580	1540	1480
$2F_7$	1320	1120	1000
$2F_8$	670	580	520
F_1+F_2	4395	4385	4375
F_1+F_3	4340	4320	4310
F_1+F_4	4225	4185	4135
F_1+F_5	3915	3900	3885
F_1+F_6	3730	3705	3670
F_1+F_7	3600	3495	3430
F_1+F_8	3275	3225	3190
F_2+F_3	2855	2835	2825
F_2+F_4	2740	2700	2650
F_2+F_5	2430	2415	2400
F_2+F_6	2245	2220	2185
F_2+F_7	2115	2010	1945
F_2+F_8	1790	1740	1705
F_3+F_4	2685	2635	2585
F_3+F_5	2375	2350	2335
F_3+F_6	2190	2155	2120
F_3+F_7	2060	1945	1880
F_3+F_8	1735	1675	1640
F_4+F_5	2260	2215	2160
F_4+F_6	2075	2020	1945
F_4+F_7	1945	1810	1705
F_4+F_8	1620	1540	1465
F_5+F_6	1765	1735	1695
F_5+F_7	1635	1525	1455
F_5+F_8	1310	1255	1215
F_6+F_7	1450	1330	1240
F_6+F_8	1125	1060	1000
F_7+F_8	995	850	760

here, and Raman data and infrared absorption spectra of other compounds have been used to supplement the present absorption measurements on the ethyl halides.

It is a striking fact that the fundamental nature of the vibration between two atoms is affected only slightly by vibrations located in other parts of the molecule. Double bonds and other structural features do exert considerable influence, but they are not involved in the present discussion of the ethyl halides. A given vibration is affected only to a slight or negligible degree by a substitution of atoms in a part of the molecule removed from the immediate vibration. When,

however, atoms of different weight are substituted in positions adjacent to the vibrating atoms the effect is more marked; and, if one of the atoms directly involved in the vibration is substituted, the change in frequency may be large. This fact has been used in choosing the types of vibration from the shifting of frequency caused by the chloride, bromide, iodide substitutions. The fundamental frequencies expressed in wave-numbers ($\bar{\nu}$) have been given in Table I and are arbitrarily referred to as F_1 , F_2 , F_3 , etc., starting with the highest frequency. The types of vibration which are believed to correspond to each of these fundamentals are pictured graphically in Fig. 3. Obviously these models represent simplified approximations and they are not to be taken literally.

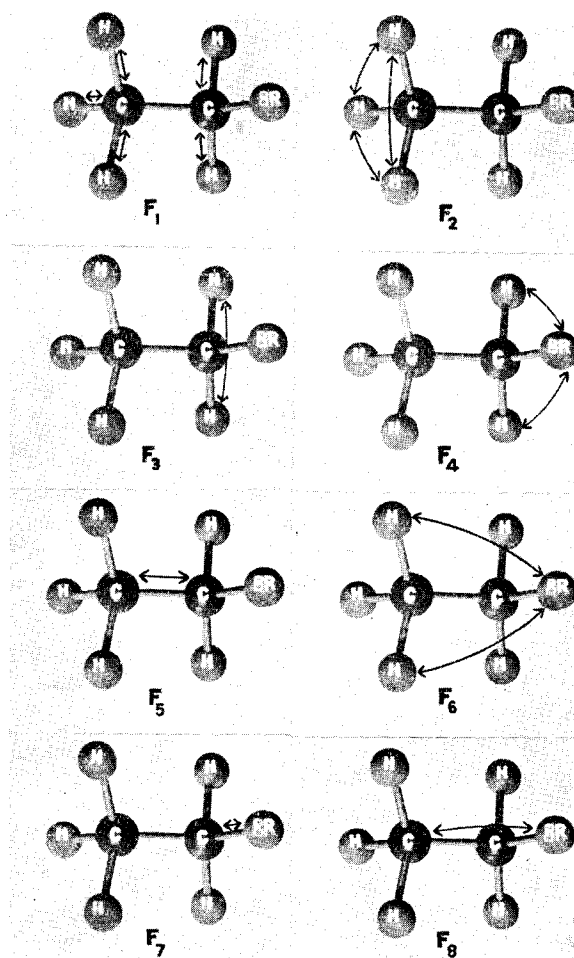


FIG. 3. Important features of the motions associated with the fundamental frequencies.

