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A REPRESENTATION OF THE DYNAMIC PROPERTIES OF MOLECULES BY MECHANICAL MODELS

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Abstract

Mechanical models have been constructed to represent the dynamical systems believed to exist in the molecule. Assuming that the intramolecular forces lie along lines associated with the chemical bonds and that for small vibrations they obey Hooke's law and have the mechanical character of spiral springs, it is possible to get a picture of the forces and masses which can be represented on a large scale by steel balls and spiral springs. Models have been constructed for some of the simpler nonpolar molecules. They are found to have characteristic frequencies which correspond very closely to the frequencies observed in the Raman spectra, and it is possible by this means to identify the Raman lines with definite types of motion of particular atoms in the molecule. This substantiates the view that Raman lines correspond very closely to characteristic fundamental molecular frequencies.

Introduction

THIS paper describes an attempt to make some mechanical models of the dynamical systems of forces and masses which are found in real molecules. The possibility of doing this lies in the fact that according to optical and thermal data the smaller nonpolar molecules are dynamically rather simple.[2,3] This simplicity is brought about in several ways. In the first place the only effective masses in the molecule are the nuclei of the atoms which may be regarded as point masses. The space relations of these masses to each other can be deduced to a large extent from the studies of the crystal lattice by means of x-rays. In the second place the forces in the molecule also appear to be simple in nature, lying for the most part along the lines which join the nuclei and which have been associated with the chemical bonds. In fact, the forces of the bonds are so much greater than any of the other forces acting on the atoms that they alone are of importance dynamically.

The problem is further simplified by the nature of the bond itself which behaves in a manner very analogous to a spiral spring. Thus for the small displacements with which we deal in studying the behavior of the molecule in the lowest vibrational levels we can see that the bond forces will obey

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[1] The results reported here were arrived at largely as a development of the concepts of molecular structure originated by the senior author (C.F.K.). The success of the project is due chiefly to the cooperation of the many members of the laboratory staff who assisted in both the mechanical and physical part.

[2] J. W. Ellis, Jour. Franklin Inst. **208**, 517 (1929); E. O. Salant, Proc. Nat. Acad. Sci. **12**, 334, 370 (1926).

[3] D. H. Andrews, Proc. Roy. Acad. Amsterdam **29**, 744 (1926); Chem. Reviews **5**, 533 (1928), Phys. Rev. **34**, 1626 (1929); **36**, 544 (1930).

Hooke's law with regard to the extension or compression of the bond. There is, however another feature of the mechanical nature of the bond which has been largely neglected heretofore. The organic chemist in trying to explain the behavior of ring compounds has suggested that the bonds from a carbon atom will normally bear certain spatial relations to each other. This normal position has been generally accepted as that in which the bonds make the tetrahedral angle with adjoining bonds. In a cyclic compound such as a ring composed of four carbon atoms, it has been assumed that a strain is introduced by the alteration of the angles between the bonds. The concept has thus arisen that, in addition to elasticity of stretching, the bond has also elasticity of bending. This idea has been substantiated by recent data from the Raman spectra which show the force necessary to bend a bond is about one fifth that necessary to stretch it.

Data from the Raman and infrared spectra, as well as from specific heats,[3] have also indicated another regularity in the nature of the bond which simplifies considerably the construction of a mechanical model. It is found that the restoring force due to the stretching of a normal nonpolar bond is always about the same whether the bond be between two hydrogens, a hydrogen and a carbon, two carbons, a carbon and an oxygen, or any other similar position. It thus would appear to be possible to represent all the bonds in a mechanical model by means of the same kind of spiral spring. If the ratio of the stretching force constant to the bending force constant were chosen correctly it should be possible to make a model which would quite closely represent the actual molecule.

Until recently the data have been quite incomplete from which one could find the fundamental mechanical frequency in a molecule. Developments[3,4,5] in the study of the Raman spectra, however, indicate that the frequencies found there do correspond rather closely to real mechanical frequencies in the molecule. It therefore seems probable that if a mechanical model of a molecule were correctly constructed the characteristic frequencies found in it should correspond term by term to the frequencies observed in the Raman spectra. We should be able to get from a Raman frequency to a model frequency and *vice-versa* by multiplying or dividing by the proper constant which depends on the ratio of the mass of the molecule to the mass of the model, and of the force of the chemical bond to the force of the spring which represents it.

