A new class of spectra due to secondary radiation
Part I

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[Plates 1–3]

1. Introduction

The discovery of a new type of secondary radiation, distinct from either the classical scattering or ordinary fluorescence, has been recorded in an address delivered recently by one of us and published in the previous issue of this Journal.[1] Whenever light is diffused by the molecules of a transparent medium, the scattered radiations contain not only the wavelengths present in the incident light but also radiations of modified frequency. The effect is most striking when the scattering medium is a dust-free liquid, and the incident radiations consist of sharply defined spectral lines, e.g. the light of a quartz mercury lamp. It is then found that in the spectrum of the scattered light we have besides the incident lines also other new lines which are usually quite sharp. A continuous spectrum may also be observed and is specially noticeable in certain liquids. The scattered radiation of altered wavelengths is partially polarised. Though the effects mentioned above are most readily studied with liquids, other media such as vapours, crystals and even amorphous solids exhibit the modified scattering, which is thus a universal phenomenon. The explanation was tentatively put forward that the new type of secondary radiation is produced when the incident quantum of radiation is partly absorbed by the molecule, shifting it to a higher level of energy, and is partly scattered. The difference between the frequencies of the incident and scattered radiations would thus correspond to a characteristic frequency of the molecule. Accepting this explanation it follows that corresponding to a given frequency of the incident radiation, we should expect a new line in the spectrum of the scattered radiation for each one of the characteristic frequencies of the molecule, that is to say, for each incident frequency we should

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[1] A New Radiation by C V Raman, *Indian J. Phys.* 1928 **2**, p. 387. See also C V Raman and K S Krishnan, *Nature (London)* 1928 **121**, p. 501.

expect as many lines of modified frequency as the molecule has characteristic electronic frequencies. Further, when the incident radiation contains several spectral lines, we should expect several sets of such modified lines in the scattered spectrum. The new type of secondary radiation should thus create for us a whole new class of spectra, and indeed as many new spectra as there are chemical substances suitable for study, multiplied by the number of spectral lines available in the light-source used.

The discovery of the new radiation thus opens up a wonderful avenue of research in spectroscopy. During the past few weeks we have succeeded in obtaining a number of spectrograms of the scattered radiation with the following liquids selected for their importance, namely, benzene, toluene, pentane, ether, methyl alcohol and water. The spectrograms obtained with benzene have been measured. It is proposed in this paper to detail the highly significant results which have emerged from the detailed study of the spectrograms for benzene, and from a qualitative study of the spectra obtained with the other liquids.

2. Experimental methods

As the source of illumination we used a commercial 3,000 C.P. mercury vapour lamp in quartz, made by the Hewittic Electric Company, which was found to be thoroughly reliable and efficient in its working. The light of the lamp was concentrated by an 8-inch glass condenser into a bulb containing the dust-free liquid under examination. The larger the bulb the more satisfactory are the conditions of observation and it is therefore desirable to use a bulb of clear non-fluorescent glass, having a diameter at least as large as the image of the quartz lamp formed by the condenser. On the other hand, a large bulb involves the use of a large quantity of the liquid and correspondingly greater expense. With liquids such as water or the common chemicals such as benzene, this is not a serious consideration. But in the case of the more costly chemicals it sets a limit to the size of the bulbs to be employed.

It is of importance that the liquid to be used for study should be chemically the purest available. For purpose of further purification, it is placed in a second large bulb connecting with the observation bulb, and transferred to the latter by distillation in *vacuum*. If the bulbs have been thoroughly cleansed before filling, a single distillation may suffice. It is usually advisable however to wash back the distilled liquid from the observation bulb to the distillation bulb several times. The distillation should be conducted at as low a temperature as possible. For this purpose the initial vacuum should be good, and the observation bulb is cooled with ice, so that the distillation occurs quickly when the second bulb is only moderately warmed. The final distillate is then obtained as a very clear liquid free from dust or other fluorescent impurity and is then used immediately for the optical observations.

The modified lines in the scattered spectrum can easily be seen with a pocket spectroscope. The most convenient direction of observation is that transverse to the path of the beam of light through the liquid, though of course any other direction of observation is theoretically permissible. The maximum intensity is obtained when the axis of the spectroscope is pointed along the direction of the image of the quartz lamp formed within the liquid, as the greatest depth of illuminated liquid is obtained in this way. For purpose of visual observation, it is helpful to exclude wavelengths greater than 4358·3 A.U. from the incident light by placing in its path a violet glass, which completely cuts out the blue, green and yellow regions of the mercury spectrum. The spectrum of the modified scattering (lines and in some cases also bands and continuous spectrum) is then very conspicuous in the blue-green region of the spectrum. With a little practice the wavelengths of the brightest modified lines can even be read off on the drum of a Hilger constant deviation spectrometer. Photographic study of the spectrum is, however, obviously the most convenient and accurate method for quantitative work, and indeed for the fainter lines the only method available.

