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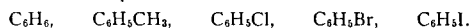
Studies with Vibrating Mechanical Models

I. Benzene, Toluene and the Phenyl Halides

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By continuing the work of Kettering, Shutts and Andrews, mechanical models have been constructed for the series of compounds:



The mechanical frequencies of the simpler types of motion show some correlation with the spectral lines, especially in the shifts of frequency in passing down the series of compounds. The types of motion observed are in fair accord with the types deduced with the aid of group theory.

KETTERING, Shutts and Andrews,¹ in their initial study of vibrating mechanical models of molecules, showed that it was possible to construct models of benzene and toluene in which the shifts of frequency caused by the introduction of the substituent group closely resembled the corresponding shifts in the spectral lines. In order to make a more extensive study of this type of shift we have constructed models of benzene, toluene, chlorobenzene, brombenzene and iodobenzene, and have observed their mechanical spectra.

In details of construction these models are similar to the previous ones,¹ the exact dimensions being given in Table I. A photograph of

constants were based on data obtained from methane and ethane.

The model representing the benzene nucleus was made with single-bond springs joining neighboring atoms in the ring, and two single-bond springs in series joining atoms para to each other.

The procedure followed was in general the same as that described in the earlier paper, the principal difference being in the type of stroboscope used, which consisted of a bright lamp placed behind a rotating disk with holes around the rim through which a beam of light passed to the model. The rotating disk was driven by a variable speed motor.

The types of motion observed are shown in Fig. 2. The drawings reproduce as closely as possible the original sketches noted when the motions were observed for the first time. In many cases these observations are somewhat inaccurate as may be surmised by comparison with the types of motion deduced from group theory which are discussed later.

The r.p.m. at which the modes of motion were excited are given in Table II and plotted in Figs. 3 and 5. In Figs. 4 and 5 there are shown plots of the Raman spectra of benzene,² toluene,³ and the phenyl halides⁴ compiled from various sources.

In order to make a comparison of the nu-

TABLE I.

	1	2
Spring type	C-H	C-C
Bond	11/64	11/64 in.
Spring wire diameter	4.5	5 cm
Outside diameter spring coil	5	5
Number of active turns	11.4	16 cm
Distance between ball centers	81	90 g
Weight of spring	5	11.4
Ratio of stretching to bending constant	C	H
Atom represented:	869	76 g
Weight of ball:		

the model of toluene is shown in Fig. 1. The atoms were represented by balls with masses approximately in the ratios of the atomic weights. The bonds were represented by two types of spring, type No. 1 being used for the carbon-hydrogen bonds and type No. 2 for the carbon-carbon and carbon-halogen bonds. The spring

¹ C. F. Kettering, L. W. Shutts and D. H. Andrews, *Phys. Rev.* **36**, 531 (1930).

² Krishnamurti, *Ind. J. Phys.* **6**, 543 (1931); R. W. Wood, *Phys. Rev.* **36**, 1431 (1930); K. W. F. Kohlrausch, *Monatshefte* **52**, 376 (1929); P. Grassman and J. Weiler, *Zeits. f. Physik* **86**, 321 (1933).

³ K. W. F. Kohlrausch, *Der Smekal Raman Effekt*, Julius Springer, Berlin (1931).

⁴ J. W. Murray and D. H. Andrews, *J. Chem. Phys.* **1**, 406 (1933); **2**, 120 (1934).

TABLE II. *Model frequencies.*

	C ₆ H ₆	C ₆ H ₅ CH ₃	C ₆ H ₅ Cl	C ₆ H ₅ Br	C ₆ H ₅ I		C ₆ H ₆	C ₆ H ₅ CH ₃	C ₆ H ₅ Cl	C ₆ H ₅ Br	C ₆ H ₅ I	
<i>X</i>		190	200	180	166	r.p.m.	<i>I</i>	1040				
<i>W</i>		200	200	180	166					1060		<i>I</i> ₂
		300	300*	340	340	<i>A</i> ₁				960	960	<i>J</i> ₁
<i>A</i>	340						<i>J</i>	960	960	920		
		340	360*	360	360	<i>A</i> ₂			1000	1000	1000	<i>J</i> ₂
<i>Y</i>		440	390	300	230		<i>E</i> ₇				1010	
<i>C</i>	510	480	480	480	500		<i>E</i> ₈	980		1100	1100	
<i>D</i> ₁	610						<i>E</i> ₄		1100			
<i>D</i> ₂	610						<i>K</i>	1160				
<i>E</i> ₁		600	540	580	510		<i>L</i>	1180				
<i>F</i>	680						<i>M</i>	1280	1400	1480	1400	1380
<i>E</i> ₂		600					<i>N</i>	1300	1200	1280	1280	1280
<i>E</i> ₃		600	610	600			<i>O</i>	1380	1280	1300	1300	1300
<i>E</i> ₅		620	620	610	610		<i>P</i>	1390				
		700	700	700	700	<i>G</i> ₁	<i>Q</i>	2060	2060	2060	2060	
<i>G</i>	790						<i>R</i>	2120	2120	2120	2100	2120
		740	780	740	780	<i>G</i> ₂	<i>V</i>	2080				
<i>E</i> ₃		810	740	880	880		<i>S</i>	2200	2200	2200	2180	2160
<i>H</i>	880	880	900	900	900							
		990	940	920	1060	<i>I</i> ₁						