THE CONSTRUCTION OF THE MODEL

The first problem in constructing the model was the determination of the ratio of the stretching to the bending force in the spring which was to be used to represent the chemical bond. In order to simplify the problem it was decided to omit the hydrogen atoms from the first series of models, thus representing only the atoms of atomic weight of twelve or greater. The hydrogens, being so light, have almost no appreciable energy at ordinary tempera-

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[4] A. Dadieu and K. W. F. Kohlrausch, Berichte der Deutschen Chemischen Gesellschaft, Jahrg. **63,** 251 (1930).

[5] A. S. Ganesan and S. Venkateswaran, Indian Journal of Physics **4,** 195 (1929).

tures, and contribute very little to the dynamical character of the system. We were thus left with the problem of determining the nature of the bond between two atoms like carbon, oxygen, or chlorine.

We have a direct indication of the strength of the carbon-carbon bond in the Raman spectrum of ethane. There is one line at 990 wave numbers which with very little doubt corresponds to the frequency of vibration of the two carbon atoms. By means of the formula,

$$\nu = \frac{1}{2\pi}\left(\frac{k}{m}\right)^{1/2} \tag{1}$$

where ν is the frequency, m is the reduced mass of the system, and k is the force constant, we can calculate what the stretching force for the carbon-carbon bond will be. It turns out to be about 4×10^5 dynes per cm. Methyl alcohol which is dynamically similar to ethane gives a similar value for the force.

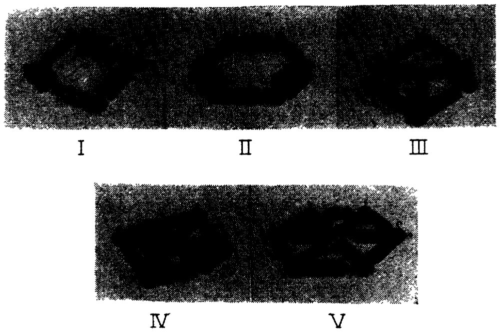

Fig. 1a.

The calculation of the bending force is quite a bit more uncertain as it is only involved when we have at least three atoms in the molecule. From the study of ethyl alcohol and benzene and its derivatives, the value of 0.66×10^5 dynes per cm has been calculated by defining the bending force as a force necessary to displace an atom in a direction perpendicular to the bond joining it to another atom which is held stationary. While this concept of the bending force may seem somewhat arbitrary, it would appear to be the best means of approach available at the time. A better knowledge of just what it is can probably be obtained as our knowledge of molecular dynamics increases.

From a consideration of these values, a helical spring to represent the bond was decided upon. It has the following characteristics:

Mean Diameter of Coil	13/16 in.
Diameter of wire	#11 (0.120)
No. of active turns	10
Free length	2-1/2 in.
Force per inch deflection	53 lbs.

The actual weight of the spring when completed was $1\frac{1}{2}$ ounces. Steel balls $1\frac{1}{8}$ in. diameter weighing 0.2 lbs. each were used to represent the carbon atoms. To obtain the desired value for the bending of the spring, the distance between the centers of the balls was set at $3\frac{3}{4}$ in. Some of the models constructed in these proportions are shown in Fig. 1a.

METHOD OF STUDY

In order to study the fundamental vibration frequencies of such models, it is necessary to activate them by means of vibrational impulses of various frequencies. This was successfully accomplished by using a rubber band to attach one of the balls to an oscillating arm having $\frac{1}{4}$ in. stroke. This arm was operated by a reciprocating yoke on an eccentric driven by a variable speed motor. The model was suspended on rubber bands in such a manner that the frequency of the natural period of the suspension was much lower than the lowest period in the model.