The spectrograms reproduced with this paper (Plates 1 and 2) were obtained with a Hilger E_2 quartz spectrograph, the reproductions being enlarged about twice from the original negatives. When sufficiently sensitive plates, e.g. Ilford Iso-Zenith are used, an exposure of a few hours is sufficient to obtain a fairly good spectrogram. In order, however, to obtain the fainter details, exposures of twelve or twenty four hours are desirable. As the quartz mercury lamp runs without attention, very long exposures can be given without any trouble or fatigue.

Usually the spectrograms are taken with the complete light from the mercury arc incident within the liquid. As the glass dome and condenser of the lamp cut out the extreme ultraviolet, the incident radiation extends from about 3400 A.U. towards longer wavelengths: Owing to the operation of the Rayleigh λ^{-4} law, the longer wavelengths (except the most intense lines) are practically suppressed in the classical or unmodified scattering, and hence the numerous lines present in the visible region of the spectrum of the mercury arc do not trouble us much. Indeed such of the brighter incident lines as appear in the scattered spectrum serve as a convenient scale of wavelengths.

If it is desired to use instead of the whole incident spectrum, only selected lines as the radiation to be scattered, this is done by placing suitable filters between the lamp and the observation bulb. A fresh strong solution of quinine sulphate followed by a blue glass serves to cut out everything except the 4358 A.U. line and its close companions, from the incident spectrum. A Corning ultraviolet glass filter (G 586) by itself passes a narrow region of the spectrum including the group of three lines near 3650 A.U.

A solution of potassium permanganate passes the strong lines 4047 A.U. and 4358 A.U. and their close companions. A strong solution of cobalt sulphocyanate in water is also useful. It transmits the group of lines near 4047 A.U. and

suppresses the other bright lines in the ultraviolet and visible regions of the spectrum.

3. Experimental results

Figure 1 in plate 1 gives the direct spectrum of the mercury arc in quartz, up to and including the two yellow lines, the exposure being such as to give a satisfactory picture in which the brightest lines are not heavily overexposed. Figures 2, 3 and 4 are the scattered spectra of benzene, toluene and pentane respectively. The two yellow lines do not appear in them while the lines in the violet and ultraviolet are somewhat overexposed. This is a natural consequence of the Rayleigh λ^{-4} law for the classical scattering. On comparing figure 1 with figures 2, 3 and 4, it will be seen that the latter contain a great many new lines not present in the direct spectrum of the mercury arc. These lines will be referred to in what follows as modified lines. It will be noticed their intensity is comparable with that of some of the weaker unmodified lines.

Figure 7 in plate 2 is another direct spectrum of the mercury arc produced for comparison with figures 8, 9 and 10 in the same plate, which are the scattered spectra from pentane, ethyl ether and methyl alcohol respectively. Figure 11 in plate 2 represents the scattered spectrum from distilled water and figure 12 the spectrum of the incident light for comparison with it. (A violet filter had been used in the incident light which cut off the lines in the blue, green and yellow regions of the incident spectrum).

Figures 5 and 6 in plate 1 are of special interest. Figure 5 represents the spectrum of the mercury arc filtered through quinine sulphate solution and a blue glass, which transmit only the 4358·3 A.U. line and its close companions (the two feeble lines of shorter wavelength appearing to the left of it are due to stray light). Figure 6 is the spectrum of the light thus filtered after being scattered by benzene liquid.

4. Qualitative study of the spectra

A general scrutiny of the spectrograms reproduced in plates 1 and 2 brings out several features of interest and importance.

In the first place it is clear from an inter-comparison of figures 2 and 6 both of which represent the scattering by liquid benzene, that when the quinine filter suppresses the bright lines in the incident spectrum, of shorter wavelength than 4358·3 A.U., it also suppresses from the scattered spectrum many of the modified lines with wavelengths both greater and smaller than 4358·3 A.U. With a potassium permanganate filter instead of quinine sulphate, we have the 4047 line in addition to the 4358 line in the incident spectrum, and several of the modified

scattered lines suppressed previously re-appear.[2] On the other hand Corning glass (G 586) ultraviolet filter, which transmits the 3650 lines and cuts out the 4047 and 4358 groups from the incident light, also cuts out all the modified scattered lines which appear when either quinine sulphate or potassium permanganate filters[3] are used. *It is thus clear that each line in the incident spectrum generates its own modified radiations in the scattered spectrum, independently of the other lines.*

All the modified scattered radiations seen in the spectrograms are generated by the intense lines lying in the region from 3650 to 4358 A.U. of the incident spectrum. That incident lines of longer wavelength are not equally effective is not surprising. For even the classical scattering of such wavelengths becomes very weak in consequence of the Rayleigh λ^{-4} law, and the modified scattering, if any, due to such wavelengths may also be expected to be feeble. Further, even if there were such lines they could hardly be expected to appear on the plates, owing to the relative insensitiveness of the photographic plate used, in the green and yellow regions. A careful visual examination may perhaps reveal them, but the attempts so far made have not been successful with the liquids studied in the present paper. The dependence of the intensity of the modified scattered lines on the wavelength of the incident lines, is a subject for further experimental research.

