The Raman Spectra of Deuteroparaldehyde and Paraldehyde

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through an increase of temperature. At a temperature of 172°C, at which, under the conditions of their experiment, the molecules were thought to exist principally as monomers, these observers reported the frequency of the band to be 1786 cm^{-1}. This frequency corresponds to a wavelength of 5.6μ. In the present work, it will be recalled, the position of the band was found to be 5.75μ for the pure liquid and 5.9μ for dilute solutions of the acid in benzene and in carbon tetrachloride. If, as is generally believed, the molecules exist principally as dimers in the dilute solutions, the difference in position and appearance of the band in the more concentrated solutions and in the pure liquid acid may indicate the presence of a more complex form.

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RAMAN spectra of deuteroparaldehyde were obtained with material prepared by Professor E. Zanetti of Columbia University. A little over 1 cc was available sealed in a quartz tube furnished with a ground and polished window. As it seemed advisable to have spectra of ordinary paraldehyde made with the same instrumental equipment, a very pure sample was prepared and distilled into a tube of Pyrex glass of the same type. This was of some importance, as there is not complete agreement between the values obtained by Petrikaln and Hochberg, Venkateswaran and Bhagavantam and others.

The technique which I now employ in making spectrograms of the Raman effect differs from that which I have previously described, and is very superior in many ways. The same apparatus can be used for large or very small quantities of fluid, requires no auxiliary cooling devices, and enables one to excite the radiation either by the total light of the quartz mercury arc, or by 4358 or 4046 alone. A Hanovia mercury arc in its metal housing is turned on its trunnions into the vertical position, and a glass tube, 5 cm in diameter and 50 cm high (closed at the bottom) is mounted about 6 cm in front of the vertical aperture through which the light of the arc emerges. This tube is half-filled with water or an absorbing solution, and serves both as a cylindrical lens and ray filter. It is closed at the top with a cork to prevent evaporation, the vapor condensing on the wall and running down. The liquid under observation is contained in a tube of the form which I have previously described in numerous papers, shown in Fig. 1.

This is mounted in such a position that the mercury arc is focused along its axis, and a concave cylindrical mirror of thin and highly polished aluminum (now obtainable commercially) is attached to the rear wall as shown. The light emerging from the window at the bottom is reflected by a right angle prism and focused on the slit of the spectrograph by an achromatic lens of about 20 cm focus mounted at a distance of 2 meters from the prism. This arrangement insures that all parts of the illuminated column of liquid are in good focus, and no light scattered by the wall of the tube enters the spectrograph. The reflecting prism is held between two stiff brass clips, and can be rocked in the vertical plane or rotated on a vertical axis into such a position that the reflected image of the illuminated fluid column is exactly horizontal and in line with the axis of the collimator of the spectrograph. In some cases a flat tube filled with a strong solution of praeseodymium is inserted between the large tube and the irradiation tube. A certain brand of tooth brush is supplied in a

flat tube of soft glass suitable for the purpose. The tube can be drawn down, filled and sealed. This filter is of use for suppressing certain parts of the continuous spectrum of the mercury arc between the lines 4358 and 4916.

Adjustments are made as follows: A "pea" electric lamp, or other small source of light is mounted in front of and close to the center of the face of the prism, and the spectrograph pointed in such a direction that the image of the flame appears at the center of the camera lens, when the eye is placed at its focus, i.e. in the spectrum. The achromatic lens is now put in place and the image of the lamp focused on the slit, giving an approximate adjustment. A convenient way of getting a comparison spectrum both above and below the Raman spectrum is to saw a notch in a small right angle prism as shown by inset at bottom of Fig. 1, and mount this against the slit in such a position as to reflect the light of an iron arc to the slit, while the image of the Raman tube is transmitted through the notch.

To make sure that no light scattered from the walls of the tube enters the slit, proceed as follows: Start the mercury arc and open the slit about 1 mm. Adjust the achromatic lens so as to bring the image of the center of the circular ring of light scattered by the wall of the tube into coincidence with the notch on the prism.

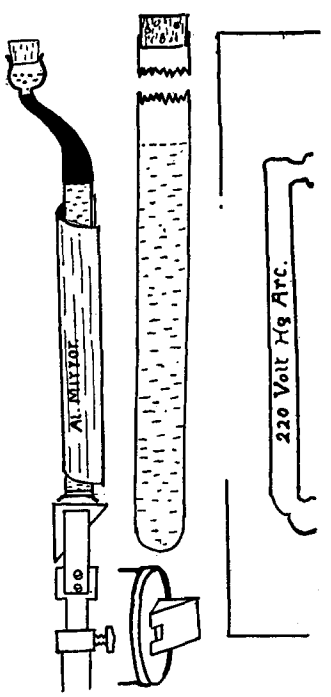

FIG. 1.

Examining the green mercury line with a short focus lens we shall then see the portion of the image of the "end-on" Raman tube that is transmitted through the notch, and can distinguish easily any portion of the relatively brilliant wall-image that gets through the slit. The lens is then to be slightly shifted until no part of the wall of the tube can be seen, or until the center of the image of the tube's cross section is coincident with the edge of the slit that remains fixed as the slit is closed. With a Raman tube of very small bore the ring of light may be wholly transmitted by the notch. In this case we shall have to be satisfied with a spectrum in which a horizontal strip along the middle is free from scattered light. This strip will be bordered above and below by the continuous spectrum of the arc.

