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[5] I. R. Rao, *Indian J. Physics*, **3**, 123 (1928).

[6] H. Nisi, *Proc. Imp. Acad. of Japan*, **5**, 127 (1929).

[7] C. Schaefer, *Zeit. Phys.*, **54**, 153 (1929).

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[9] This agreement may be fortuitous because of the fact that maxima of reflection and absorption are not quite coincident and are sometimes very appreciably removed from each other. See, for example, Havelock, *Proc. Roy. Soc.* **105A**, 488 (1924).

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RAMAN SPECTRA FROM ACETONE

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Measurements of Raman spectra from acetone have been published in a recent paper.[1] These measurements were so interpreted that out of thirteen modified lines, twelve corresponded to frequencies of observed infra-red absorptions, the thirteenth lying outside the range of the infra-red measurements. This result is surprising; for the occurrence of frequency shifts in Raman effect without the appearance of the corresponding infra-red absorptions is a very common phenomenon. We have examined Raman spectra from acetone; and as both our measurements and our interpretation disagree with those mentioned above, it seems desirable to report them.

The acetone used was Merck's "C.P." It was distilled through a 30 cm.-Eastman fractionating column the product used all coming over within 0.05° of 55.7° at 746 mm. It is important to use materials of reasonable purity; we have, for example, found it possible to bring out the strongest benzene lines from a carbon tetrachloride solution containing only 0.46% benzene.

The acetone was irradiated with light from a glass mercury arc, and the spectra photographed with a glass spectrograph having a dispersion of about 100 cm.$^{-1}$ per mm. in the blue. The iron arc was used as a standard.

The measured frequencies of the shifted lines together with their intensities are given in the second and third columns of table 1. Comparison of these measurements with those which have already been reported[1] shows considerable disagreement even among the strongest lines. Apparently seven lines are concerned in the production of these Raman lines. The wave-lengths and frequencies of these mercury lines are:

I	3650.15 Å 27388.4 cm.$^{-1}$	V	4077.8 Å 24516.1 cm.$^{-1}$
II	3654.83 Å 27353.3 cm.$^{-1}$	VI	4347.50 Å 22995.3 cm.$^{-1}$
III	3663.27 Å 27290.5 cm.$^{-1}$	VII	4358.34 Å 22938.1 cm.$^{-1}$
IV	4046.56 Å 24705.5 cm.$^{-1}$		

TABLE 1

OBSERVED RAMAN LINES FROM ACETONE —

NO.	OBSERVED FREQUENCY OF SHIFTED LINE, CM.$^{-1}$	ESTIMATED INTENSITY OF SHIFTED LINE	ASSUMED ORIGIN OF LINE	CALCULATED FREQUENCY OF SHIFTED LINE, CM.$^{-1}$
1	24464.4	Very strong	I — m	24464.6
2	24428.1	Strong	I — n	24421.8
			II — m	24429.5
3	24383.5	Medium	I — o	24382.0
			II — n	24386.7
4	24367.5	Strong	III — m	24366.7
			II — o	24346.9
5	24316.1	Weak	III — n	24323.9
			IV — a	24314.0
6	24284.7	Weak	III — o	24284.1
7	24212.9	Very weak	IV — b	24213.5
8	24174.0	Medium weak	IV — c	24175.5
9	23918.3	Strong	IV — d	23917.5
10	23727.1	Medium weak	V — d	23728.1
11	23639.0	Medium weak	IV — g	23638.1
12	23482.7	Medium	IV — h	23482.7
13	23366.5	Very weak	IV — i	(23366.5)
14	23275.5	Medium (broad)	IV — j	23275.0
15	22546.6	Medium	VII — a	(22546.6)
16	22446.7	Weak	VII — b	22446.1
17	22407.6	Medium	VII — c	22408.1
18	22207.0	Very weak	VI — d	22207.3
19	22150.9	Very strong	VII — d	22150.1
20	22032.5	Very weak	VII — e	(22032.5)
21	22009.7	Very weak	VII — f	(22009.7)
22	21869.8	Medium	VII — g	21870.7
23	21782.5	Very strong	IV — m	21781.7
24	21738.9	Medium strong	IV — n	21738.9
25	21712.0	Medium strong	VII — h	21715.3
26	21696.2	Medium strong	IV — o	21699.1
27	21590.0	Medium strong	V — m	21592.3
			VII — i	21599.1
28	21507.2	Medium strong (broad)	VII — j	21507.6
29	21227.1	Strong	VII — k	(21227.1)
30	21190.1	Very weak	VII — l	(21190.1)
31	20069.9	Very weak	VI — m	20071.5
32	20015.5	Strong	VII — m	20014.3
33	19972.4	Medium weak	VII — n	19971.5
34	19931.7	Medium weak	VII — o	19931.7

The strongest of these lines are I, IV and VII. Lines V and VI are so weak as to be involved in the production of only the most prominent Raman shifts. The modified lines are all accounted for by using the frequency differences summarized in table 2.