On figure 6 of plate 1, the modified lines due to the incident 4358·3 A.U. line are all of longer wavelength, except one, which appears feebly but quite clearly in the original negative, but is perhaps not visible in the reproductions. The existence of this line proves in a perfectly unmistakable way that *while a degradation of frequency is by far the most probable effect in light-scattering, an enhancement of frequency may also occur.* We shall have more to say about this line later on.

5. Relation of modified scattering to chemical constitution

An inter-comparison of figures 2, 3, 4, 8, 9, 10 and 11 in the plates shows in a striking way the manner in which the chemical constitution of the molecule influences the modified scattering. It is clear that each chemical substance has its own special type of modified scattering, no two of the spectra being exactly alike. Nevertheless, certain general similarities are noticeable in the scattered spectra due to compounds having similar chemical characters. For instance, in plate 2, the brightest groups of lines in the scattered spectra of the three aliphatic

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[2] See plate 1, figures 3 and 4 reproduced in the address on "A New Radiation," *Indian J. Phys.* **2**, facing p. 396.
[3] A spectrogram of the scattering by liquid benzene with the Corning glass filter in the incident light has been obtained but is not reproduced in the present paper.
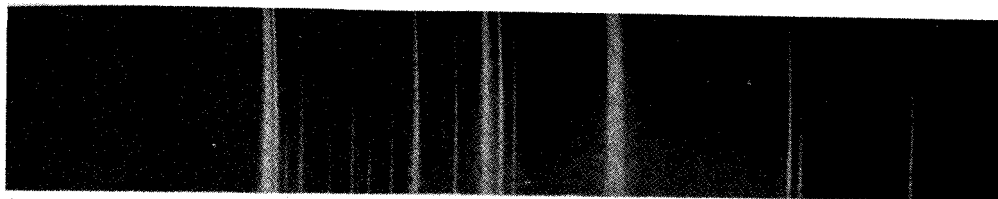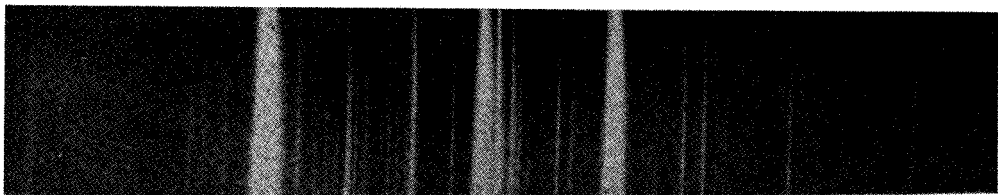
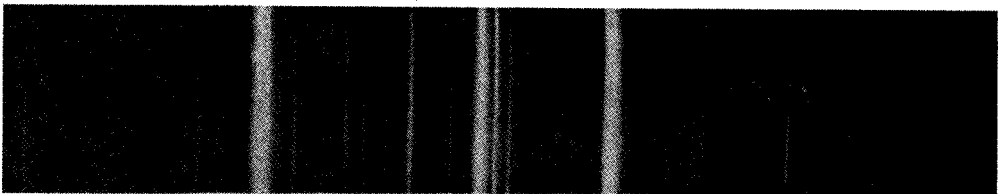Plate 1

