

## The Raman Spectra of the Sugars in the Solid State and in Solution I. The Raman Spectra of $\alpha$ and $\beta$ -D-Glucose

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Citation: *The Journal of Chemical Physics* **10**, 176 (1942); doi: 10.1063/1.1723681

View online: <http://dx.doi.org/10.1063/1.1723681>

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The strong lines near 340 and 630  $\text{cm}^{-1}$  for the monosubstituted acetylenes and near 365 for the disubstituted acetylenes were observed also for the alkylacetylenes in V. Following Crawford,<sup>13</sup> the frequency near 630 may be identified with the bending of the  $\text{C}\equiv\text{C}-\text{H}$  angle and the ones near 350 may be associated with the  $\text{C}\equiv\text{C}-\text{CH}_3$  angle.

All the present compounds, as well as four of the seven alkylacetylenes in V, have a line near

500  $\text{cm}^{-1}$ . The present compounds also have, without exception, a polarized line near 800 and lines near 1065 and 1250  $\text{cm}^{-1}$ . Lines near 1300 and 1330 were found for the four compounds having a fairly long chain (and for five of the compounds in V), but not for the two containing only ethyl groups; these two, however, have lines at 1315 and 1375  $\text{cm}^{-1}$ . The doublet observed at 1440, 1457 (mean values) for the seven alkylacetylenes in V appears here at 1436, 1457.

MARCH, 1942

JOURNAL OF CHEMICAL PHYSICS

VOLUME 10

## The Raman Spectra of the Sugars in the Solid State and in Solution

### I. The Raman Spectra of $\alpha$ - and $\beta$ -*d*-Glucose\*

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(Received December 11, 1941)

This paper presents data on the Raman spectra of anhydrous crystalline  $\alpha$ - and  $\beta$ -*d*-glucose and of equilibrium aqueous *d*-glucose solutions containing 5, 15, and 50 moles of water per mole of glucose. Ultraviolet excitation (Hg  $\lambda$ 2537A) was employed. A technique for photographing Raman spectra of crystalline organic powders and solutions with very poor scattering power is described. It consisted essentially of the use of complementary filters of aqueous succinic acid (saturated, 4 mm thick) and a mercury vapor absorption cell (10 cm long, 150°C). Thirty-six lines are reported for  $\alpha$ -*d*-glucose, 32 for the  $\beta$ , and numerous new bands including measurements of maxima and shoulders are given for equilibrium solutions. Only the obvious experimental differences are discussed as the detailed discussion will be given in a later paper of this series.

### INTRODUCTION

THE carbohydrates play such an important role in agricultural chemistry that additional knowledge about their structures and chemical and physical properties is greatly to be desired. Because of the complexity of these compounds, accurate experimental work is difficult and there is a great need for the development of new physical methods to help the investigators in this field. The Iowa Agricultural Experiment Station, therefore, in collaboration with the Chemistry Department has started a program to study the Raman spectra of the sugars and

their derivatives. It is hoped that the method and technique of the Raman effect can be developed so as to be a useful tool in this field. If the Raman spectra of the various sugars could be photographed readily in the solid state and in solution, then from the differences in their vibrational frequencies it should be possible to identify the sugars by their spectra and even to determine quantitatively the amount of one sugar in the presence of another providing the mixture was not too complicated. Chemically this can be done only with great difficulty. In addition to this if the frequencies of a given sugar in the solid state differ from those in solution, some light might be thrown on the sugar-sugar and sugar-water association. Also, since the frequencies may be compared with those of mole-

\* From the dissertation to be submitted by Robert F. Stamm to the Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† Journal Paper No. J.954, Project 696.

cules thought to be similar and having better known geometrical structures, an insight into the structures of the sugars might thus be obtained. Finally, a complete set of vibrational frequencies would permit a dynamical analysis to be made with the resultant proof of geometrical structure. This last objective presents well-nigh insuperable difficulties if carried out rigorously by the usual methods. However, as the theory develops and the newer calculating machines<sup>‡</sup> become available, even this might be accomplished if the vibratory frequencies are available.

In this, the initial paper of a series, we are reporting the Raman spectra of  $\alpha$ - and  $\beta$ -*d*-glucose in the solid state and that of equilibrium *d*-glucose in solution. This aldo-hexose is one of the most important since it is the building block of both starch and cellulose.