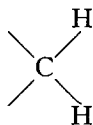
F_1 . Wave-numbers ($\tilde{\nu}$) $C_2H_5Cl=2940$,
 $C_2H_5Br=2935$, $C_2H_5I=2930\text{ cm}^{-1}$
 Wave-lengths (λ) $C_2H_5Cl=3.40$,
 $C_2H_5Br=3.41$, $C_2H_5I=3.42\mu$.

This frequency has long been associated with the carbon-hydrogen bond. Coblenz⁶ in his classical examination of over a hundred organic compounds observed this intense band at about 3.4μ in every case where there was a simple linkage between carbon and hydrogen. In reality this band represents an average of 3 or 4 bands between 2850 and 3050 cm^{-1} in the case of the ethyl halides, but the average value is sufficient for the present purpose.

As shown in Fig. 3 this F_1 frequency is attributed to a stretching vibration of the carbon and hydrogen atoms toward and away from each other. This is perhaps the most common linkage in organic compounds and when, as is frequently the case, there are several such groups in a single molecule, the band becomes particularly prominent.

F_2 . $\tilde{\nu}=1455, 1450, 1445\text{ cm}^{-1}$ *
 $\lambda=6.87, 6.90, 6.92\mu$
 $\tilde{\nu}_{(\text{Raman})}=1450, 1440, 1430\text{ cm}^{-1}$.

This frequency occurs only when the



group is present. For example, in chloroform ($CHCl_3$) F_1 is present but F_2 is missing. As shown in Fig. 3, this frequency is attributed to two hydrogen atoms swinging laterally at the side of a carbon atom. But as brought out in the next paragraph, it seems likely that this frequency is restricted to the bending vibration of pairs of hydrogen atoms in the CH_3 group only.

F_3 . $\tilde{\nu}=1400, 1385, 1380\text{ cm}^{-1}$
 $\lambda=7.14, 7.22, 7.25\mu$.

This frequency is very nearly the same as that of

* These values in the following paragraphs are given in the order ethyl chloride, ethyl bromide, and ethyl iodide respectively, as indicated after F_1 .

F_2 , but it is distinguished from it by being slightly lower and particularly in being more easily influenced by the halogen. For this reason, as shown in Fig. 3, the vibration is attributed to the bending vibration of two hydrogen atoms not in the CH_3 group but in the $-CH_2Br$ group.

F_4 . $\tilde{\nu}=1290, 1255, 1210\text{ cm}^{-1}$
 $\lambda=7.75, 7.96, 8.26\mu$
 $\tilde{\nu}_{(\text{Raman})}=1276, 1240, 1197\text{ cm}^{-1}$.

The very large change produced in this frequency by substituting for bromine the lighter chlorine or the heavier iodine leads to the conclusion that the halogen atom is directly involved in the vibration. A bending vibration of halogen and hydrogen pivoting around the carbon atom is suggested for this vibration as shown in Fig. 3.

F_5 . $\tilde{\nu}=975, 965, 955\text{ cm}^{-1}$
 $\lambda=10.26, 10.36, 10.47\mu$
 $\tilde{\nu}_{(\text{Raman})}=966, 960, 951\text{ cm}^{-1}$.

The small change produced in this frequency by changing the halogen shows that the halogens are not directly involved. Furthermore, this frequency is found in ethane where no halogen is present. The fact that it is not found in methyl compounds shows that it is not due to a simple carbon-hydrogen vibration. All this evidence indicates that the F_5 frequency is due to a stretching vibration of the two carbon atoms along a line joining their centers as shown in Fig. 3.

This frequency seems to occur in all ethyl compounds except ethyl alcohol. This exception may be due to the fact that the two end groups, the OH and the CH_3 groups, having nearly equal physical properties, tend to interact and produce types of vibration in which the local features give way to features involving the whole molecule.

F_6 . $\tilde{\nu}=790, 770, 740\text{ cm}^{-1}$
 $\lambda=12.65, 13.00, 13.5\mu$.

The F_6 frequency, like the F_4 frequency, changes so markedly with substitution of the different halogens that vibration of the halogen atom must be directly involved. This frequency is not found in methyl halides. Accordingly, a bending vibration involving the halogen atom and a hydrogen atom on the second carbon atom is tentatively proposed as shown in Fig. 3.

$$F_7. \quad \tilde{\nu}_{(\text{Raman})} = 655, 560, 500 \text{ cm}^{-1} \\ \lambda = 15.3, 17.8, 20.0\mu.$$

This frequency is beyond the range of the spectrometer because it falls in the region where rocksalt is no longer transparent. It is taken from Raman data alone. Since this frequency is changed so much by substitution of the halogen, it must be connected directly with a vibration of the halogen; and the low frequency suggests that heavy atoms may be involved. Harkins and Bowers¹⁰ and others have suggested that this frequency is due to a stretching vibration of the carbon and halogen atoms.