TABLE 2

FREQUENCY SHIFTS FROM ACETONE

DESIGNATION OF SHIFT	FREQUENCY SHIFT, CM. $^{-1}$	RELATIVE INTENSITY OF SCATTERING	λ RAMAN μ	λ I. R. μ	RELATIVE INTENSITY OF ABSORPTION
a	391.5	Medium	(25.6)		
b	492.0	Weak	(20.3)		
c	530.0	Medium	(18.9)		
				13.10	2.3
d	788.0	Very strong	12.69	12.63	2.2
e	905.6 (?)	Very weak	11.03	11.30	1.2
f	928.4 (?)	Very weak	10.77	10.90	4.0
				10.40	0.2
				9.70	0.2
g	1067.4	Medium	9.38	9.10	2.0
h	1222.8	Medium strong	8.17	8.30	4.0
i	1339.0 (?)	Very weak	7.47	7.60	0.3
				7.30	0.5
j	1430.5	Medium (broad)	6.99	6.98	0.4
				6.60	0.5
k	1711.0	Strong	5.84		
l	1748.0 (?)	Very weak	5.72	5.75	5.2
				4.70	1.5
m	2923.8	Very strong	3.42	3.41	4.0
n	2966.6	Strong	3.37		
o	3006.4	Strong	3.27		

In the fifth column of table 1 are given calculated frequencies of modified lines obtained assuming the various lines to originate in the way indicated in the fourth column. (For example, I—*m* is the mercury line I of frequency 27388.4 cm.$^{-1}$ shifted by the amount 2923.8 cm.$^{-1}$ which is shift *m*.) It may be seen that the assumed origins of the lines are such that modified lines corresponding to any one shift have qualitatively (allowing for the smaller sensitivity of the plate toward the green) the same relative intensities as the mercury lines producing them. Several of the lines in table 1 (Nos. 2, 3, 4, 5 and 27) should result from the approximate superposition of two or more modified lines; measurements of these have been disregarded in selecting the best values given in table 2.

The fairly strong shift *k* ($\Delta\nu$ = 1711.0) occurs only once (line 29); Hg 4046 shifted by this amount would produce a line almost coincident with Hg 4347. If, however, a different origin were assumed for line 29 we should expect to find other lines not occurring on the plate. To account for lines 13, 15, 20, 21 and 30 corresponding to shifts *i*, *a*, *e*, *f* and

l we have also found it necessary to assume five frequency shifts not otherwise employed. When a potassium chromate filter was used, line 15 was greatly strengthened compared with, for example, lines 12 and 14; this leaves little doubt that line 15 arises from Hg 4358 modified by shift *a*. There remains, possibly, some ambiguity in the origin of lines *e, f, i* and *l*. We have attempted to remove this ambiguity by using the potassium chromate filter; but because of the extreme weakness of these lines we have not been entirely successful.

In the fourth column of table 2 are given calculated infra-red wavelengths corresponding to the frequency shifts. In the fifth and sixth columns are the wave-lengths and intensities of the maxima of infra-red absorption observed by Coblentz.[2] If a latitude of 0.3μ be allowed, all of the observed Raman shifts can be brought into agreement with infrared absorption maxima in so far as the investigated regions overlap. In view of the considerable number of frequencies involved in both spectra, the necessity of allowing so much latitude leaves some of the coincidences unconvincing. In any case, the intensities in scattering and in absorption bear no evident relation. This question has been discussed elsewhere.[3]

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[2] Coblentz, "Investigation of Infra-red Spectra," *Carnegie Inst. Publications*, 1 (1905).

[3] Dickinson, Dillon and Rasetti, *Phys. Rev.*, 34 (1929).

THE THERMAL DECOMPOSITION OF ACETONE IN THE GASEOUS STATE

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In the field of reaction kinetics, the study of unimolecular homogeneous gas reactions is, from a theoretical standpoint, most interesting. At the present time but few really homogeneous, unimolecular reactions are known and this work was undertaken with the object of extending the number of organic decompositions of this type. In all the investigations of such decompositions made so far, the method used to follow the reaction has been to measure the rate of increase of pressure and from this to obtain the velocity constant. This method has two obvious disadvantages: (1) we must know what the products of decomposition are, and (2) these must not decompose or react with each other appreciably at the temperature of the experiment. Unfortunately in the case of organic compounds, these conditions seriously limit experimental work so that the decomposi-