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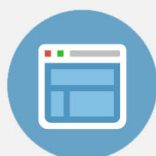
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TABLE IV. Bond angle α , observed Raman frequencies ν_1 , ν_2 , ν_3 and ν_4 in cm^{-1} . Calculated force constants K , H , K' and H' in dynes/cm and calculated interatomic distances in Angstroms for trihalides.

	α	ν_1	ν_2	ν_3	ν_4	$K \times 10^{-5}$	$H \times 10^{-5}$	$K' \times 10^{-5}$	$H' \times 10^{-5}$	R_0	$R_0 - R$ (obs)
(a) PF_3	100°	890	531	840	486	4.56	1.07	0.39	0.04	1.64	0.09
(b) PCl_3	102°	510	257	480	190	2.11	0.31	0.28	0.06	2.15	0.12
(c) PBr_3	104°	380	162	400	116	1.62	0.27	0.05	0.07	2.31	0.07*
(d) AsF_3	97°	707	341	644	274	3.90	0.40	0.34	0.06	1.80	0.08
(e) AsCl_3	96°	410	193	370	159	2.01	0.23	0.19	0.02	2.24	0.03
(f) SbCl_3	94°	360	165	320	134	1.75	0.17	0.16	0.02	2.30	-0.10*
(g) BiCl_3	93°	288	130	242	96	1.17	0.10	0.15	0.02	2.46	-0.04*

* $R(\text{obs})$ for these molecules taken from Pauling's tables of covalent radii. These values are probably somewhat high for these molecules.

Source of assignments:

(a) D. M. Yost of this laboratory, unpublished results. (b) and (e) See Kohlrausch, *Der Smekal-Raman-Effekt*, p. 201, Julius Springer, Berlin, 1931. (c) Cabannes and Rousset, *Ann. de physique* **19**, 272 (1933). (d) Yost and Sherborne, *J. Chem. Phys.* **2**, 125 (1934). (f) Braune and Engelbrecht, *Zeits. f. physik. Chemie* **B19**, 303 (1932). (g) Bhagavantam, *Ind. J. Phys.* **5**, 66, 86 (1930).

means of the relation found by Badger¹⁰ connecting the force constant and the interatomic distance in diatomic molecules. The last column

¹⁰ R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934).

of Table IV gives the difference between these values and the distances obtained either from electron diffraction or from Pauling's table of covalent radii.

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A Photographic Method for the Study of Mechanical Models of Vibrating Molecules

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(Received July 25, 1934)

IN the study of the vibrations of complex molecules the mechanical models developed by Kettering, Shutts and Andrews¹ have proved useful as a general aid to the interpretation of spectra and particularly as a means of obtaining suggestions regarding the different possible modes of vibration. One of the chief disadvantages in this method, however, is the difficulty of making certain by means of visual observation just what is taking place when the model vibrates. To overcome this defect a photographic

method has been developed for recording the types of motion, as shown in Fig. 1.

White dots, 2 mm diam., are painted with enamel on the balls B, B, B which represent the atoms. A 300 watt lamp L is placed so that the greater part of the light from it can be thrown on the model with the help of a mirror M and lens. The latter is so arranged that the light beam passes across the reciprocating bar K which runs from the motor P to the model to transmit the energy of agitation, and is reflected back on the model. It is brought to a rough focus at a point about two centimeters above the bar on which a screen S is placed so that at one end of the stroke it cuts down the intensity of the light by 75 percent. The resultant effect is that, when the model is executing a characteristic mode of vibration in phase with the agitating bar, the intensity of the light falling on it at one extreme of the phase is about four times that at the other extreme.

A camera C is placed about five feet from the model and arranged so that a time exposure may be taken while the model is vibrating. With

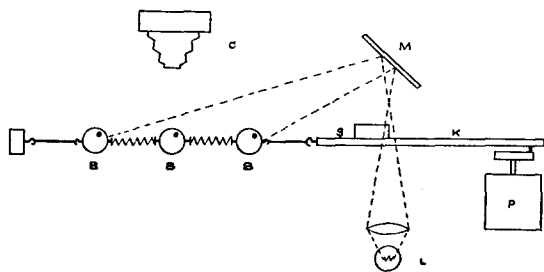


FIG. 1.