This frequency changes only slightly (less than 10 percent) in going from the methyl halides to the ethyl halides and remains practically constant for the normal halides of the higher members of the series. The fact that the addition of more carbon atoms has so little effect on the frequency may be taken to strengthen the view that the motion is essentially along a line joining the halogen and the carbon atom to which it is bound, as shown in Fig. 3.

$$F_8. \quad \tilde{\nu}_{(\text{Raman})} = 335, 290, 260 \text{ cm}^{-1} \\ \lambda = 29.9, 34.5, 38.5\mu.$$

This low frequency revealed by Raman data is likewise beyond the range which can be measured with the spectrometer used in the present investigation. The large change produced by the substitution of the different halogens indicates that the halogen is one of the vibrating atoms, and the low frequency suggests a bending vibration with heavy atoms involved. This frequency does not occur in methyl compounds, but it does occur in various ethyl compounds in which a halogen, OH or SH group is involved. As shown in Fig. 3, a bending motion is suggested in which the halogen and the second carbon atom oscillate at the side of the CH₂ group.

As pointed out before, there are no doubt other fundamental frequencies which have missed detection because they are considerably weaker than the ones described here and designated as F_1 to F_8 . For example, a Raman line is found at 1070, 1065 and 1050 cm⁻¹. This was missed in the first absorption measurements, but, after a special search, using different absorbing thickness, it became plainly evident in ethyl bromide at 1065

cm⁻¹. This frequency shows little change with the halogen substitutions and it is not found in the methyl halides. It may be attributed, tentatively, to a bending vibration between a hydrogen and the second carbon atom. It is not shown in Fig. 3. If this is a correct interpretation, it seems strange that the line is not more intense because there should be opportunity for several different atoms to contribute to this frequency.

THEORETICAL DISCUSSION

Each type of vibration has been represented as involving only two or three atoms, but, when a molecule is exposed to continuous radiation in the infrared region, all the fundamental frequencies and those corresponding to the various harmonics and combinations are absorbed, so that several different vibrations may be occurring simultaneously. Likewise, when the molecule becomes activated by collision or by other agency, several of these vibrations may be brought into play at the same time.

It is hoped that a knowledge of these types of vibration, such as those depicted in Fig. 3, will be helpful, eventually, in predicting ways in which chemical changes can take place. Some of them coincide with concepts of organic chemistry suggested long before there was physical evidence for their existence.

Andrews¹² has been quite successful in reproducing the fundamental frequencies of the Raman spectra with mechanical models excited to small amplitudes, a fact which indicates that the mechanical models and classical mechanics do give an approximate representation of the vibrational structure and behavior of the molecules. However, amplitudes as small as those employed by Andrews are connected with the chemical reactivity only in an indirect manner.

If, as is suggested by Rice and Ramsperger¹³ and others,¹⁴ molecules which decompose unimolecularly do so when a sufficient amount of energy becomes localized in a particular bond or type of vibration, it would seem logical that the

¹² Andrews, Ind. Eng. Chem. **23**, 1232 (1931).

¹³ Rice and Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1927).

¹⁴ Kassel, *Kinetics of Homogeneous Gas Reactions*, Chapters V and X, Chemical Catalog Co., New York, 1932.

particular vibration should be a bending vibration rather than a stretching one, since the bending motion will bring close together certain parts of the molecule which may be able to interact with each other. A rearrangement to give new molecules may result. For example, it has been established¹⁵ that ethyl bromide decomposes according to the equation $\text{C}_2\text{H}_5\text{Br} = \text{C}_2\text{H}_4 + \text{HBr}$ and that the reaction is definitely unimolecular.

It follows, therefore, that this decomposition would more likely take place by the oscillation of a hydrogen and a bromine atom toward each other transversely than by a mechanism wherein the first step is dissociation into a radical and a free atom by a stretching vibration such as F_1 or F_7 . Such a disruption into free atoms should require considerably more energy. Furthermore, the absence of detectable amounts of side products such as higher hydrocarbons and various bromine derivatives supports the view that the dissociation involves a single molecule rather than an associated complex. The rupture could take place in the same manner, however, even if a complex unit of two or more molecules were involved.

