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IMPROVED TECHNIQUE FOR THE RAMAN EFFECT

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Abstract

Mercury-arc excitation of Raman spectra. The unfiltered light from a mercury arc is not well suited for an analysis of Raman spectra. The confusion of interpretation which may result is illustrated in the case of benzene.

Filters for use with mercury arc.—The object of a filter is two-fold: the limitation of the excitation to light of a single wave-length (if possible) and the suppression of the continuous spectrum in the region in which the Raman spectrum appears. Raman spectra of benzene excited by the mercury arc through various filters are reproduced. Suggestions concerning the proper design and manipulation of arc, filter tubes and scattering tubes are given.

Helium-arc excitation of Raman spectra—The use of the General Electric Company's hot cathode helium arc as a source for Raman spectra excitation is described. The Raman spectrum of benzene excited by this source through a nickel-oxide glass filter is reproduced.

THE ideal source of light for the study of the Raman effect should have a single very bright spectrum line, widely removed from other lines, and situated preferably in the region between 4000 and 4200A. The nearest approach to this is the hot-cathode helium arc, brought out by the research laboratory of the General Electric Company at Schenectady, with which I have been experimenting during the past winter. A number of photographs of Raman spectra made with a spiral helium discharge tube and a filter of nickel-oxide glass were published in the Philosophical Magazine for 1929,[1] and in this paper I stated that apparatus was in preparation for excitation by the helium arc.

The mercury arc which has been used exclusively heretofore, suffers from a number of disadvantages, but as it will doubtless continue to be used by the majority of investigators, it appeared to be worthwhile to improve the technique for this method of excitation.

MERCURY ARC EXCITATION

In the first place it is a great mistake to employ the total radiation of the arc without filters. Consider, for example, the region between the 4358 mercury line and wave-length 5100, shown in Fig. 1B which is the Raman spectrum of benzene excited by the mercury lines 4046–4077 and 4358–4348–

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[1] R. W. Wood, Phil. Mag. **7**, 744 (1929).

4339, the light being filtered through a concentrated solution of praseodymium which absorbs the continuous spectrum of the arc in the region of the Raman spectrum, and enables us to photograph fainter lines than would be recorded otherwise. It is obvious that more lines appear in this photograph than in any of the numerous ones of benzene that have been reproduced heretofore. This is due simply to the very perfect suppression of the continuous background, which ordinarily drowns out the fainter lines, a matter which will be taken up in detail presently.

As is now well-known the Raman spectrum of a large majority of organic compounds excited by Hg4358, consists of a group of lines in the region 4400–4700 and from one to three or more strong broad lines at about 5030 which, for brevity I shall call the 3.3μ band, the region between being free of lines. As I showed, however, in the paper on helium excitation,[1] the 3.3μ band is, in some cases accompanied on both sides by companion lines or doublets and the work of the past winter with the helium arc has shown, in the case of benzene at least, that the companions extend down nearly half way across the region usually regarded as free of lines. This is shown by ig. 1F—the Raman spectrum of benzene excited by the helium arc filtered through a nickel-oxide glass tube. Excitation is by the 3888 line at the left, two other helium lines appear (indicated) but all of the others are Raman lines. The spectrum has been enlarged to such a scale as to coincide with Fig. 1B, the spectrum of benzene already referred to. The "coincidence" is for lines of the Raman spectrum and not for wave-lengths, of course. The complexity resulting from the circumstance that in case B the spectrum is excited by five mercury lines is at once apparent. Its analysis is shown by the diagram above and by the two spectra below, Fig. 1, C and D. The former excited by 4358–4348–4339 and the latter by 4046–4077.

The spectrum of the mercury arc, in the region near the 3.3μ band at 5030 is shown by Fig. 1A′, No. 1 being the 4915 line. The short wave-length component of the 3.3μ band is in coincidence with mercury line No. 3, and its relative intensity is thus enhanced unless this spectral region is filtered out of the exciting radiation, since all radiations present in the exciting light are scattered with an intensity several hundred times that of the strongest Raman lines to which they give rise. We see from the diagram at the top of Fig. 1 that the main part of the Raman spectrum excited by the 4358 group is overlaid with the 3.3μ band and its companions, i.e., *n* and *r* are the 3.3μ bands excited by 4046 and 4077, and correspond to the 3.3μ band excited by 4358, near mercury line No. 3 of Fig. 1A′. If now there are numerous companions of the 3.3μ band, as is the case with benzene, the confusion resulting is obvious, and it is this circumstance that has been responsible for the numerous disputes over the assignment of the fainter lines of this substance.