3650·1   4046·6   4358·3   4916·1   5460·7
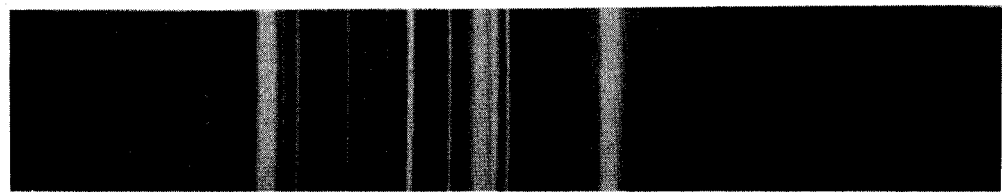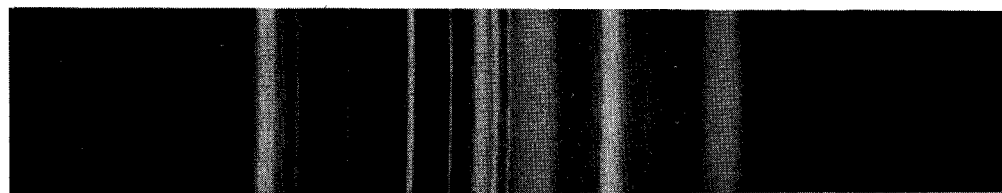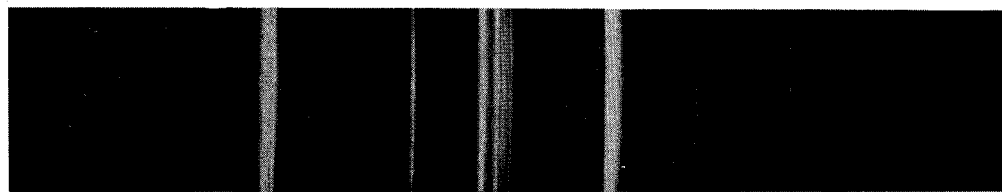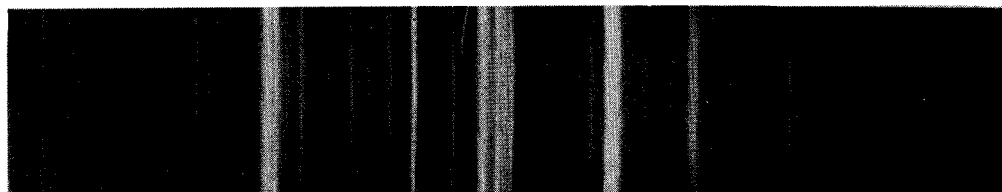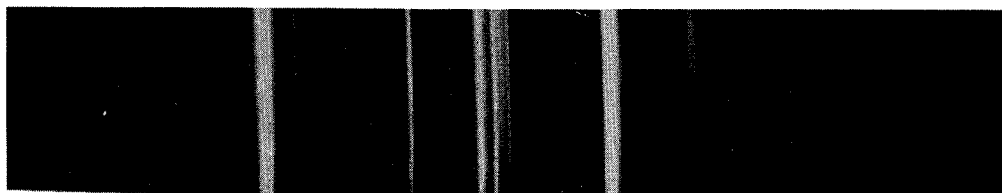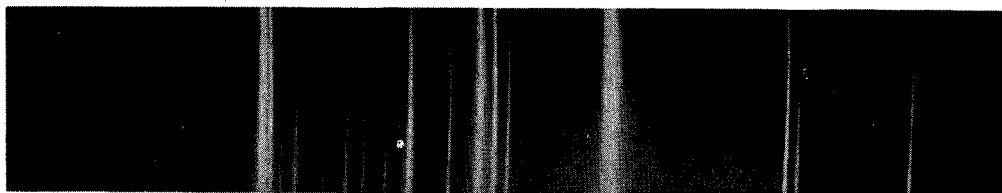
Plate 2

Modified lines | Benzene | Incident lines

Modified lines:
5029·6

4683·5

4593·9

4555·1

4476·4

4178·5

Incident lines:
4916·1

4358·3

4108·9

4077·8

4046·6
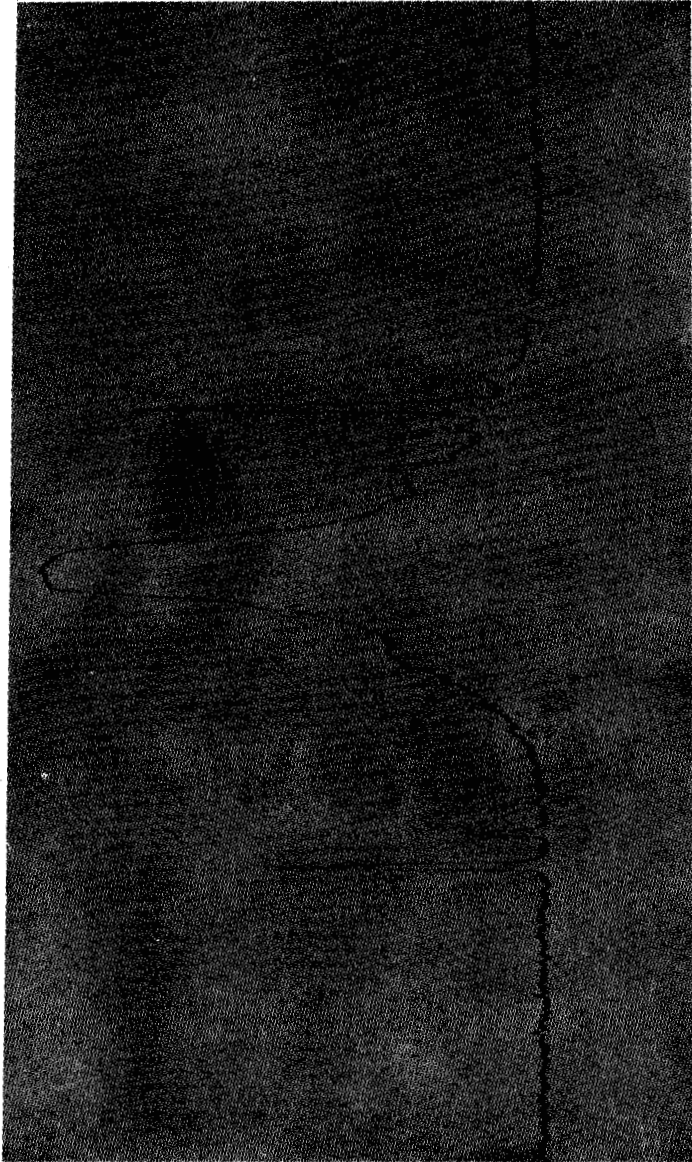
Microphotometered Spectrum of Scattering