The types of vibrations suggested for F_6 or F_8 and shown in Fig. 3 would both lead to a close approach of an atom of bromine and an atom of hydrogen from the second carbon atom, and, with sufficient amplitude, this might lead to a rearrangement of the forces within the molecule and result in the formation of ethylene and hydrogen bromide.

If chemical rupture of the molecule can be brought about by the proper type of vibration between the atoms, it might seem at first sight that infrared radiation should be photochemically active, but the experimental facts, thus far, show that infrared radiation is photochemically inactive.^{16, 17} The fundamental frequencies described in the present communication correspond to displacement of the atoms only to the first quantum state, and the first harmonics involve displacements to the second quantum state. These displacements fall far short of giving suf-

ficient amplitude of vibration to bring about the chemical dissociation already described.

Speaking specifically of ethyl bromide, the energy of activation calculated from the temperature coefficient of the thermal dissociation rate is 54,800 calories per mol.¹⁵ This energy of activation would correspond to a wave number of $19,300 \text{ cm}^{-1}$ (in the green part of the visible spectrum) whereas the wave number of the fundamental frequency F_6 is only 770. In other words, it would take at least the 25th harmonic (perhaps the 30th or 40th with due allowance for an anharmonic factor) to provide sufficient energy to disrupt the molecule of ethyl bromide, assuming such a mechanism of disruption for both the thermal and the photochemical dissociations. But, as has been shown, the first harmonics are much less intense than the fundamental, and the second harmonics are still very much weaker. The absorption of any of the higher harmonics in the region of the 25th harmonic would be utterly negligible. For example, Ellis¹⁸ found it necessary to use a tube of liquid chloroform 4.5 meters long in order to detect even the sixth harmonic of the carbon-hydrogen fundamental, designated here as F_1 .

In other words, no matter how great the radiation density, the fundamental frequencies cannot decompose the molecules because the energy of the quantum is not large enough; and a harmonic having sufficiently high frequency to give decomposition is not absorbed. Consequently it is unlikely that a molecule can be disrupted by radiation which acts only in causing the atoms to oscillate. The critical vibration of large amplitude (high-quantum states) leading to chemical dissociation must be effected in other ways,—by violent collisions from thermal agitation or by electronic excitation, for example.

Although it has been shown that the fundamental frequencies of given types of vibration are relatively independent of the nature of the remainder of the molecule, it is by no means implied that the energy terms of a given type are independent of the degree of excitation of the various other types of vibration when the amplitude is large and the motion is anharmonic. Indeed, it would seem more in keeping with the

¹⁵ Vernon and Daniels, J. Am. Chem. Soc., in press.

¹⁶ Daniels, J. Am. Chem. Soc. **48**, 607 (1926); Chem. Rev. **5**, 54-56 (1928).

¹⁷ Taylor, J. Am. Chem. Soc. **48**, 577 (1926).

¹⁸ Ellis, Phys. Rev. **32**, 906 (1928).

modern view of the energy relationships of such systems to believe that there might be considerable influence exerted between the highly excited states. Thus, although a certain amount of energy localized in a given type of vibration may be sufficient to cause the decomposition of a molecule, it may be true that a smaller amount of energy in that type, when accompanied by additional energy in certain other types, will cause the decomposition to take place. Since little is known of the vibrational energy states of complex molecules, or the nature of the interchange of energy between the different types of vibration, a quantitative treatment of the problem is not possible at this time.

In closing the authors wish again to emphasize the fact that the speculations based on their experimental facts are tentative and incomplete. Exact analysis of the systems studied may alter the interpretation given here, but such analysis is as yet impossible. Chemists find it helpful to try

to connect physical and chemical properties with molecular models, although physicists often object to such models because they are inadequate in more quantitative fields.

The present hypotheses regarding atomic motions in the molecule are offered in the hope that further discussion and additional experiments may justify the incomplete picture as useful until a more complete one is possible.

The slight differences in the spectra of the structurally similar ethyl halides have been helpful in interpreting the spectra. Likewise, a comparison of the dissociation rate of ethyl iodide and chloride with that of the bromide may be helpful in the study of kinetics. These systems then seem particularly favorable for an extended study of the relation between molecular structure and chemical reaction.

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