Since the vibrations of the models covered a range of frequencies from 200 to 3500 cycles per minute, it was necessary to use some special means of observation in order to determine the characteristic motion of the various vibration periods. This was accomplished by illuminating the model with a neon lamp of a specially constructed stroboscope giving a large field of illumination. The circuit breaker of the stroboscope was geared to the activating motor shaft so that the neon lamp flashed at a frequency 2% slower than the exciting frequency applied to the model. Thus when the model was vibrating, a slow motion image, 1/50th of the actual frequency, was obtained. Thus at a frequency of 3000 cycles per minute, the model would appear to move through one cycle per second making it very easy to study the characteristics of the motion.

The tuning was found to be very sharp. When the motor was running at a speed which did not correspond to a characteristic frequency, the model was absolutely quiet. When the motor speed came within about five percent of a characteristic frequency, however, the balls began to move over the paths characteristic of that frequency and with closer tuning would generally vibrate with an amplitude of the order of 1/2 in. This, of course, depends on the type of motion and the point of activation to some extent. The tuning was sharp enough, though, so that the characteristic frequencies could be determined to within two or three percent, and it was easy to see just what type of motion corresponded to that frequency.

There was little complication because of harmonics. One or two of the lowest frequencies would sometimes appear when the speed of the motor was double their fundamental value, but could easily be recognized as harmonic because the balls were vibrating with twice the frequency which they should have had for that motor speed. The amplitude of these harmonics was always small. There seemed to be a little trouble from spurious vibrations, that is, vibrations occurring because the springs actually had mass. These are called spurious because they would not be found in the real molecule where the only mass is in the nuclei. They were easily recognized by studying the motion of the springs under the neon light.

The method of study consisted in activating the model starting with a frequency of about 100 r.p.m. and raising the motor speed continuously to the maximum of 3600. As the characteristic frequencies were reached, they would be recognized by the appearance of motion of the balls under the neon light and the frequencies of revolution would be tabulated as read from a tachometer connected to the motor shaft. After going through the range of frequencies, a further study would be made by approaching each frequency carefully from above and below and observing as accurately as possible the motions of the balls at that frequency. The same model would be vibrated at several different positions by attaching the activating rubber band in various ways. It was found that while this sometimes altered the amplitude of the various frequencies, their values and number remained the same. In this way we have secured data on the characteristic frequencies of models of a number of the commoner organic compounds. A discussion is given in detail in the following paragraphs.

RESULTS

MODELS WITHOUT HYDROGEN REPRESENTED

Benzene. Benzene was chosen as one of the compounds for study because of the uncertainty regarding its structure. Five different models of benzene, illustrated in Fig. 1a, were constructed as follows:

I. The Kekulé formula. The six balls representing the carbon atoms are arranged in a hexagon, and joined with alternate single and double bonds so placed that the tetrahedral angle is formed between any two adjoining bonds. The double bonds are made by putting two of the standard springs in parallel. The result is a "puckered" hexagon.

II. The Kekulé formula, plane. This is similar to model I except that the bonds are so arranged that the balls form a hexagon in a plane.

III. Centric formula. In this model the six balls are joined by single bonds into a "puckered" hexagon. There are in addition three cross bonds joining carbon atoms opposite each other in the ring. Each of these cross bonds is formed of a standard spring with a sufficient extension of wire on one end to give it the necessary length. In model IIIa the three cross bonds can slide over each other freely. In model IIIb they are clamped together in the center.

IV. Centric formula. This is the same as the preceding model except that the cross bond is formed by two standard springs joined together in the center. In IVa the bonds slide freely at the center and in IVb they are clamped together.

V. Centric formula. This is similar to the preceding model except that the bonds are so arranged that the six balls lie in a plane.

In order to compare the frequencies found in these models with the Raman spectra, it is necessary to calculate a conversion factor for passing from r.p.m.

to wave numbers This conversion factor C may be expressed in terms of the masses and elastic constants by means of the equation

$$C = \frac{\nu\ \text{r.p.m.}}{\bar{\nu}} = 60c\left(\frac{k_s}{k_m}\cdot\frac{m_m}{m_b}\right)^{1/2} \qquad (2)$$

where $\bar{\nu}$ is the frequency in wave nos., ν r.p.m. is the frequency in r.p.m., k_m is the elastic constant for the bond in the real molecule, k_s is the elastic constant of the spiral spring, m_b is the effective mass of the ball, m_m the mass of the nucleus, and c the velocity of light.