We may take for example lines *o*, *p*, and *q* of Fig. 1B. Pringsheim and Rosen list only *o* and *q* giving incorrect assignments for both. This error was based on the assumption that *r* was excited by 4358 as well as by 4077, *o* and *q* being considered as excited by the companions of 4358, all of which is incorrect. Kohlrausch and Dadieu list *o* and *q*, give a wrong assignment to *o*, deducing a frequency difference $\Delta v = 3160$ which is non-existent—and give no assignment for *q*. Bär claims that *o* does not exist, does not mention *p*, and gives a correct assignment for *q*. Söderquist omits *o*, and gives correct assignments for *p* and *q*, thus verifying the doublet companion on the long wave-length side of the 3.3μ band $\Delta v = 3046$–3060 which I found last year with helium excitation and which shows beautifully in Fig. 1, E and F, the former excited by the green mercury line and the latter by helium 3888.

The 3.3μ band has a strong companion on the short wave-length side $\Delta v = 2947$. In Fig. 1B this line, as excited by 4046 coincides with the line *m* excited by 4358 which gives $\Delta v = 1178$. Kohlrausch and Dadieu state in their paper that I "failed to find this line as can be seen by reference to their table of lines found by previous investigators." Though absent in *their* table it was present in *mine*, and showed as well as a strong line in the reproduction of the spectrogram, though they state that it was not present. We thus see that *m* and *o* are the short wave-length components *n* and *r*, (the 3.3μ bands excited by 4046 and 4077 respectively), while *p* and *q* constitute the long wave-length component (doublet) of *n*, the corresponding component of *r* being hidden by the strong doublet *st* excited by 4358. They appear as faint lines in Fig. 1D at the extreme right, in which case 4358 has been filtered out of the exciting light.

Uncertainties and errors such as those enumerated above are almost certain to occur with unfiltered mercury arc excitation, and can be avoided only by the use of suitable filters. Even with filters we have to contend with the difficulty that all strong Raman lines excited by 4358 are accompanied on the short wave-length side by two fainter companions excited by 4348 and 4339, while those excited by 4046 have a faint companion on the long wave-length side, due to 4047 excitation.

Lines in Fig. 1B not mentioned above are as follows:

a, the 3.3μ band excited by Hg 3906

bc, *hi*, *kl*, short wave-length companions of *d*, *j*, and *m* excited by 4358 (due to multiple excitation)

e, *f*, excited by 4046, $\Delta\nu 2542$–2597 (see following paper).

Filters for Hg-arc excitation:—We will now take up the subject of filters and how best to apply them. While the 4358 line is about four times as intense as 4046 it suffers from the disadvantage that the 3.3μ band (with its real companions) which it excites falls in a region of very low sensibility of most photographic plates and of only moderate dispersion of the prism spectrograph. The 4046 line, however, projects its entire Raman spectrum in the region of high and moderately uniform sensibility of the ordinary plate. The mercury lines 4077, 4108 and 4140 are superposed on the Raman spectrum and are liable to conceal important lines. Some substances, however, cannot be excited profitably by 4046 on account of strong fluorescence. The object of the filter is two-fold, the limitation of the excitation to the light of a single wave-length (if possible) and the suppression of the continuous spectrum of the mercury arc in the region in which the Raman spectrum appears.

The most convenient mercury arc that I have found for Raman spectra work is the new model brought out recently by the Hanovia Company of Newark, New Jersey. Both electrodes are of mercury, which obviates the tungsten blackening, and the burner is enclosed in a metal housing which can be rotated on trunnions, which in turn have an up and down adjustment of several inches. With the housing in the horizontal position the burner is just below and close to a narrow rectangular aperture in the top and the Raman tube can thus be brought very close to it, with interposed filters. At first I used shallow glass dishes of "Pyrex" (Petri dishes used by the biologists, superposing one above the other, when two solutions were used). The evaporation was rather rapid, however, even with air cooling by an electric fan.