The quartz tube containing the deuteroparaldehyde was about 6 mm in diameter and 25 cm long, with a liquid column at the bottom 5 cm high. The empty portion of the tube was wrapped with black tape, and there was no bend at the top. A small amount of light is reflected from the meniscus, but not enough to give serious trouble.

A spectrogram excited by the 4358 mercury line is reproduced in Fig. 2a. (Fe comparison.) The liquid used for the cylindrical condenser was a saturated solution of sodium nitrite, which absorbs all of the radiations of shorter wavelength. The $\Delta\nu$ values are given in Table I, each line numbered to correspond with the numbers on the photograph. The relative intensities of these lines can be seen from the spectrogram.

Spectrograms of paraldehyde were made with a much larger tube of Pyrex glass as shown in Fig. 1. The one made with 4358 excitation is reproduced in Fig. 2b. The spectrum excited by the total radiation was also photographed, as a control. Many lines not listed by previous investigators were found, twenty-three in all, against ten listed by Kohlrausch, two of which (900 and 1020) are nonexistent. The values are given in Table II.

We must now account for the discrepancies between the present values and those given by

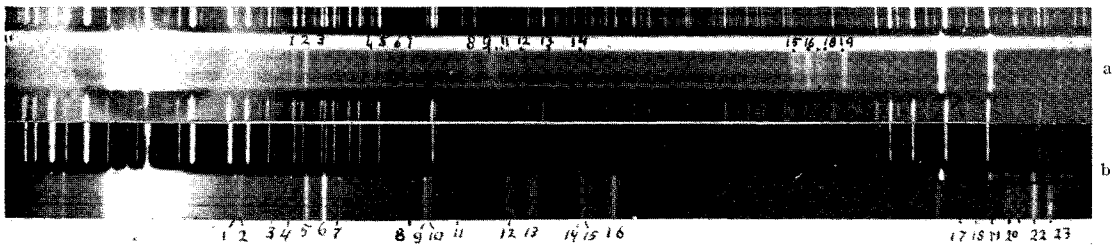

FIG. 2.

previous observers and listed in Kohlrausch's book on the Raman effect.

Petriakin gives a line 1015 and Vankateschar one at 1025. Kohlrausch gives the mean —1020. Both authors attribute this line to a line $\lambda = 4562$ excited by Hg 4358. Now there is *no* line 4562 by pure 4358 excitation. (If present it would come half-way between lines 10 and 11 in Fig. 2b.) It shows up, however, by excitation by the total radiation, and attributing it to 4046, we get $\Delta\nu = 2782$.

With 4358 excitation the corresponding Raman line would coincide with the mercury line 4960 and would hence be missed. It seemed worthwhile to look for this line and another spectrogram was made on a special plate sensitized for this region of the spectrum. A gelatine filter strongly dyed with ethylviolet was interposed between the sodium nitrite tube and the Raman tube. In this way the mercury lines 4915 and 4960 were eliminated from the esciting radiation. The result is shown at the right of Fig. 2b, this small region of the spectrum being pasted over the other (which shows as a narrow strip at the top, the two strongest lines to the left being 4915 and 4960). It is clear from the relative intensities that the latter line could not possibly register, as 4915 is quite faint, yet there is a clearly recorded line at this point in the original negative (line 19) giving a value of 2782 as required. This brands the line 1020 as spurious. Venkateschar and Bhagavantam record also a line 900, given by attributing $\lambda = 4536$ to 4358 excitation. I find a line at 4536 only with 4046 excitation, giving $\Delta\nu = 2665$, while with 4358 excitation we find a very faint line (No. 17) giving $\Delta\nu = 2660$. This disposes of the 900 line.

Their value $\Delta\nu = 845$ is the mean of the two clearly resolved lines 9 and 10 in Fig. 2, and their line 1178 corresponds to the middle of the broad band with sharp edges (No. 13, Fig. 2b) which is perhaps an unresolved triplet.

TABLE I.

No.	$\Delta\nu$	No.	$\Delta\nu$	No.	$\Delta\nu$
1	428	7	794	13	1262
2	470	8	981	14	1348
3	518	9	1043	15	2072
4	671	10	1063	16	2119
5	711	11	1077	17	2158
6	751	12	1144	18	2176
				19	2251

TABLE II.

	Wood	P.H.	V.B.		Wood	P.H.	V.B.
1.	258			11.	944	1015	1025
2.	274	276		12.	1108		1105
?3.	371			*13.	1162		
4.	424				1196		1178
5.	470	474	472	14.	1341		1350
6.	525	526	525	15.	1370		
7.	575		735	16.	1450	1452	1455
?8.	754		776	17.	2660		
9.	837	838	840	18.	2734		
10.	857		900	19.	2782		
				20.	2843	2863	2850
				†21.	2882		
				22.	2940	2942	2945
				23.	3000	3002	3000

* 13 is probably an unresolved triple line. Values given for the two edges.

† Probably excited by Hg 4347, i.e. to be excluded.