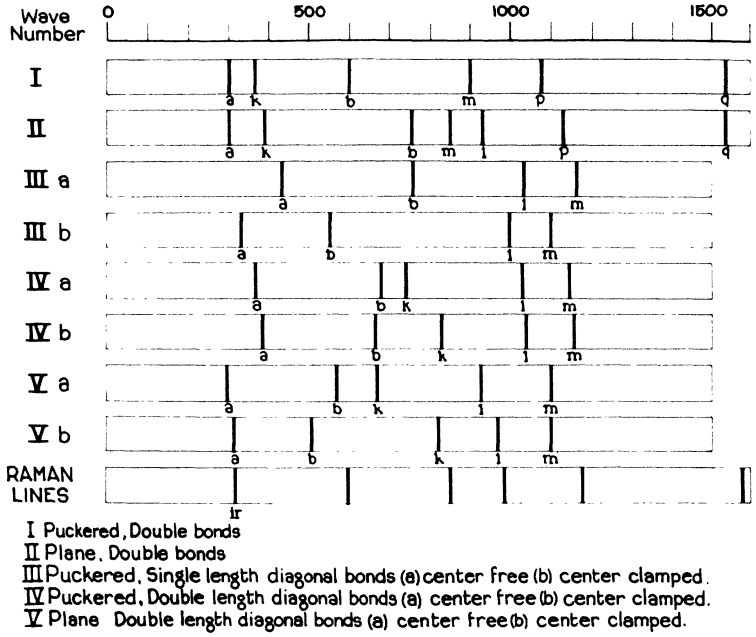

Fig. 1b. Models of benzene.

In the case of the fastest motion in benzene, the effective mass will be approximately that of a ball plus one and one-half springs. Of course this effective mass will be different for different types of vibration, but this seems to be sufficiently close approximation. Using the proper values, we find that C has a value of 3.1, which may be considered equal to three, within our limit of error.

The results of the study of these models are shown in Fig. 1b. The Raman spectrum for benzene is shown in the last line of the figure. The lines at 1500 cm^{-1} and at 3000 cm^{-1} (not shown) are almost surely due to the hydrogen which is not represented in this model. The four lines between 600 and 1200 cm^{-1} have been reported by almost everyone studying benzene and are known quite accurately. There seems to be also considerable evidence for a frequency in the neighborhood of 360. A series of bands observed in the infrared[6,7] indicate a fundamental frequency at 360 cm^{-1} and the specific heat[3] of benzene also gives very strong evidence for a frequency in this neighborhood. These five frequencies then seem to be the characteristic frequencies due to the vibration of the carbon atoms in benzene.

As may be seen in Fig. 1b, the centric models are in fairly good agreement with the Raman spectrum. They show five fundamental frequencies of the type indicated in Fig. 2. These types of motion are also in agreement with those which had previously been assigned to benzene[3] on the basis of its specific heat and Raman spectra. The degrees of freedom observed in the different types of motion add to give the correct number for the six carbon atoms, namely, twelve.*

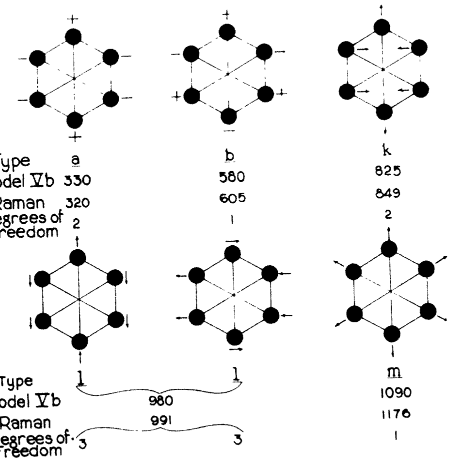

Fig. 2. Types of motion in benzene. + and − indicate motion out from and into plane of paper.