Several investigators of Raman spectra have worked with the sugars, including *d*-glucose, in the past with partial success. Whiting and Martin<sup>1</sup> examined a dextrose solution of 500 g per liter. They found no Raman lines, only an undiminished continuum. Kutzner<sup>2</sup> obtained three lines of very low intensity accompanied by a heavy continuum after 30 hours' exposure. Wiemann<sup>3</sup> used charcoal to decolorize a 30 percent dextrose solution which he then filtered through sintered glass and reported that very little continuum was present in his pictures. He found eleven bands in solution. A. L. Sundara Rao<sup>4</sup> reported twelve lines for *d*-glucose solution, two of them broad. Only the last investigator reported any lines in the C—H and O—H regions and he stated that the spectra were so faint that it was difficult to distinguish them from the background.

Since the glucose frequencies can also be observed in infra-red absorption, it should be mentioned that Coblenz<sup>5</sup> studied molten dex-

trose and obtained a band from 3–4 $\mu$  and a maximum at 4.8 $\mu$ . Rogers and Williams<sup>6</sup> used saturated solutions 0.002 mm thick and investigated the region 2–12 $\mu$ . They reported seven bands but could not resolve details in the C—H and O—H regions. Barr and Chrisman<sup>7</sup> evaporated saturated solutions on cover glasses and used the resulting syrups. Two bands were found by them for each of a series of sugars including *d*-glucose.

The phenomenon of muta-rotation leads to the conclusion that in aqueous glucose solutions both the  $\alpha$ - and  $\beta$ -forms of the pyranose ring are present in equilibrium with one another and perhaps in equilibrium with other forms. Therefore any spectrum of the solution will be composed of a superposition of the spectra of all the various forms present and many of the bands observed will in reality be envelopes of several lines or bands from these forms. Since all of the above work (that of Coblenz excepted) was done with equilibrium solutions, the values of the vibrational frequencies obtained by them should be compared with our solution values in Table I.

The  $\alpha$ - and  $\beta$ -forms of *d*-glucose are geometrically different and should possess different vibrational frequencies. It is therefore desirable to study the spectra of the pure forms alone. This can be done with the sugars in the solid state.

## EXPERIMENTAL

From the work of Kwiencinski and Marchlewski<sup>8</sup> and especially from that of V. Henri and Schou<sup>9</sup> it was decided that pure *d*-glucose does not absorb light of wave-lengths longer than 2300Å and that the 2537 mercury line could therefore be used as a primary exciter of the Raman lines. We employed one of the low pressure argon-mercury arcs.<sup>10</sup> Unfortunately the direct light from this arc decomposes all sugars so that all light below 2300Å has to be removed by a filter.

<sup>‡</sup> Those used for evaluating secular determinants.

<sup>1</sup> Whiting and Martin, Trans. Roy. Soc. Can. III [3] 25, 87–98 (1931). (Visible Hg excitation, quinine sulphate filter.)

<sup>2</sup> Kutzner, Naturwiss. 20, 331–332 (1932). (Super-saturated solution at 20°C, quartz Hg arc, visible excitation.)

<sup>3</sup> Wiemann, Comptes rendus 203, 789–791 (1936). (Visible Hg excitation.)

<sup>4</sup> A. L. Sundara Rao, Indian J. Phys. 14, 207 (1940). (Visible Hg excitation.)

<sup>5</sup> W. Coblenz, Carnegie Inst. of Wash. Pub. 65 (1906).

<sup>6</sup> Rogers and Williams, J. Am. Chem. Soc. 60, 2619–2621 (1938).

<sup>7</sup> Barr and Chrisman, J. Chem. Phys. 8, 51–55 (1940).

<sup>8</sup> Kwiencinski and Marchlewski, Bull. Soc. Chim. 43, 725–743 (1928).

<sup>9</sup> V. Henri and Schou, Zeits. physiol. Chem. 174, 295 (1928).

<sup>10</sup> The Hanovia Chemical and Manufacturing Company, Newark, New Jersey (Helicoidal type, 0.1 amp. at 4400 v).

TABLE I.