* Identification of the type of motion not certain.

merical values somewhat easier a scale of wave numbers has been added in Fig. 3 so placed that the value of 992 cm⁻¹ falls at the line for the *H* motion in benzene. As will be shown in the following paper, there is considerable evidence that this strong line in benzene corresponds to the *H* type of motion.

Figs. 3 and 4 show certain apparent correlations between the mechanical frequencies and

the Raman spectra. The *X-W* motions in the phenyl halide models agree quite well in position and relative shift with the series of lines lying at the extreme lower limit of the Raman spectra. The corresponding motion in toluene lies somewhat lower than the Raman line apparently associated with it. This appears to be due to the weight of the three springs representing the carbon-hydrogen bonds of the CH₃ group, which makes the total weight of the CH₃ group relatively too great.

There is a correspondence between the positions and shifts of the *Y* type of motion and the series of lines starting at about 500 cm⁻¹ in toluene and ending at about 250 cm⁻¹ in iodobenzene. The identification of these lines with the motions of the substituent groups is in general accord with the conclusions drawn by Kohlrausch⁵ and his associates in their noteworthy series of investigations on the Raman spectra of phenyl derivatives.

There is a superficial resemblance between the series of lines in the Raman spectrum starting with 607 cm⁻¹ in benzene and the series in the mechanical spectrum labeled *C*. We believe, however, that this is not a true correlation. As will be shown in the next article of this series there is considerable evidence that the series starting at

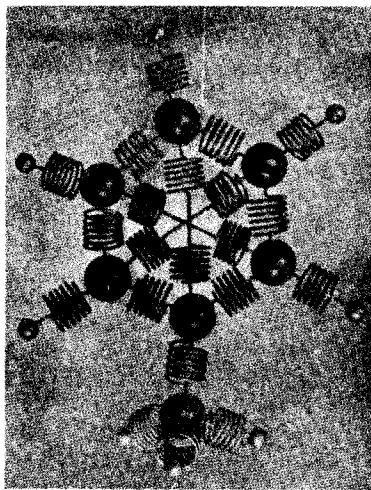


FIG. 1. Model of toluene.

⁵ K. W. F. Kohlrausch and A. Pongratz, Sitz. Ber. Akad. Wien [Ib] **142**, 637 (1934).

607 cm^{-1} is due to deformation vibrations in the plane of the ring.

Kohlrausch and Pongratz² point out that there is evidence for a series of lines starting with 849 cm^{-1} in benzene. With the exception of the line in $\text{C}_6\text{H}_5\text{Br}$ the series of mechanical vibrations starting with F and ending with E_1 show a close relation to these Raman lines.

The relative shifts of the H motion correspond to the shifts of the series of strong lines in the Raman spectra which start with the 992 cm^{-1} line in benzene. Since the shifts are so small, it is not very positive evidence.

There is another slight resemblance possibly worth noticing, namely, that between the series of mechanical vibration $I-I_1$ and the series of Raman lines starting at 1176 cm^{-1} in benzene and ending at 1062. Kohlrausch and Pongratz include the 1209 cm^{-1} toluene line in this series instead of the 1154 cm^{-1} line.

Fig. 5 shows the mechanical frequencies and Raman spectra for the 3000 cm^{-1} region usually associated with the motions which result primarily in stretching the carbon-hydrogen bond. The scale of wave numbers has been placed so as to make R in C_6H_6 fall at 3063 cm^{-1} . Although there is some evidence in the Raman spectra for three principal series of lines such as are shown by the models, the correlation between the shifts is not particularly good.