It is a little difficult to say just which model is in best agreement with the Raman spectrum. The evidence is perhaps a little in favor of *Vb*. This would be in accord with other observations which favor a plane hexagon for benzene. The double bond models, Kekulé formula, are distinctly different from the others in the higher frequencies. As may be seen in Table I, there is a frequency (p) which arises from a stretching of the single bonds. We would also expect a frequency (q) arising from a stretching of the double bonds. It was not possible with the present appratus to excite this frequency because of the speed limitation of the motor, but calculation shows it would correspond to about 1540 cm^{-1}. As shown in the last column, there is fair agreement between these frequencies and the Raman frequencies at 1176 and 1592 cm^{-1}. It is true that we had assumed the latter to be close to a lateral motion of the

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[6] J. W. Ellis, Phys. Rev. **27**, 298 (1926).

[7] L. Marton, Zeits. f. Phys. Chem. **117**, 97 (1925).

* The six carbon atoms with three degrees of freedom each give eighteen degrees of freedom in all. Substracting six for the translation and rotation of the molecule as a whole, we should have twelve internal degrees of freedom.

TABLE I. *Models without hydrogen represented.* $3\bar{\nu} = (r.p.m.)$.
Benzene

Model	I	II	IIIa	IIIb	IVa	IVb	Va	Vb	Raman[5]
a	300	320	435	340	385	400	325	335	360*
b	615	770	755	—	650	665	580	585	605
k	390	400	—	550	735	850	680	815	849
l	950	940	1035	1000	1015	1015	945	955	991
m		865	1160	1150	1150	1150	1090	1080	1176
p	1080	1135	—	—	—	—	—	—	(1176)
q	(1540)	(1540)	—	—	—	—	—	—	(1592)

* Value from infrared spectra, see reference 6.

Toluene

Type	Model	Raman[5]
t_1	205	215 cm^{-1}
t_2	235	
a	400	345
		520*
b	635	622
k_1	750	730
k_2	835	786
l_1	960	1005
l_2	990	1029
m	1150	1162

* Not observed by all investigators.

Models with chlorine $1.8\nu = (r.p.m.)$.

Carbon tetrachloride		Chloroform	
Model	Raman[5]	Model	Raman[5]
220	216 cm^{-1}	235	261 cm^{-1}
305	313	360	367
—	459	—	669
—	762	—	762
1000	791	1195	1218
1540	1535	1750	1441

Models with hydrogen represented. $\bar{\nu} = (r.p.m.)$.

Ethane			Ethylene			Acetylene		
Model		Raman[9]	Model		Raman[8]	Model		Raman[9]
C-C	1275	990 cm^{-1}	C-C	1725	1623	C-C	2025	1960
H_t	725 870	1460	H_t	775 825	1342	H_t	750	
H_l	2800 3000	2890 2950	H_l	3000	2880 3019 3240 3272	H_l	2960 2980	

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[8] R. G. Dickinson, R. T. Dillon, and F. Rasetti, Phys. Rev. **34,** 582 (1929).
[9] M. Daure, Compt. Rend. **188,** 1452 (1929).

Methyl alcohol			Ethyl alcohol		
Model		Raman[5]	Model		Raman[5]
C-O	1200	1031 cm^{-1}	C-C-O x	250	450 cm^{-1}
H_t	875	1257	y	1125	884
		1360	z	1350	1047
H_t CH_3	2900	2834	H_t	750	1461
OH	3000	2939			1165
					1276
			CH_3	2940	2872
			H_t CH_2	2960	2930
			OH	3025	2973

hydrogens, but this is not absolutely certain. We may conclude that there is some evidence in favor of the double bonded structure, but until we are a little more certain of the correct way to represent the double bond, too much weight must not be placed on this evidence.

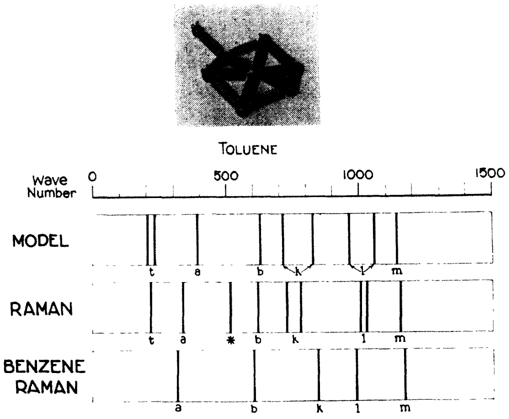


Fig. 3. Models of toluene.