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

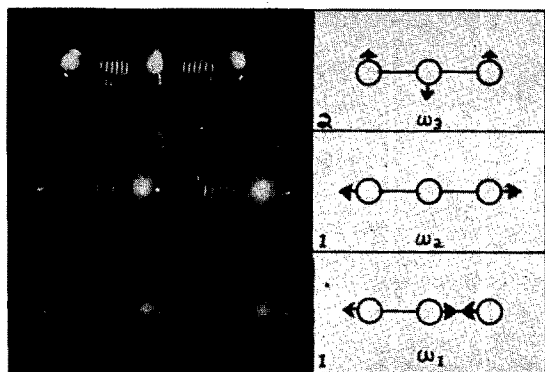
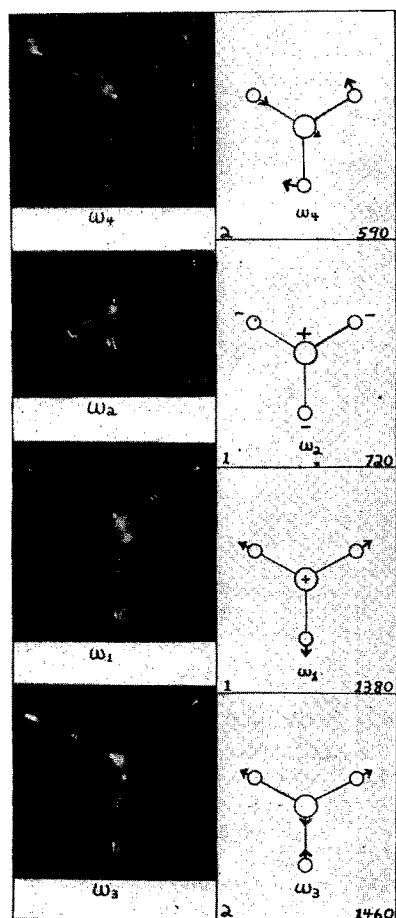


FIG. 2.

FIG. 3. Vibrations in NH_3 .

exposures of about one or two seconds the dots trace out the paths over which the atoms are vibrating, the intensities at the ends of the paths indicating the phase relations.

Fig. 2 shows the three modes of vibration in a

linear triatomic model composed of three balls of equal mass and two springs of equal strength. Fig. 3 illustrates the four modes of vibration in a model of the ammonia molecule. In the case of the degenerate types of vibration, ω_3 and ω_4 , only one mode of motion is excited.

The values of the observed frequencies for NH_3 are given in Table I. It seems either that ω_4 does not appear in the Raman spectra as might be expected from Placek's selection rules or that in the molecule the frequencies ω_2 and ω_4 have about the same value. There also appears to be some kind of doublet instead of a simple frequency for ω_3 .

The spring was designed to have roughly the ratio of bending to stretching force observed in a number of the C-H vibrations. The numbers given in the left-hand corner opposite each type of vibration indicate the number of degrees of freedom, and in the right hand corner the r.p.m. at which the motion was photographed. The latter have been converted by means of an arbitrary constant (calculated so as to bring ω_1 , and the corresponding model frequency* into

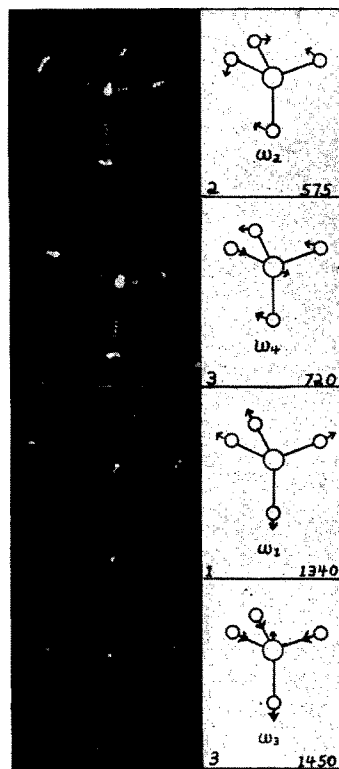
FIG. 4. Vibrations in CH_4 .