Plate 3

compounds pentane, ethyl ether and methyl alcohol, are in approximately the same positions, one group of lines appearing in the region 4076 A.U. to 4100 A.U., a second group in the region 4500 A.U. to 4600 A.U., and a third group (visually very bright, but only very faintly visible in the photographs) in the region 4900 A.U. to 5000 A.U. Comparing the scattered spectra of the two aromatic compounds benzene and toluene, we see that toluene gives many more lines than benzene, but that the lines due to toluene are less intense, some of the brighter lines due to benzene and toluene are in nearly identical positions, and these differ distinctly from the positions of the brighter groups of lines obtained with the aliphatic compounds. On the other hand, a close comparison of the spectra due to toluene and ether shows certain similarities evidently connected with the presence in both the compounds of the methyl group CH_3.

The scattered spectrum of water (plate 2, figure 11) is very remarkable, as it shows bright bands instead of sharp lines. It is very interesting that methyl alcohol shows in addition to sharp lines, also diffuse bands, one of which is seen in figure 10, plate 2 in the region 4100 A.D. to 4105 A.D., that is to say, in the same region as the first and brightest band obtained with water. We may presumably attribute this similarity to the presence in methyl alcohol, of the hydroxyl group OH.

Further discussion of the relationship between chemical constitution and the scattered spectra must evidently be postponed till a large number of compounds have been studied, and the positions and intensities of the modified lines observed with them have been determined and tabulated. Even the preliminary work described above, however, makes it clear that the scattered spectrum is practically a description in spectroscopic form, of the chemical constitution of the molecule. Since the lines are in many cases sharp and can therefore be very accurately measured, the frequency differences between the incident and modified lines can be accurately determined. The study of the scattered spectra thus promises to be of great importance for the future of chemistry as an exact science.

6. Measurements of the benzene spectrum

The spectrum of the light scattered by liquid benzene, which is reproduced in figure 2 of plate 1, was measured with a Hilger travelling micrometer, and such of the lines appearing in it as were present in the direct spectrum of the mercury arc were located and identified by comparison with the photograph reproduced in figure 1. From the known wavelengths of the standard lines thus identified, the wavelengths of the modified scattered lines appearing only in figure 2 and not in figure 1 were determined from the measurements, using the Hartmann simplified interpolation formula. The wavelengths of the modified scattered lines thus measured are probably accurate to 0·5 A.U. in the case of well-exposed lines, and to within 1·0 A.U. in the case of faint or diffuse lines. Greater accuracy should be

possible if an iron arc be used as a comparison and the wavelengths determined from the nearest standard lines by interpolation. The quartz spectrograph used provides in the blue region a dispersion of about 50 A.U. per mm on the original negative. In view of the brightness and sharpness of the modified scattered lines, a dispersion much greater than this should prove useful and make a greater accuracy of measurement possible. The present work being of a preliminary nature, we have contented ourselves with determinations of wavelength to within 0·5 A.U. or 1·0 A.U. With the improvements mentioned above, a ten- or a hundred-fold increase of accuracy might well be hoped for.

In Table I, the wavelengths of the lines in the scattered spectrum of benzene have been separated into two classes and shown under the headings "Unmodified lines" and "Modified lines" respectively, the former being the original lines present in the incident spectrum and the latter the additional lines present only in the scattered spectrum. Under the heading "Origin of the modified lines" are indicated the wavelength of the incident line which gives rise to each modified line, and the difference in wave-number between the incident and the modified lines in question. The identification of the exciting line corresponding to each modified line is assisted and confirmed by observations and photographs with light-filters placed in the path of the incident light.

In Table II are shown the wavelengths of the modified lines excited when only the 4358·3 A.U. line and its close companions are present in the incident spectrum.

In Table III is given an analysis of the data given in Tables I and II; against each of the strong lines present in the mercury arc spectrum, are shown the differences in wave-number between it and the modified lines to which it gives rise.

7. Interpretation of results

From the analysis of the measurements given in Table III several striking results emerge.