A much better method is to enclose the filter solution in a glass tube 5 cm in diameter, which when mounted between the mercury arc and the Raman tube and as close to each as possible, acts as a cylindrical lens and filter combined. If two solutions are used, one of them is contained in an inner tube of smaller diameter, which is hermetically sealed. A concentrated solution of cuprammonium sulphate sealed up in a large tube looks very promising as a filter but I have not fully tried it out. An electric fan placed close to the lamp and blowing over the top is sufficient to keep the tubes cool. The Hanovia Company has obtained excellent results with a chimney attachment to the lamp, which I suggested they make up, and which causes a "down draught" through the slot in the top of the housing. With this attachment I hope to be able to dispense with the fan. (See Fig. 3.)

Raman spectra of benzene made with various combinations of filters are reproduced in Fig. 1. Spectrum B was obtained with a tube 3.5 cm in diameter filled with a saturated solution of the praseodymium double salt furnished by the Welsbach Light Company of Gloucester City, Pennsylvania. In this case the excitation is by 4046 and 4358, the filter absorbing the region between 4375 and 4800 where most of the Raman lines are found. Spectrum C was obtained with a combined filter of praseodymium and sulphate of quinine in dilute sulphuric acid, which absorbs 4046 and 4077, the excitation being by 4358. Spectrum D was made with a filter composed of a solution of cobalt sulphocyanate, made by adding a strong solution of ammonium sulphocyanate to one of cobalt chloride. This filter reduces the intensity of 4358 to the point at which it fails to yield Raman lines, though the group of three lines records itself in the spectrum. A strong solution of iodine in carbon tetrachloride is even better for removing 4358 and a spectrum made with this filter is reproduced (Spectrum H.) This spectrum, however, shows strong fluorescence to the right of the 4358 group, which is at the middle of the spectrum. This fluorescence is due to the 3650 group of mercury lines. A less concentrated solution of iodine transmits 4358 freely, and can be used for the suppression of the continuous background. Spectrum G was made with a double filter, the inner tube filled with a very dilute solution of potassium chromate and the outer with the iodine solution. Potassium chromate can be used only if diluted to the point at which it shows only a trace of