Toluene. The model for toluene is the same as model IV_b of benzene, with a ball and spring added to represent the methyl group. This group is attached so that it lies in the plane of the ring. The results are shown in Fig. 3. The addition of the methyl group causes a splitting of two of the frequencies which involve several degrees of freedom into doublets. Apparently one of the lines represents a motion which has its principal axis through the pair of carbon atoms in the ring which are in line with the methyl group, and the other two correspond to types of motion with the principal axis passing through the other two carbon atoms in the ring. This splitting may be seen by comparing the Raman spectra of benzene and toluene, and the model duplicates it almost exactly. There are also two low frequencies which represent the motion of the methyl group like a tail wagging. This interpretation has been verified by the heat capacity[3] which shows a large value at low temperatures which must be due to the presence of low frequencies.

Carbon tetrachloride. In order to investigate the effect of changing mass in the model, a representation of carbon tetrachloride has been constructed, the chlorine atoms being balls, the weight of which bears the proper ratio to the standard ball which represents the carbon atom. The results are shown in Fig. 4. If we use the same conversion factor of three, there is a discrepancy between the model frequencies and the Raman frequencies. This seems to be due to the fact that the force constant for the carbon-chlorine bond is somewhat smaller than for the carbon-carbon. An arbitrary conversion constant was therefore used which was somewhat smaller than the other one. There is no frequency in the model for the Raman line at 452 cm^{-1}. It seems quite possible that this is a first harmonic of the line at 216 cm^{-1}.

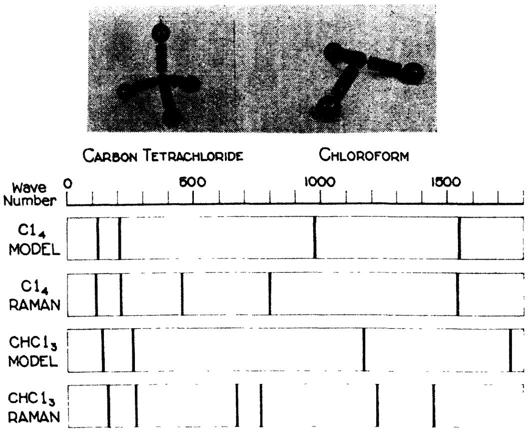


Fig. 4. Models of chlorine compounds.

Chloroform. This is just like the model for carbon tetrachloride except that the one chlorine atom has been omitted. If the value of the conversion constant suitable for the carbon-chlorine bond is used, the lines are in fair agreement with the Raman spectra.

MODELS WITH HYDROGEN REPRESENTED

In order to make a model in which the frequencies of the hydrogens could be represented and could be observable with the means at our disposal, it was necessary to change the scale of the model. For convenience we used, to represent the hydrogen, the ball which had previously represented the carbon, and carbon was now represented by a ball of twelve times the mass of the small ball. A spring of the same wire and same number of turns as before was used to represent the bond. Its length was, however, shortened by a third because in the molecule the distance separating C-H is 1A, while that separating C-C is 1.5A. With this means, models were constructed and vibrated and the results are as follows:

Ethane. In the model of ethane it was found that there was one frequency corresponding to the vibration of the two carbon atoms with respect to each other, also vibration of the hydrogen atoms at approximately three times the frequency of the carbon atoms. Of course, a new conversion constant must be used now that the mass has been changed. It might be calculated from the one previously adopted, but the difficulty of correcting for the mass of the springs makes this almost impossible. Since we are primarily interested in the ratio of the frequencies, it seemed wiser to adopt an arbitrary constant, and as it happens that in this model r.p.m. corresponds almost exactly to wave numbers, we have taken the conversion constant to be unity for the sake of simplicity.

As may be seen in Fig. 5, the ratio of the carbon frequencies (C-C) to the longitudinal hydrogen frequencies (H_l) is approximately that found in the Raman spectra for longitudinal vibrations. The model, however, shows transverse frequencies for the hydrogen (H_t) around 800 cm^{-1}. The line in the Raman spectrum which has been identified with this vibration lies at 1420 cm^{-1}. The reason for this discrepency between the model and the spectrum is hard to explain. Apparently the force constant for lateral displacement of the hydrogen is quite a bit larger than the corresponding force in the carbon-carbon bond. We can not hope, of course, for a perfect representation of the real molecule, and it seems that we must be content here with having the number of frequencies correspond while the numerical value of this type of frequency lies considerably lower in the model than it does in the spectrum.