TABLE I. *Vibrations in NH₃.*

	Raman spectra ²	Model
ω_1	3210 cm ⁻¹	3210*
ω_2	1580	1675
ω_3	3310 }	3400
	3380 }	
ω_4	1580(?)	1370

TABLE II. *Vibrations in CH₄.*

	Spectra ⁴	Model
ω_1	2915 cm ⁻¹	2915*
ω_2	1304	1260
ω_3	1520	1575
ω_4	3022 }	3180
	3070 }	

agreement) to values comparable with the spectral frequencies. Only the qualitative agreement is significant.

Fig. 4 shows the vibrations observed in CH₄ and the frequencies either observed or deduced from spectra are given in Table II.

The method has been applied with considerable success in the study of some metal carbonyls and alkyls by Duncan and Murray³

² P. Daure, *Ann. de physique* **12**, 375 (1929).

³ A. B. F. Duncan and J. W. Murray, *J. Chem. Phys.* **2**, 636 (1934).

and in the study of the motions of the benzene ring to be discussed in a forthcoming article. It should be especially useful in unsymmetrical compounds such as hydrogen compounds consisting partly of protium and partly of deuterium where the lack of symmetry makes an analytical solution by means of determinants or group theory extremely difficult.

⁴ The authors' interpretation of the results of D. M. Dennison, *J. Astrophys.* **62**, 73 (1925) and Dickinson, Dillon and Rasetti, *Phys. Rev.* **34**, 582 (1929).

The Raman and Ultraviolet Absorption Spectra of Some Metal Carbonyls and Alkyls

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(Received July 17, 1934)

The Raman spectra of nickel carbonyl, iron pentacarbonyl, lead tetramethyl, and lead tetraethyl and the ultraviolet absorption spectra of nickel carbonyl, lead tetramethyl and lead tetraethyl have been studied. The symmetry number of nickel carbonyl has been calculated. The vibrations of a mechanical model of a plane XY₄ mol-

ecule have been studied. The correlation of the observed Raman lines with modes of vibration is discussed. It is concluded, from the observed spectrum and the vibrations shown by the mechanical model, that nickel carbonyl has a plane rather than a tetrahedral structure.

THE structure of compounds containing metal-carbon homopolar bonds has received little attention. The question is of interest not only from a purely scientific standpoint, but also because these substances are noted for their "anti-knock" properties when used in small concentrations in gasoline. We have obtained new optical data on nickel carbonyl, iron pentacarbonyl, lead tetramethyl and lead tetraethyl which we wish to report here.

The Raman spectrum of nickel carbonyl has been obtained previously by Dadieu and Schneider,¹ and by Anderson.² The former

¹ Dadieu and Schneider, *Anzeiger der Acad. der Wiss. in Wien, Math. Naturwiss. Klasse* **68**, 191 (1931).

² J. S. Anderson, *Nature* **130**, 1002 (1932).

authors also attempted to obtain the Raman spectra of cobalt tetracarbonyl and iron pentacarbonyl without success. The lead alkyls have not been examined from this viewpoint heretofore. The ultraviolet absorption spectrum of nickel carbonyl has been examined by Thompson and Garratt³ whose findings are confirmed by our work. The ultraviolet absorption of the other compounds treated in this work have not been investigated previously.*

³ H. W. Thompson and A. P. Garratt, *J. Chem. Soc.* (1934), 524.

* H. W. Thompson (*J. Chem. Soc. London*, 1934, 790) has recently reported a system of discrete bands belonging to lead tetraethyl which lies on the long wave side of the continuum observed by us and by him. Although we used a slightly longer path and corresponding pressures, we