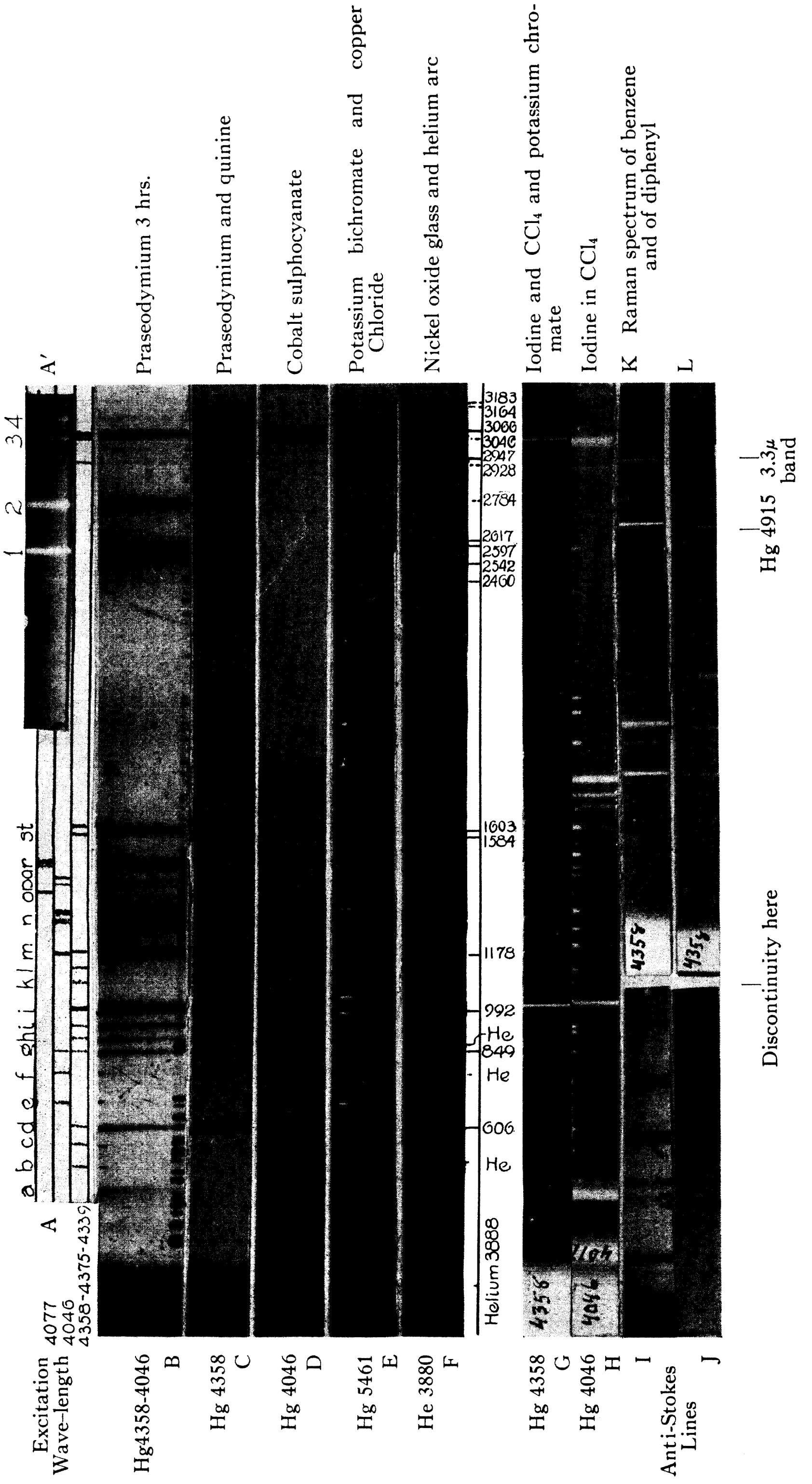

Fig. 1. Raman Spectra of benzene under various types of excitation.

yellow by daylight with the thickness employed, otherwise it absorbs 4358 too powerfully. In this concentration it only partially suppresses the 4046 group. Quinine sulphate in dilute sulphuric acid can be made sufficiently concentrated to completely suppress 4046 with practically no absorption of 4358 but it turns yellow rapidly and requires renewal every half hour.

The Zeiss Company makes a fluorescent glass (used in filter "C" in combination with cobalt glass) which appears to be similar to the Corning Noviol glass plates. I believe that a tube of this glass filled with a solution of iodine in carbon tetrachloride of moderate concentration, will prove the best filter for excitation 4358, and for 4046 excitation a strong solution of iodine contained in a tube of Corning "Noviol" 0, or "Nultra" of such thickness as to absorb 3660 and transmit freely 4046. If tubes of these glasses should not be available the iodine solution can be used in a tube of ordinary glass with a plate of the ultraviolet absorbing glass interposed between it and the Raman tube. I am informed by the Corning Company that their "Noviol A" is opaque to 4046 and transmits 50 percent of 4358, but I have not yet had the opportunity of comparing it with the Zeiss filter C. None of these glasses that I have tried however is much better than a solution of potassium chromate. By increasing the concentration of the solution 4046 can be practically abolished but only at the cost of increased time of exposure.

The absorbing power of a potassium chromate solution for 4046 and 4358 has been investigated by Mrs. M. Goeppert-Mayer in my laboratory. Her results are given in the following table, in which the two lines are regarded as having equal intensity with no filter. c = concentration in grams per liter, d = thickness of the filter in centimeters.