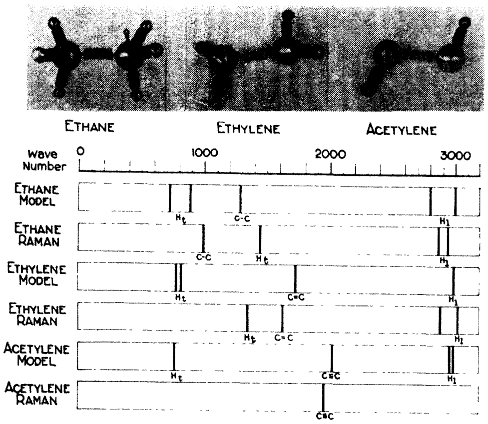


Fig. 5. Models with hydrogen represented.

Ethylene. By putting a double bond between the carbon atoms, we shift the carbon-carbon frequency to about 1700 cm^{-1}. This corresponds to the shift observed in the Raman spectrum. The frequencies of the hydrogen are but slightly affected as the spectrum also shows.

Acetylene. Putting a triple bond between the carbon shifts the frequency to a little over 2000 cm^{-1}. This corresponds to the spectrum observed.

Methyl alcohol. Dynamically, this is quite akin to ethane. We find about the same frequency for the vibration of the two heavy atoms and the frequencies in the same region for the vibration of the hydrogens as shown in Fig. 6. Again transverse vibrations of the hydrogens lie considerably lower than the lines ascribed to them in the Raman spectra.

It is very interesting to see the distinction between the two lines around 3000 cm^{-1}. When the model is vibrated at 2900 cm^{-1} the three hydrogens of the methyl group move in toward and out from the carbon while the hydrogen attached to the oxygen stays quiet. At 3000 cm^{-1} the three methyl hydrogens become quiet and the hydroxyl hydrogen vibrates. Since the masses and forces are the same in each case, this difference in frequency must be due to the fact that we have three balls reacting against the central ball in the one case and only one in the other case. It would, therefore, look as if the lines in the Raman spectrum could be positively identified with specific atoms in the molecule.

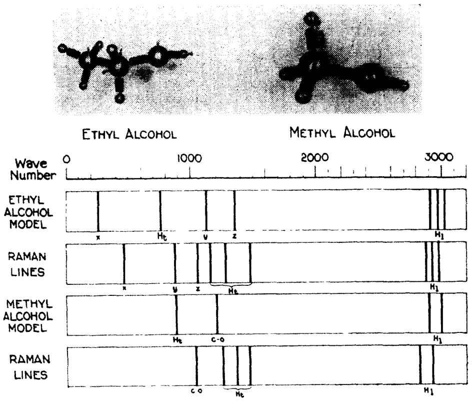
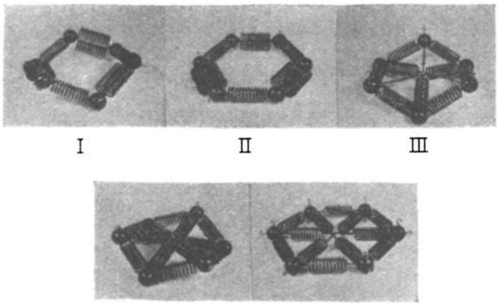


Fig. 6. Models with hydrogen represented.

Ethyl alcohol. This was constructed in the same way as the preceding models. We now have however, the possibility of three types of frequencies involving the large balls. The spectrum has the same general character as that of methyl alcohol. We now, however, find three lines around 3000 cm^{-1}. The lowest of these frequencies makes the three hydrogens in the methyl group vibrate while the others stand still. The next makes the two hydrogens in the CH_2 group vibrate, and the highest vibrates the hydrogen of the hydroxyl while the others remain quiet. We thus have a confirmation of the identification of these Raman lines with individual atoms. The transverse vibrations of the hydrogen again are lower than the lines identified with them in the Raman spectrum. The two upper vibrations (y, z) of the heavy atoms agree fairly well with the corresponding Raman lines. The lowest of the three (x) lies somewhat lower than the corresponding Raman line. This is probably due to the fact that in the model the mass is not distributed in space in the same way as in the molecule.