It is interesting to compare the types of motion observed in the models with the modes of motion deduced by E. Bright Wilson, Jr.,⁶ from group theory as shown in Fig. 2b. In seeking correspondences between the two sets of data several facts must be borne in mind. In the first place, Wilson has not given all his results in the form of complete types of motion. It is necessary to add together certain of his figures in

⁶ E. B. Wilson, Jr., Phys. Rev. **45**, 707 (1934).

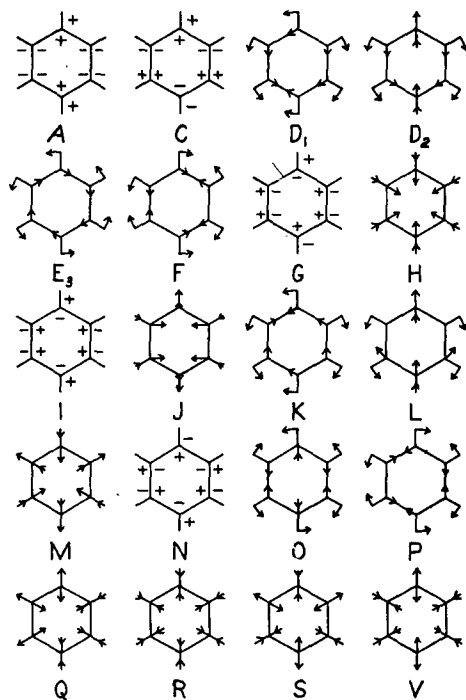


FIG. 2a. Benzene, model motions.

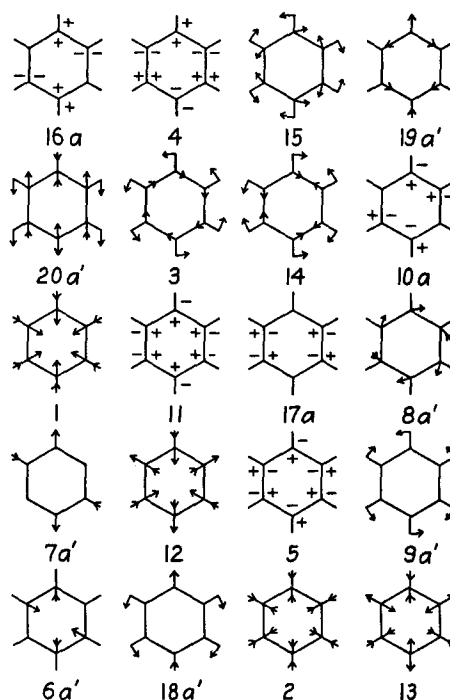


FIG. 2b. Benzene, group theory motions.

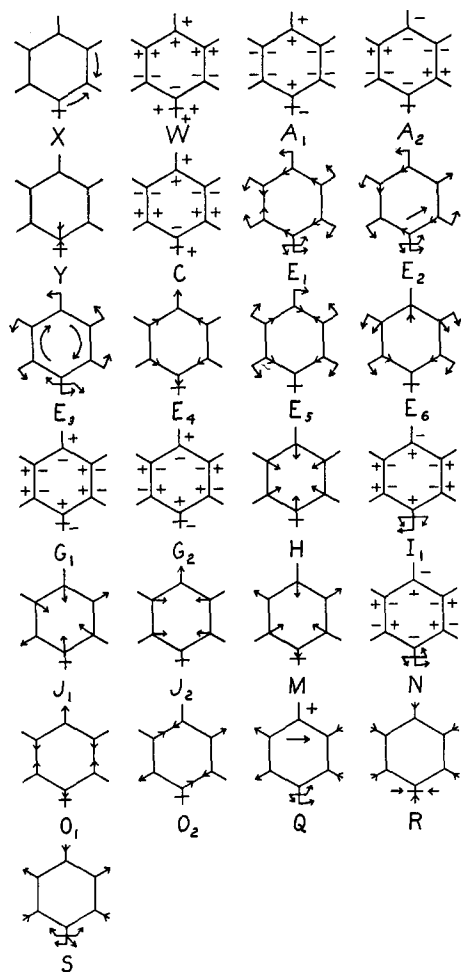


FIG. 2c. Toluene.