Anhydrous $\alpha$ -D-glucose	Int.	Anhydrous $\beta$ -D-glucose	Int.	5 moles H <sub>2</sub> O: mole glucose	Int.	15 moles H <sub>2</sub> O: mole glucose	Int.	50 moles H <sub>2</sub> O: mole glucose	Int.	Previous investigators solutions only
142	1	137	1	i. 96		121		i. 90		
168	1	163 <sup>1</sup>	1	i. 171	1	187		i. 172	1	
224	1			247		252		255		
				288				255		
				i. 302	0			i. 290	0	
				316				325		
				322		327		336		
363	0			i. 345	1	m. 349	1	i. 349	1	
				368		359		363		
395	4			386		371		389		
405	4	404	3	sh. 410		m. 385	1	m. 404	3	
441 <sup>1</sup>	1	425	0	m. 423	7 <sup>2</sup>	m. 407	6	m. 421	6 <sup>2</sup>	423(R)
		462	0	m. 445	6	m. 423	8 <sup>2</sup>	m. 447	4	435 $\pm$ 25(W), 454(K)
				467		m. 448	6	m. 464	3	
				483		469		471		
				sh. 502		483		486		
542	8	523	3	m. 518	6	m. 498	5	m. 497	4	
				sh. 540	1	m. 518	8	m. 520	5	519 $\pm$ 11(W), 513(K)
		567	0	m. 550	0	m. 542	6	m. 541	4	549 <sub>a</sub> (R)
				m. 562	0	m. 562	0	m. 559	0	
580	0			m. 584	0	m. 588	0	m. 573	2	
				589		597		m. 586	0	
				628		628		609		
				i. 640	0	m. 636	2			624 <sub>i</sub> (R)
				652		658				
				702		? 694	0	i. 687		
				m. 715	2	m. 705	0	i. 707	0	
				730		m. 720		727		
774	2			m. 760	2	m. 739	1	i. 750	2	
				m. 775		m. 744		773		
				794		m. 768		796		
				798		795				
				m. 804	1					
				812		m. 814	1			
				829		829				
842	8	825	0	m. 845	4	m. 856	3	m. 835	3	
				m. 858	4			m. 850		856(R), 853 $\pm$ 10(W)
		870	0	sh. 870				m. 868	3	
				872		878		875		
887	0	901	3	sh. 894		m. 899	5	m. 905	4	
913	6	914	0	m. 911	5	m. 914	5	m. 916	4	919(R), 911 $\pm$ 14(W)
		941	0	sh. 930	3	sh. 937		937		
				951		951				
				970						
				m. 986	2			m. 982		
				1016		999		m. 998	3	1000(RW)
1020	1	1025	1	m. 1029	5	m. 1016	6			1020 $\pm$ 10(W)
? 1038 <sup>1</sup>	1			sh. 1038	6	m. 1033	7			
1057	5	1051	3	m. 1066	8	m. 1063	10	m. 1069	7	1064 <sub>7</sub> br. (R), 1067 $\pm$ 12(W)
1072	6			sh. 1080	7	sh. 1076		sh. 1082		
				1085		1089		1089		
1109	5d.			1091		1089		1095		
		1118	4					sh. 1101		1100(RW)
1122	6			m. 1124	11	m. 1126	13	m. 1124	11	
1149	4	1130	4							
		1151	0	sh. 1152	6	sh. 1155		sh. 1158		1159 <sub>10</sub> br. (R), 1145 $\pm$ 9(W),
				1179		1176		1184		1140(K)
				1187		1193				
1203	1	1209	0	m. 1200	2	i. 1206	2			1200(W)
						1219				
? 1227 <sup>1</sup>	1			sh. 1230	3	m. 1233	4	m. 1222	3	
				sh. 1252				m. 1233	4	
1273	2	1268	2	m. 1265	5	m. 1263	6	m. 1247	5	1270(R), 1262 $\pm$ 8(W)
				sh. 1284	1			m. 1269		
				1286		1292		1285		

This was done by circulating a saturated (30°C) aqueous solution of succinic acid continuously through a fused-quartz filter jacket interposed between the arc and the Raman tube. The thickness of the filter solution was 4 mm and it was circulated by means of a midget centrifugal

pump.<sup>11</sup> A number of other solutions were tried but proved unsatisfactory; e.g. sodium succinate tended to give off gas which permitted the short ultraviolet light to get through where the bubbles

<sup>11</sup> Obtainable from the Eastern Manufacturing Company, New Haven, Connecticut.

TABLE I—Continued.