CONCLUSION

The general agreement which we have found between the characteristic frequencies of the models and the lines in the Raman spectra substantiates the character of the dynamical system in the molecule which we assumed in building the models. It seems reasonable to conclude that the molecular forces are directed along the lines associated with the chemical bonds and that mechanically, they are analogous to spiral springs. It appears also that the great majority of Raman lines have values of the frequency closely corresponding to fundamental mechanical frequencies in the molecule. Some of these frequencies are determined largely by the character of the whole molecule while others correspond to individual atoms or small groups of atoms. The mechanical model should prove very valuable in making these identifications and in ascertaining the structure of the molecule.



I II III

IV V

Fig. 1a.

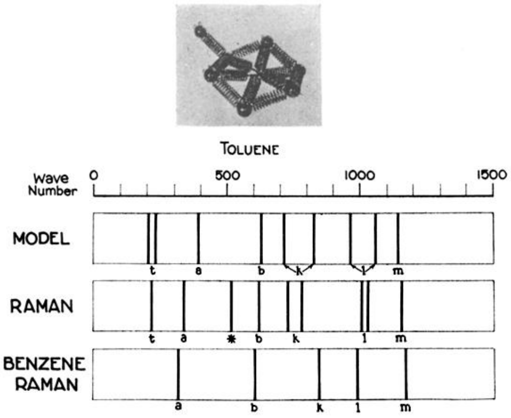


Fig. 3. Models of toluene.

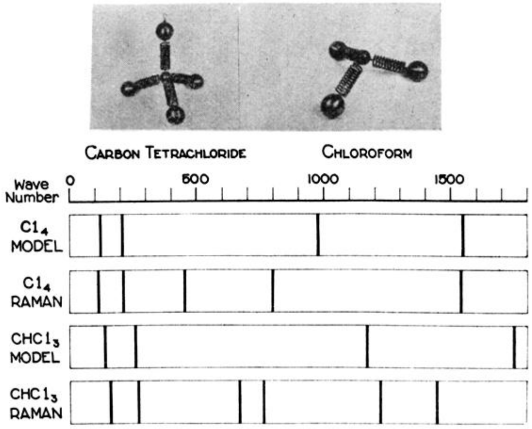


Fig. 4. Models of chlorine compounds.

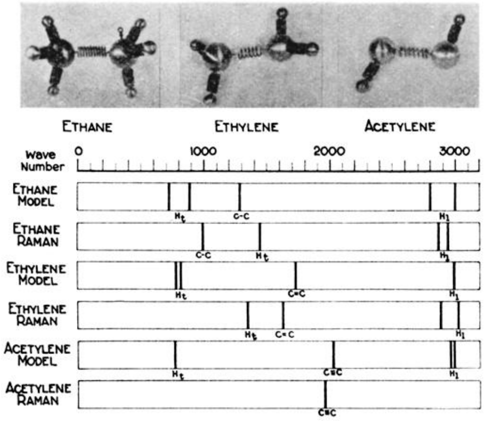


Fig. 5. Models with hydrogen represented.

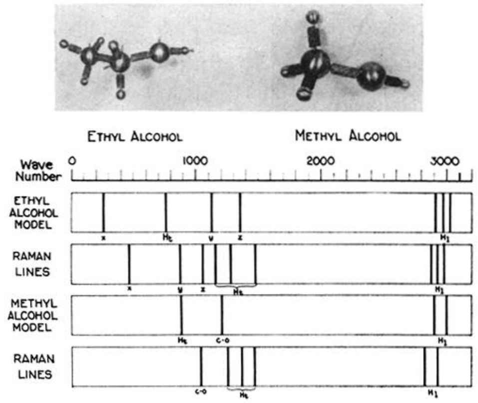


Fig. 6. Models with hydrogen represented.