$c\ d$ concentration times thickness	I 4046	I 4358	Ratio
0	1	1	1
0.127	$\frac{1}{10}$	$\frac{1}{1.7}$	6
0.177	$\frac{1}{25}$	$\frac{1}{2.1}$	11
0.215	$\frac{1}{50}$	$\frac{1}{2.45}$	24
0.253	$\frac{1}{100}$	$\frac{1}{2.9}$	34
0.304	$\frac{1}{250}$	$\frac{1}{3.54}$	70
0.342	$\frac{1}{500}$	$\frac{1}{4.15}$	120
0.361	$\frac{1}{750}$	$\frac{1}{4.55}$	165
0.380	$\frac{1}{1000}$	$\frac{1}{4.87}$	205

This table shows very clearly just what can be accomplished: for example, 4046 is reduced to 1 percent with a reduction of 4358 to 34 percent almost exactly the same figures as given for the Zeiss C filter. If the mercury arc is of the type that operates only in the vertical position the filter tube can be mounted alongside of it, and the cooling accomplished by the convection currents in the fluid. The higher the tube, the more perfect the cooling. A tube 4 cm in diameter and 70 cm in height will be found sufficient to carry off the heat. If there is no objection to water cooling, a shorter tube can be used, the upper end wrapped with several layers of tin-foil on which is wound a close spiral of copper or lead tubing, as shown in Fig. 2.

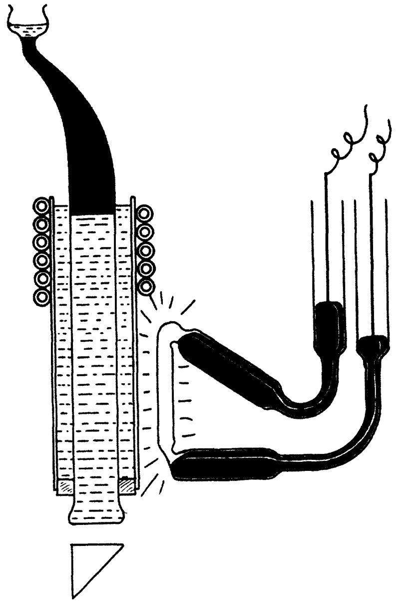

Fig. 2.

One of the most important points is to prevent any stray light from reaching the slit of the spectrograph. The entire optical path, from the window of the Raman tube to the slit should be enclosed by tubes of black paper, as diffused light, reflected from the window of the tube, or the lens used in forming the image on the slit, gives rise to a continuous background. The arc should be operated in a light-tight box, well ventilated, however, and placed as close as possible to the aperture in the wall.

If only very small quantities of material are available for study (10 cc or less) a form of tube which I described in a communication to the Faraday Society last year, may be used. It is shown one half natural size in Fig. 3. The Raman tube should be made of thin walled soft glass tubing (not Pyrex) about 13 mm in diameter, one end blown round and then flattened by holding it absolutely vertical above the tip of a very small bunsen flame which is burning quietly without flickering. If the tube is drawn off sharply at a right angle preliminary to blowing the bulb the objectionable drop of glass at the center is avoided. Windows can be made in this way which give almost no distortion. A water-jacket tube about 23 mm internal diameter surrounds this tube, which is held in place by a rubber gasket at the bottom. These gaskets can be turned on a lathe from rubber stoppers with a sharp pen-knife as described in my first paper on the Raman effect[2] where more complete directions for making the flattened bulb are also given. After slipping the gasket over the tube the upper portion is drawn down as shown and painted with black "Duco." The upper portion of the large tube is wrapped in tinfoil wound with a copper tube 3 or 4 mm in diameter, the space between being filled with water or a filter solution. Cooling is effected by water circulating in the copper spiral. A concave 3/4 inch cylinder of polished sheet aluminum is slipped around the inner tube on the side opposite the lamp, unless a filter solution which attacks aluminum is being used. The tube is illuminated with a capillary quartz mercury arc, almost in contact with the outer tube.

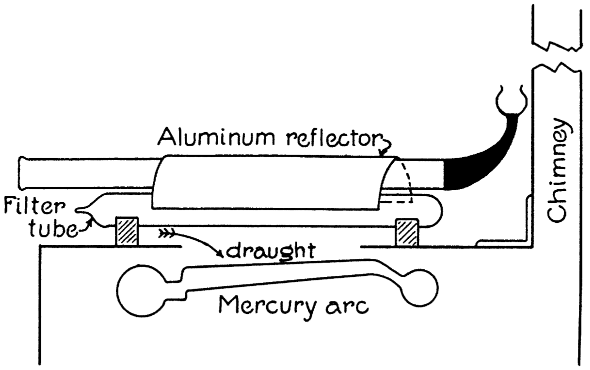

Fig. 3.