The first and most significant result is that the shift of the modified line with respect to the exciting line (measured in wave-numbers) is independent of the frequency of the exciting line. This is shown by the fact that the shift is the same for all exciting lines, within the limits of error in measurement.

The second most significant result is that very similar groups of lines are generated by each incident line in the spectrum. This is shown by the fact that for each incident line, modified lines are to be found in known positions relative to it, or else, if they are absent, an adequate explanation is forthcoming, e.g. insufficient intensity of the incident line, or of the modified line, or of both, or else the obscuration of a modified line by strong lines in the incident spectrum.

Table I. Spectrum of benzene-scattering

Unmodified lines			Modified lines			Origin of the modified lines	
Wavelength (in A.U.)	Wave-number (in *vacuo* per cm)	Inten-sity	Wavelength (in A.U.)	Wave-number (in *vacuo* per cm)	Inten-sity	Exciting lines (in A.U.)	Difference of wave-numbers
3341·5	29918	1					
3543·4	28213	3					
3561·7	28068	3					
3579·7	27927	0					
3598·0	27824	1 (Band)					
3615·8	27649	1					
3650·1	27389	100					
3654·8	27354	30					
3663·3	27290	30					
3680·0	27166	3					
3704·3	26988	6					
			3732·8	26782	2	3650·1	607
			3737·7	26747	1	3654·8	607
			3746·6	26683	0	3663·3	607
3751·7	26647	5					
			3767·7	26534	0	3650·1	855
3771·0	26511	1					
			3787·1	26399	15	3650·1	990
3789·8	26379	10					
3801·7	26297	6					
			3813·4 imperfectly	26216 resolved	2	3650·1	1173
			3815·8	26199	2	3654·8	1155
3820·4	26168	5					
			3828·0	26116	0	3663·3	1174
3860·3	25897	5					
			3875·3	25797	1 (very broad)	3650·1	1592
			3891	25693	1	4046·6	− 988
3895·3	25665	2					
3902·0	25621	6					
3906·5	25591	20					
3984·0	25098	8					
4046·6	24705	100					
4077·8	24516	30					
4108·9	24331	10					

Table I. (Contd.)
Spectrum of benzene-scattering

Unmodified lines			Modified lines			Origin of the modified lines	
Wavelength (in A.U.)	Wave-number (in *vacuo* per cm)	Inten-sity	Wavelength (in A.U.)	Wave-number (in *vacuo* per cm)	Inten-sity	Exciting lines (in A.U.)	Difference of wave-numbers
			4115·1	24294	3	3654·8	3060
			4125·1	24235	4	3663·3	3055
			4147·7	24103	1	4046·6	602
			4178·2	23927	0	4358·3	−989
			4190·6	23856	0	4046·6	849
			4215·5	23715	10	4046·6	990
			4248·8	23529	5	⎰4077·8	987
						⎱4046·6	1176
			4282·1	23346	0	4108·9	985
4339·2	23039	15					
4347·5	22995	30					
4358·3	22938	200					
			4476·4	22333	1	4358·3	605
			4525·8	22089	0	4358·3	849
			4548·3	22004	0	4347·5	991
			4554·9	21948	10	4358·3	990
			4593·6	21763	2	4358·3	1175
			4618·6	21646	10	4046·6	3059
			4658·9	21458	1	4077·8	3058
			4683·0	21348	1 (very broad)	4358·3	1590
1916·1	20336	5					
4960·4	20154	1					
			5029·6	19877	1	4358·3	3061
5460·7	18308	1					

Thirdly, the order of the relative intensities within each group of modified lines appears to depend but little on the frequency of the line which excites the group. The shifts of + 990 and of 3059 in wave-number give rise to the brightest modified lines in every case.

A fourth and most interesting result is that while most of the modified lines are *degraded* in frequency relatively to the exciting lines, an *enhancement* of frequency is also possible, though such modified line of enhanced frequency is usually of extremely low intensity. Further the *enhancement* of frequency of such line is equal to the *degradation* of frequency of another modified line. This is shown by the identity in magnitude (within the limits of accuracy of measurements) of the shifts of opposite signs shown in the first and fifth columns of Table III.

Table II. Spectrum of benzene-scattering
(Only the 4358 A.U. group of lines were incident)

Unmodified lines			Modified lines			Origin of the modified lines	
Wavelength (in A.U.)	Wave-number (in *vacuo* per cm)	Inten-sity	Wavelength (in A.U.)	Wave-number (in *vacuo* per cm)	Inten-sity	Exciting line (in A.U.)	Difference of wave-numbers
			4178·5	23925	0	4358·3	− 987
4339·2	23039	15					
4347·5	22995	30					
4358·3	22938	200					
			4476·4	22333	1	4358·3	605
			4524·3	22097	0	4358·3	841
			4534·5	22047	0	4339·2	992
			4543·4	22004	0	4347·5	991
			4555·1	21947	10	4358·3	991
			4593·9	21762	2	4358·3	1176
			4683·5	21316	1 (broad)	4358·3	1592
			5029·6	19877	1	4358·3	3061

A fifth and rather curious result, which is probably not an accident, is that one of the shifts in wave-number (1591) is approximately the sum of two others (606 + 990 = 1596). It may be significant to note that the modified lines showing this shift appear distinctly more diffuse on the plate than other modified lines.