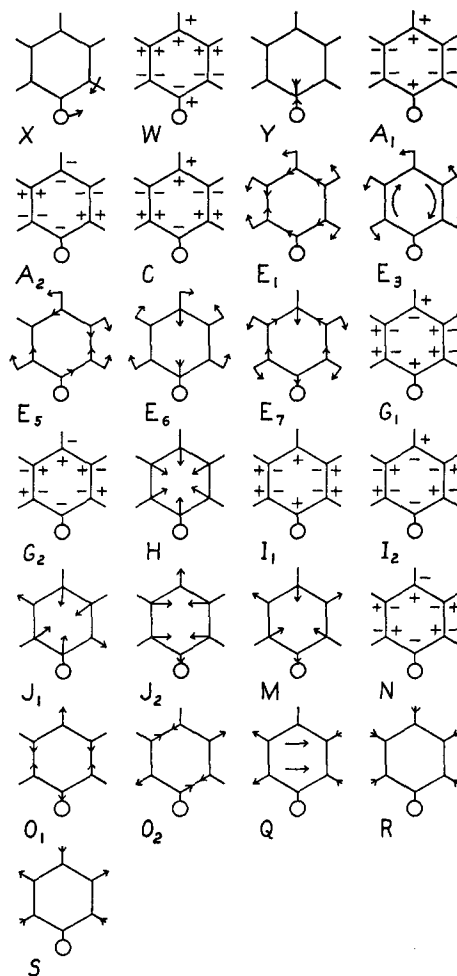


FIG. 2d. Halogen derivatives.

order to obtain the final result which gives the actual manner of vibration. In the second place, Wilson's results are based on the Pauling resonance formula for benzene so that in certain types of motion one would expect differences between his results and the behavior of the centric model. Finally one must remember that the precise direction of motion depends on the relative elasticity of the various bonds with respect to bending and stretching. Since we have

almost no information on this point at the present time we may expect considerable deviation in angle between any two methods which attempt to predict these motions.

With these facts in mind, one must conclude that the resemblance between the two sets of motions is quite striking. There are the following exact correspondences: $C=4$, $M=12$, $H=1$, $F=14$, $E_s=3$, $N=5$, $P=15$, $R=2$, $S=13$. By adding together certain of Wilson's incomplete

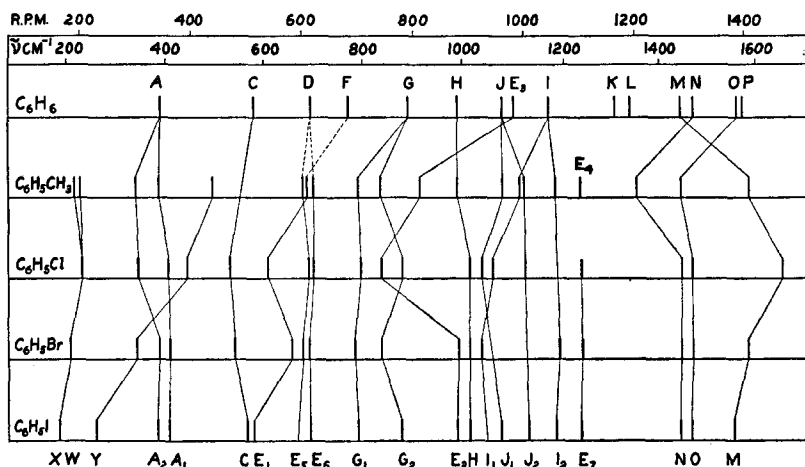


FIG. 3. Model frequencies.

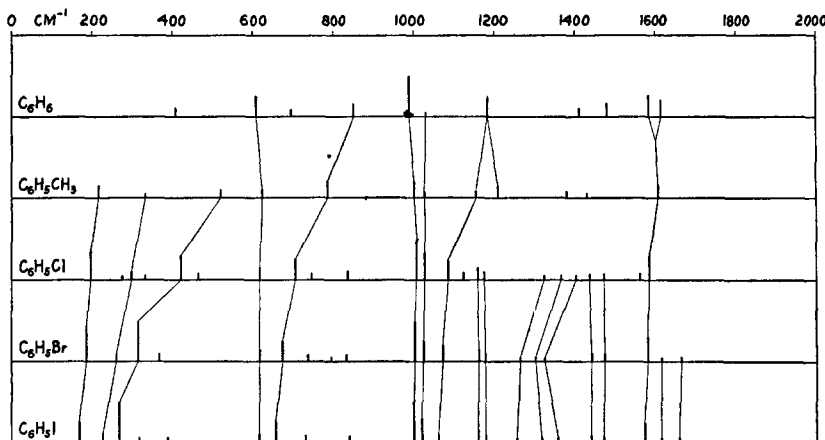


FIG. 4. Raman frequencies.