A few words regarding the best method of pointing the collimator of the spectrograph down the axis of the illuminated tube and forming the image on the slit may be found helpful.

In general, when the source of light is a long cylinder, seen end-on it is important to mount it at such a distance from the spectrograph that both ends of it can be fairly well focussed on the slit simultaneously. This means that the distance from the source to the lens should be much greater than the distance from the lens to the slit. If this condition is not fulfilled we are not utilizing all of the available light.

With the eye in such a position that it is looking exactly down the axis of the tube, bring the end of the match stick (mounted in a clamp stand) directly in front of the pupil. This marks the position of the spectrograph slit. The The collimator is now pointed at the end of the tube, and the slit brought into coincidence with the end of the match.

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[2] R. W. Wood, Phil. Mag. 6, 729 (1928).

Now look into the spectrograph from the position of the plate (i.e. from the focal plane of the camera) and if the aim has not been very bad, the end of the tube will appear as a small circle of light somewhere in the field of the camera lens. Next shift the spectrograph until the circle of light is in the center of the lens, keeping the slit position fixed.

To form an image of the end of the tube on the slit two methods are available. If a large spectrograph is being used, a small circle of paper should be mounted over the end of the tube and strongly illuminated with a lamp. This can then be focussed at once on the slit. With small spectrographs I have found the following method very convenient. The lens is first mounted practically in contact with the slit and the spot of light in the camera lens watched. As the lens is moved towards the tube and away from the slit the spot of light graudally enlarges, finally filling the entire field of the lens, The lens should be moved so as to keep the spot centrally placed in the field, and when the whole field is uniformly illuminated, the lens is in the correct position. This method enables us to utilize the brightest part of the source, if the illumination is not uniform, for, as the spot enlarges the attention can be focussed on the bright portion and this is then made to fill the field.

Helium Arc Excitation

Through the courtesy of Dr. Dushman of the Research Laboratory of the General Electric Company I was supplied with a hot cathode helium arc. This is more troublesome to operate than the mercury arc, as it requires a current of 9 amperes for heating the filament and 220 volts direct current for excitation. The filament current was supplied by a very inexpensive transformer, operated from the 110-volt A.C. mains, and the lamp started by spraying the tube with sparks from a small high-frequency apparatus (leak tester).

A tube of Pyrex glass with a window fused to one end was surrounded by a tube of nickel-oxide glass and mounted as close as possible to the helium arc, the whole being surrounded by a cylindrical tube of very thin and highly polished sheet aluminum, made by rolling up a rectangular piece of suitable size on a cylinder somewhat smaller than the size desired. The tube springs open to the desired diameter and can be still further opened and slipped over the other tubes. Sheet aluminum of this description is now obtainable commercially and is most useful for making reflectors of various shapes. There seems to be little point in going to the trouble of ellipsoidal reflectors as some investigators have done. Equally good illumination can be secured as described above, for the source is so large that only a small fraction of it is at the focus point, and the ellipsoid functions only for radiations originating at the focus. With the cylinder practically all of the light emitted by the arc gets into the Raman tube, with the exception of that lost by absorption. A large tube of Pyrex glass, silvered on the outside, similar to the reflector which I described many years ago in connection with the excitation of the resonance spectra of iodine, would give rather stronger illumination, but the aluminum is less troublesome and easier to fit over the tubes. The helium arc was supported in V-shaped notches lined with asbestos on two wooden upright supports, and the Raman tube, with its cover of nickel-oxide glass held in an iron clamp as shown. The end of the tube was drawn off obliquely and expanded into a bulb, to take care of expansion of the fluid. The tapering portion was painted with black "Duco" to secure a black background. Cooling was accomplished with the blast of an electric fan, directed into the aluminum cylinder by a paste-board cone. I have found nothing as good as this arrangement for investigating the region in the vicinity of $\Delta\nu = 3060$. The only objection is the presence in the Raman spectrum of the helium lines 3964 and 4026. The Raman spectrum of benzene excited in this way is reproduced in Fig. 1, Spectrum F, which will be more fully considered in the following paper.