8. Origin of the modified spectrum

The results set out above definitely prove the correctness of the explanation of the new type of secondary radiation advanced by one of us previously,[4] namely, that the incident quantum of radiation is partly absorbed and partly scattered by the molecule. The shift of frequency would then correspond to some characteristic frequency of the molecule and would therefore be independent of the frequency of the exciting radiation. The latter is, with the liquids under study, far removed from either the characteristic ultraviolet or infrared frequencies of the molecule, and hence the phenomenon we are studying is a pure scattering effect and does not partake of the nature of resonance radiation. The great differences in the

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[4]*Indian J. Phys.*, 1928, **2**, p. 395.

Table III. Analysis of the modified lines
(The numbers within brackets give the relative intensities of the lines)

Shift of wave-number of the modified lines	Incident lines (in A.U.)	Shift of wave-number of the modified lines					
	3650·1 (100)	607 (2)	855 (0)	990 (15)	1173 (2)	1592 (1)	falls on an incident line
	3654·8 (30)	607 (1)		falls on an incident line	(?) 1155 (2)		3060 (3)
	3663·3 (30)	607 (0)		”	1174 (0)		3055 (4)
−988 (1)	4046·6 (100)	602 (1)	849 (0)	990 (10)	1176*		3059 (10)
	4077·8 (30)			987* (5)			3058 (1)
	4108·9 (10)			985 (0)			
	4339·2 (15)						
	4347·5 (30)			991 (0)			
−989 (0)	4358·3 (200)	605 (1)	849 (0)	990 (10)	1175 (2)	1590 (1)	3061 (1)
	4339·2 (15)			992 (0)			
	4347·5 (30)			991 (0)			
−987 (0)	4358·3 (200)	605 (1)	841 (0)	991 (10)	1175 (2)	1592 (1)	3061 (1)
Mean shift of wave-number −988		606	849	990	1176	1591	3059
Wavelengths corresponding to the frequency of the shifts 10·13 μ		16·50 μ	11·78 μ	10·10 μ	8·57 μ	6·28 μ	3·268 μ

*The two modified lines marked with * coincide in position.

brightness of the different modified lines produced by a given incident line must presumably be ascribed to the differences in the "Einsteinian coefficients of probability" of the transitions induced by the incident radiation.

The existence of lines of enhanced frequency referred to above may be regarded as a definite experimental proof that *negative* transitions may be induced by incident radiation, that is to say, that a molecule may pass to a state of *lower* energy as the result of radiation falling upon it. This of course will be possible only if it be initially in a state of higher energy than the normal. As the number of molecules in a liquid in the state of higher energy at any instant would be only a fraction of the number present in the normal state, the feebleness of the modified line corresponding to such negative transition is readily understood. The fact that the negative shift of frequency is equal to the positive shift of frequency for some other modified line is also intelligible if we assume that the initial state of higher energy is identical with one of those to which the molecule might be raised from the normal state by the incident radiation. As the result of the existence of thermal agitation within the fluid, a certain fraction of the molecules (which may be taken as $\exp(-w/kT)$, where w is the increase of energy) exist in the higher level of energy under consideration and tend under the action of the incident radiation to return to the normal state. Multiplying the observed shift of frequency by Planck's constant, the energy difference w is readily calculated. Thus corresponding to a shift of wave-number equal to 990, $\exp(-w/kT)$ comes out as about 1/120 at room temperature (viz. 30° C), which is of the same order of magnitude as the relative intensities of the two modified lines with positive and negative shift of frequency.

As the modified lines of enhanced frequency do not appear very clearly in the reproductions of the spectrograms (though they are quite definite in the original negatives) it was thought advisable to exhibit the same with a microphotometric record of the spectrogram appearing as figure 6 of plate 1. This is reproduced as plate 3. The line of enhanced frequency (4178·5 A.U.) is seen as a small but perfectly distinct hump in the record. Its feebleness in comparison with the line 4554·9 is quite evident, the latter being the most intense of all the modified lines in the spectrogram.

9. Infra-red spectrum of benzene

From Table III we extract below in Table IV the shifts of wave-numbers and the wavelengths to which they correspond.

Of these the two marked with a star give us the shifted lines of greatest intensity.

The curves of absorption of liquid benzene obtained by Coblentz[5] with a rock-

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[5] Quoted by J W Ellis, *Phys. Rev.* 1926, **27**, p. 305.