Anhydrous $\alpha$ -D-glucose	Int.	Anhydrous $\beta$ -D-glucose	Int.	5 moles H <sub>2</sub> O: mole glucose	Int.	15 moles H <sub>2</sub> O: mole glucose	Int.	50 moles H <sub>2</sub> O: mole glucose	Int.	Previous investigators solutions only
? 1302	0	1312	0	1295		1292		1302		
		1336	0	m. 1331	5	m. 1337	8	m. 1333	7	
1345	6	1350								
		1363	2							
1374	1	1377		m. 1370	10	m. 1371	11	m. 1373	8	1370(R), 1373 $\pm$ 19(W),
br.d. 1417	1	br. 1407	1	sh. 1411	5	m. 1413	6	1417		1370(RW)
				m. 1430	3	1427				
				1436						
				1444		1444		1449		
1461	5	1452	2	m. 1462	7	m. 1460	8	m. 1465	5	1463(R), 1464 $\pm$ 7(W)
		1507	0	1490		1496		1485		
		$\nu_8$ (H <sub>2</sub> O)		1605	0	1584	3	1588	5	1590(RW)
				i. 1646		i. 1642		1646		
				1688		1701		1706		1670(RW)
		(H <sub>2</sub> O)		2057	3	2065	2	2053	3	2080(RW)
				i. 2168		i. 2140		i. 2172		
				2280		2214		2292		
				2447	0					
				2528						
				2549						
				2556						
				br.m. 2625	4			2596		
2640						2669		i. 2641	3	
i. 2700	1			br. 2706		i. 2710	2	2686		
2761				i.flat 2744	7	2750		2686		
2833				m. 2781				i. 2737	6	
i.d. 2856 <sup>1</sup>	1							2788		
2879				sh. 2801		2805				2805 <sub>2</sub> br. (R)
2879	15	d. 2876 <sup>1</sup>	4					br. 2876		
2893	20	2895	20	br.m. 2896	20	m. 2902	20	m. 2890	20	
2916	8	2908	20					2904		
		2929	4							
2946	19	2947	13	br.m. 2945	16	m. 2943	17	m. 2953	16	
2961	12	2977	13	3022		3015		2991		
				3047		3015		3011		3030(RW)
				3189	20	c. 3237	20	br. 3168		3260 br. (R)
3396	4			3276		m. 3349		i. 3271	30	
				3349		c. 3434	24	m. 3374		
		3503		br.m. 3439	30	br. 3619				
		3556	1	3522						
				3714				3738		

<sup>1</sup> Observed on only one plate.<sup>2</sup> From the relative intensities of Hg  $\lambda$ 2563.9 and 2578.4A, we conclude that this maximum is not the mercury line 2563.9A but is a Raman line. br. broad, c. center, d. diffuse, i. center interpolated, m. maximum, sh. shoulder, ? doubtful. (K) Kutzner, reference 2, (R) Rao, reference 4 (subscripts are his intensities), (RW) Rogers and Williams, reference 6, (W) Wiemann, reference 3.

formed and the sugar was then decomposed because the bubbles did not always leave the cell immediately. The succinic acid<sup>12</sup> proved very satisfactory. The ultraviolet arc emits the 1850A line of mercury with considerable intensity. This in turn generates ozone in the air which tends to cut down the intensity of ultraviolet light reaching the spectrograph. The difficulty was overcome by having a strong suction just above the arc so that the ozone was removed as soon as it was formed.

The sugar crystals were contained in a fused-quartz tube of 6 mm inside diameter with a fused-quartz window sealed on the end. The length of the sample was about 5 mm. Longer

<sup>12</sup> The quantitative absorption data can be found in the paper by Ley and Arends, Zeits. f. physik. Chemie **B17**, 177 (1932).

samples were not needed since very little light penetrated to the window from distances greater than 5 mm. In order to prevent light which had not penetrated the crystals from reaching the spectrograph a brass collimator containing two diaphragms of 4-mm aperture placed 3 inches apart was affixed to the tube with Duco cement. The interior of the collimator was painted a flat black. To gain better light transmission some of the very fine crystalline powders were moistened with absolute methyl alcohol. Only one line of the methyl alcohol appeared on any of the plates ( $\Delta\nu$  2836 cm<sup>-1</sup>). With the dispersion used, no change in the frequency of the sugar vibrations could be detected when this procedure was used and the exposure time was cut frequently by a third.