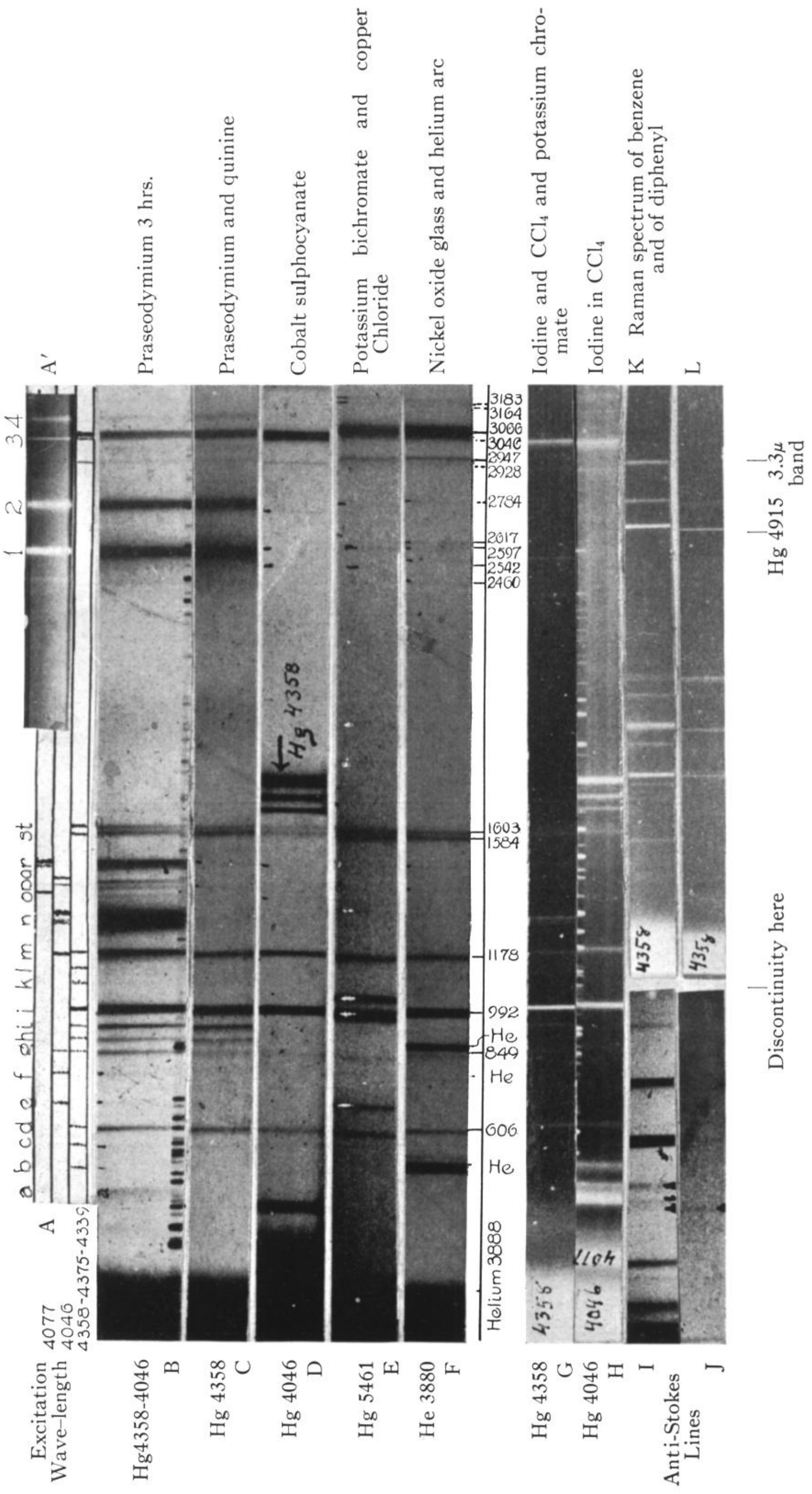

Fig. 1. Raman Spectra of benzene under various types of excitation.