Table IV

Shift of wave-number	3059	1591	1175	990	849	606
Wavelength (in μ)	3·268*	6·28	8·51	10·10*	11·78	16·50

salt spectroscope show rather broad troughs lying roughly at the wavelengths 3·3 μ, 5·5 μ, 6·8 μ, 8·7 μ, 9·9 μ and 11·9 μ, the most prominent of these being the one at 9·9 μ. Bell[6] gives tan absorption curve for benzene obtained with his infrared spectrometer in which a series of absorptions appear at 3·3 μ, 5·1 μ, 5·5 μ, 6·2 μ, 6·7 μ, 7·2 μ, 8·5 μ, 9·7 to 10·2 μ and 11·8 μ respectively. Of these the absorption at 3·3 μ is the sharpest and most prominent and may be certainly identified with the 3·268 μ shown in Table IV. The absorptions at 8·5 μ and 11·8 μ are also very prominent and have wavelengths agreeing very closely with those shown in Table IV. The absorption between 9·7 μ and 10·2 μ forms a very prominent feature. We may reasonably identify it with our wavelength 10·10 μ. In Bell's curve for benzene, the absorption at 6·2 μ is more shallow than that at 6·7 μ; but he points out that the absorption band at 6·2 μ is prominently shown by certain wavelength 6·28 μ, with which it may be identified, appearing in our Table IV, and not 6·7 μ. The absorptions at 5·1 μ, 5·5 μ and 7·2 μ also fail to appear in our Table IV. The reason for this is yet to be found.

From the foregoing comparison, it is clear that the wavelengths appearing in Table IV correspond to certain fundamental frequencies of absorption of light by the benzene molecule. *Further it is evident that the shift of the modified lines in scattering by liquids, furnishes us with an extremely accurate method of determining these fundamental infrared frequencies of the molecule* and of the changes produced in it by varying the chemical constitution.

Attempts have been made by Ellis, Andrews and others to identify the infrared frequencies of the molecule with the frequencies of relative oscillation of the chemically bonded atoms in the molecule. For instance, Bates and Andrews[7] identify the wavelengths 3·3 μ and 9·9 μ respectively with the oscillations of the hydrogen-carbon bond and the carbon-carbon bond in benzene, and the latter[8] has even attempted to calculate the specific heat of liquids on the abasis of certain assumed fundamental frequencies of vibration of the molecule. The relation between the modified scattering of light and the structure of the molecule, and

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[6]F K Bell *J. Am. Chem. Soc.* 1925, **57**, p. 2814.

[7]J R Bates and D H Andrews *Proc. Natl. Acad. Sci.* Washington 1928, **14**, p. 128.

[8]D H Andrews, *Proc. R. Acad.* Amsterdam 1926, **29**, p. 744.

specially its bearings on Franck's[9] recent work on photochemical decomposition will form the subject of a separate paper.

10. Summary and conclusion

(a) The paper concerns itself with a new class of spectra observed when light from a quartz mercury lamp is diffused within a liquid and the scattered light is spectroscopically analysed. A large number of new lines are observed in the scattered spectrum which are not present in the incident spectrum.

(b) The scattered spectra from benzene, toluene, pentane, ether, methyl alcohol and water have been photographed.

(c) Each liquid shows a distinctive scattered spectrum, but certain general similarities are exhibited by liquids having chemically similar groups in their composition.

(d) The scattered spectrum of benzene has been measured and analysed. From the measurements and also from special spectrograms obtained with single-line filters in the path of the incident light, it is shown that corresponding to each unmodified line in the spectrum there are seven modified lines observable, of which two are specially prominent. The frequency differences between the unmodified and modified lines are independent of the wavelength of the incident lines.

(e) Six out of the seven in the group of modified lines have frequencies lower than that of the exciting line while one has a higher frequency, the increase of wave-number being numerically the same for it as the decrease of wave-number for one of the six lines of degraded frequency.

(f) The shift of frequency of the modified lines is found to agree with certain characteristic infrared frequencies of the molecule and in fact the method is capable of yielding extremely accurate measurements of these frequencies.

(g) The observations are explicable on the supposition that the incident quantum of radiation may be absorbed in part and scattered in part by the molecule. If the molecule is initially in the normal state, the transition induced by the radiation must naturally be to a higher level of energy, and hence the scattered radiation will have a degraded frequency. But if the molecule is initially in a level of energy higher than the normal, the radiation will induce a return to the normal level, and in this case we get a modified scattered radiation of higher frequency than the incident. The possibility of such negative transitions induced by

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[9] J Franck, *Trans. Faraday Soc.* 1925, **21**, p. 536.

radiation is proved by the observations. The comparative feebleness of the modified line of higher frequency is readily explained on a thermodynamic basis.

We have much pleasure in acknowledging the valuable assistance received from Mr S Venkateswaran in the course of the experiments described in this paper.