The sugar solutions were filtered through sintered glass and placed in a fused quartz Wood's tube with a flat, polished window.<sup>13</sup> This tube had a diameter of 15 mm and a possible active length of 5 inches. A half-inch length of the front of the tube and the horn were painted a flat black thus leaving a 3-inch effective length for irradiation. The solution tube had a collimating tube also and was used in conjunction with the filter jacket mentioned above. The mercury arc was surrounded with a polished sheet aluminum reflector, and the entire assembly was located in a large box. The collimator tube projected through the box, thus eliminating the possibility of light from the arc getting into the spectrograph. In the case of powders there can be no (or at most only a very short) dead optical space in the front end of the sample, for unless the powder near the window is illuminated, the secondary radiation cannot get through to be photographed. Thus with the powders considerable primary light (except 2537 which was especially removed) got into the spectrograph due to multiple reflections from the crystal faces, and the continuum on each side of 2537 was strong as were the rest of the mercury lines. Since this arc yields a particularly strong resonance line (the makers claim it to be nearly 80 percent monochromatic 2537), on long exposures, we found that the usual practice of having mercury vapor in the spectrograph to absorb the 2537 line was not efficient enough and we therefore employed a mercury vapor absorption cell. This cell was electrically heated, had an absorbing column 10 cm long, and when heated to *ca.* 150°C with a drop of mercury in it, completely obliterated the 2537 line.

The spectrograph employed was a Bausch and Lomb medium quartz type. In the region used the linear dispersion ran from around  $7\frac{1}{2}$ –9 Å/mm. The room housing the spectrograph was thermostated to within 1°C.

The sugars used were anhydrous  $\alpha$ -*D*-glucose,<sup>14</sup>  $[\alpha]_D^{0.2^\circ\text{C}} = 110.4$  initial rotation (Lit. 111.5);  $[\alpha]_D^{30^\circ\text{C}} = 52.2$  final rotation (Lit. 52.7);  $\alpha$ -*D*-

glucose monohydrate,<sup>15</sup>  $[\alpha]_D^{0.2^\circ\text{C}} = 100.8$  initial rotation (Lit. 101.4);  $[\alpha]_D^{30^\circ\text{C}} = 47.5$  final rotation (Lit. 47.9); anhydrous  $\beta$ -*D*-glucose (two samples), one (from The Pfanstiehl Chemical Company),  $[\alpha]_D^{0.2^\circ\text{C}} = 18.5$  initial rotation (Lit. 18.4);  $[\alpha]_D^{30^\circ\text{C}} = 52.5$  final rotation; another (prepared according to Hudson and Dale<sup>16</sup>),  $[\alpha]_D^{0.2^\circ\text{C}} = 18.5$  initial rotation;  $[\alpha]_D^{25^\circ\text{C}} = 51.8$  final rotation. The literature specific rotation values given were taken from the paper by Isbell and Pigman.<sup>17</sup> Unfortunately their figures do not agree exactly with those of other investigators and the discrepancies are of the same magnitude as those between our values and those of Isbell and Pigman. Therefore, all we can say about the purity of our  $\alpha$ - and  $\beta$ -sugars is that any impurities or other forms present must be there in such small amounts that their Raman spectra would not be observed. The solution pictures were made with *D*-glucose purified by the method of Hudson and Dale<sup>16</sup> using "Cerelese" as starting material.<sup>18</sup> A solution of "Cerelese" is usable but is slightly yellow originally and is a very bright yellow after a 24-hr. exposure. Also the impurities which can be removed by clarification and recrystallization increase the exposure time and give rise to fluorescence thus tending to hide the fainter Raman lines.

It was found difficult to measure the lines under our comparator since due to its magnification and to the low contrast of the fast plates used, the lines tended to wash out. Therefore the spectrograms were enlarged about sevenfold on high contrast paper and the wave-lengths of the Raman lines found by the Hartmann formula. Such was not the case, however, for the solution bands since they were frequently envelopes of a number of lines often diffuse and ill defined. It was found better to microphotometer these plates with a tenfold enlargement and to measure the band edges, shoulders, and maxima on the curves and to determine their wave-lengths by means of the Hartmann formula. Checks of the solution measurements were made on enlarge-

<sup>13</sup> Prepared according to Hudson and Yanovsky, J. Am. Chem. Soc. **39**, 1013 (1917).

<sup>14</sup> Hudson and Dale, J. Am. Chem. Soc. **39**, 320 (1917).

<sup>17</sup> Isbell and Pigman, J. Research Nat. Bur. Stand. **18**, 158 (1937).

<sup>18</sup> In the clarification both "Norit" and SO<sub>2</sub> were used prior to the concentration and subsequent crystallization.

<sup>13</sup> This and the filter jacket were obtained from The American Instrument Company.