types of motion one also finds the following correspondences: $A = 16_{ar} + 16_{al}$; $D_2 = 18_a + 19_a$; $I = 17_{ar} + 17_{al}$; $J = 6_{ar} + 6_{al} + 7_{ar} + 7_{al}$; $V = 6_{ar} + 6_{al} - 7_{ar} - 7_{al}$; $G = 10_{ar} + 10_{al}$. The subscripts r and l refer to right-handed and left-handed types of motion. Finally there are the two correspondences which are incomplete in the part indicated by the asterisk: $L = 18_a + 19_a^*$; $O = 9_a + 6_a^*$. The types of motions D_1 , K and Q were not found by Wilson.

It is interesting to remember that, quite apart

from any relation which they bear to real molecules, the models are directly related to group theory, since they constitute a vibrating mechanical system which is amenable to treatment by this branch of mathematics. The models thus provide a means of testing the postulates of group theory without passing through the indirect and frequently uncertain medium of spectroscopic analysis.

After the work with these models was completed an attempt was made to study this same

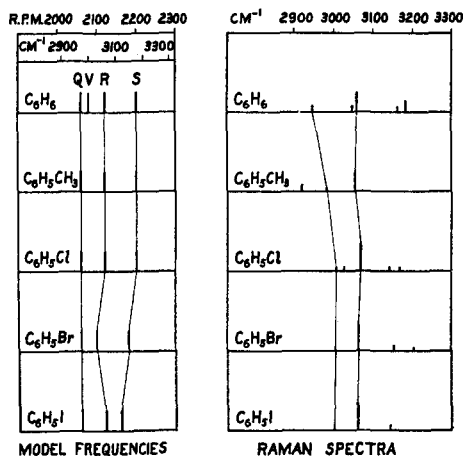


FIG. 5.

series of compounds with two other sets of models in which the springs representing the benzene ring correspond, respectively, to the Kekulé and to the Pauling resonance formulas.

The results were quite unsatisfactory. As found in the earlier model studies,¹ it is very difficult to get vibration in a steady state at a sharp resonance frequency if the molecule is what may be called the "floppy" type such as a long hydrocarbon chain. The model of the centric formula was compact enough to avoid this difficulty, the cross bonds acting to stabilize the vibration, but the models representing the Kekulé and Pauling resonance formulas were very unstable and yielded results that appeared to be incomplete and unreliable.

From this we may conclude that the usefulness of the models will be restricted largely to the study of certain relatively simple and stable types of vibration such as the *X*, *Y* and *H* movements where one can expect to get qualitative evidence of the effect of a change of mass on the frequency.

The authors wish to thank Mr. Charles F. Squire for the study which he made of the resonance and Kekulé models in connection with the work reported here.

Studies with Vibrating Mechanical Models

II. The Series: C₆H₅Cl—C₆Cl₆

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Mechanical models have been constructed for the following molecules based on the Pauling resonance formula for benzene: C₆H₆; C₆H₅Cl; *o*-, *m*-, *p*-C₆H₄Cl₂; (1, 2, 3)-, (1, 2, 4)-, (1, 3, 5)-C₆H₃Cl₃; C₆Cl₆. The mechanical spectra of these models have been observed and compared with the Raman spectra. The shifts in frequency observed in passing down the series are the same in both mechanical and Raman spectra in a number of cases. This makes possible the identification of several of the lines connected

with the motions of the chlorine atoms and of the line at 992 cm⁻¹ associated with the symmetrical expansion of the benzene ring. The types of motion show an evolution from the symmetrical group of C₆H₆, which can be correlated with group theory, through the various doublets and triplets associated with the less symmetrical intermediate compounds, to the group connected with C₆Cl₆ which is similar to that of C₆H₆ except for the inversion of frequency order due to the increased mass of the substituent atoms

IN studying the variation of characteristic frequencies with structure, some of the most interesting shifts in frequencies are those associated with the change in position of substitution in the benzene ring. Since a rather complete series of Raman spectra are available for the various chloro-derivatives of benzene, this group of compounds was selected as the basis for an

extension of the work with the vibrating mechanical models.

The atoms and bonds were represented by the same types of ball and spring used in work by Teets and Andrews¹ reported in the previous article of this series. The procedure followed for

¹ D. Teets and D. H. Andrews, *J. Chem. Phys.* 3, 175 (1935).