<sup>14</sup> "Cerelese" from the Corn Products Company, New York.

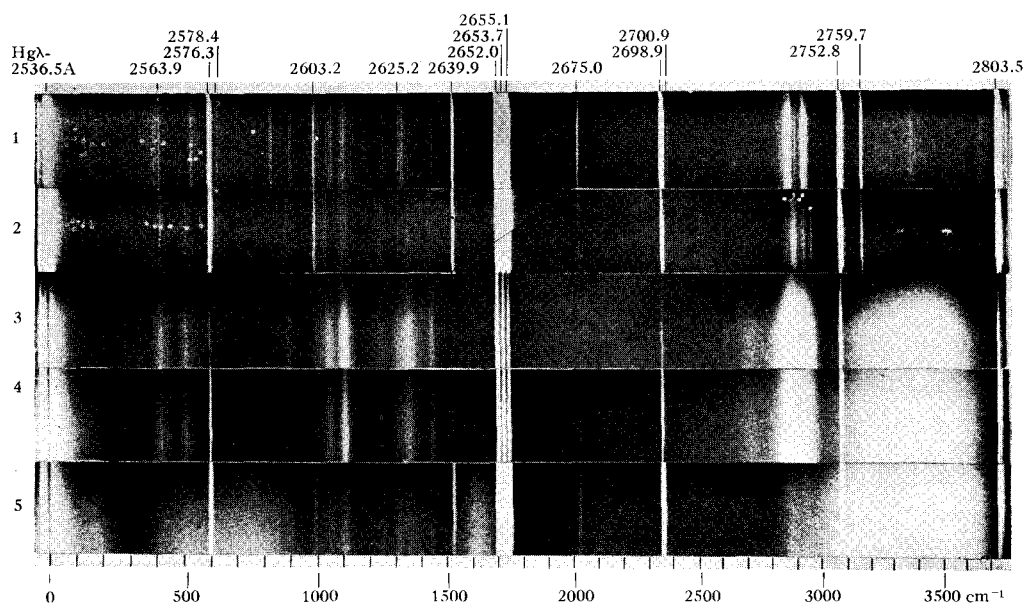


FIG. 1. Enlargements representative of the Raman spectra obtained by Hg  $\lambda$ 2537A excitation. 1. Anhydrous  $\alpha$ -*D*-glucose. 2. Anhydrous  $\beta$ -*D*-glucose. 3. 5 moles  $H_2O$ /mole glucose. 4. 15 moles  $H_2O$ /mole glucose. 5. *ca.* 520 moles  $H_2O$ /mole glucose (0.1 molar). The two bands in 1 and the higher of these two bands in 2 lying to the low side of Hg 2803.5A belong to a band system in the arc which encroaches slightly on the O-H region.

ments to be sure that no false information (due to scratches or flaws on the plates) would be conveyed by the curves. Too much stress must not be put on these band edges since their position varied slightly with the time of exposure. The low frequency "crystal" lines on the crystal plates were measured on the comparator after first pricking the lines with a fine needle.<sup>19</sup> In general the measurements are judged to be accurate to within  $\pm 2$   $cm^{-1}$ . The intensities are qualitative only and are based on a scale of 0 to 20 with 2893, 2895–2908, and the 2900- $cm^{-1}$  band of the  $\alpha$ -,  $\beta$ -, and solution plates respectively being given an arbitrary rating of 20. Plates were made of the direct arc in order to be sure which lines originated in the arc and which in the sugar.

Below is given a resumé of plates measured. After the number of the plate, the words "dry" or "moistened" indicate whether the powder was photographed dry or moistened with absolute methyl alcohol. Next is given the slit width on

the spectrograph and finally the number of hours which the plate<sup>20</sup> was exposed.

$\alpha$ -*D*-glucose anhydrous (all I-O plates): (1) dry, 0.025 mm, 35 hr. (2) dry, 0.02, 25 (3) moistened, 0.02, 15 (4) moistened, 0.02, 25.

$\beta$ -*D*-glucose anhydrous (all I-O plates): (1) moistened, 0.02, 24 (2) dry, 0.02, 60 (3) dry, 0.04, 72 (4) moistened, 0.03, 40 (5) dry, 0.03, 42 (6) dry, 0.03, 72.

Saturated equilibrium *D*-glucose (*ca.* 5 moles  $H_2O$ /mole glucose): (1) I-O, 0.025, 25 (2) 103-O, 0.04, 75 (lines also confirmed on two other plates not measured).

Dilute equilibrium *D*-glucose (*ca.* 15 moles  $H_2O$ /mole glucose): (1) 103-O, 0.03, 84.

Dilute equilibrium *D*-glucose (*ca.* 50 moles  $H_2O$ /mole glucose): (1) 103-O, 0.03, 47 (lines confirmed on other plates not measured).

The results are summarized in Table I. The strong lines were observed and measured on all plates mentioned. In the first three columns the weaker lines were observed and measured on at least two plates unless marked by a superscript 1 in the table.

<sup>20</sup> All Eastman plates.

<sup>19</sup> Some of these low  $\Delta\nu$  lines seen in the reproductions may arise in the arc. They are  $\Delta\nu$  47, 79, 111, 191, and 380  $cm^{-1}$ . These arc lines are sharp but faint and probably too many crystal frequencies were rejected by being assigned to these weak lines in the source. We have leaned over backwards in this respect.

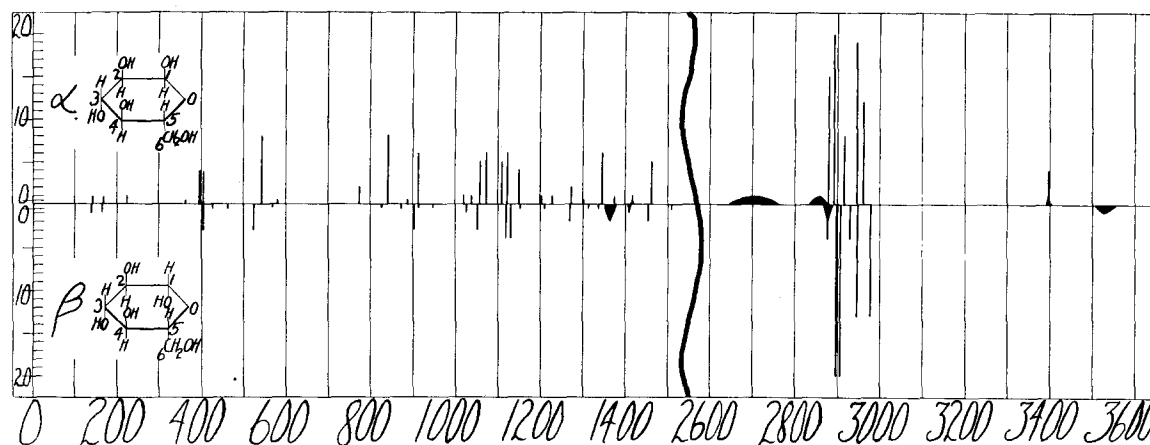


FIG. 2. Comparison of the Raman frequencies (in  $\text{cm}^{-1}$ ) of anhydrous  $\alpha$ - and  $\beta$ -D-glucose. Intensity estimates plotted vertically.

### DISCUSSION OF RESULTS

In the crystals there is only a fair one-to-one correspondence among the vibrational frequencies of  $\alpha$ - and  $\beta$ -D-glucose below  $1500\text{ cm}^{-1}$ . One notable discrepancy is the absence of a strong frequency in the  $\beta$ -D-glucose near the rather intense  $842\text{-cm}^{-1}$  line of the  $\alpha$ -form. While it is a fact that a strong frequency exists in this region for a whole series of six membered heterocyclic ring compounds and corresponds to the breathing frequency, we do not wish to make any conjecture about the absence of a strong frequency of the  $\beta$ -form in this region until more intense spectrograms have been taken along with accurate intensity measurements and polarization characteristics of the lines. We hope to carry out these experiments if we are successful in growing large single crystals free from fluorescent

impurities and flaws. The most striking difference between the two crystalline forms is exhibited in the  $2900\text{-cm}^{-1}$  region where the form of sugar may be identified by a glance at the spectra. The O—H frequency region is nearly bare for both forms with only one line in the  $\alpha$  and one band in the  $\beta$ . On the best plates, which we have reproduced in Fig. 1, there is some evidence in the  $\alpha$  for another frequency of slightly smaller value than the O—H frequency mentioned. Rough preliminary measurements on the  $\alpha$ -monohydrate seem to show no marked differences from the anhydrous  $\alpha$ . This seems astounding and we are investigating the spectra further. We do not feel that speculation as to the identity of the various frequencies or as to their appearance or non-appearance would be very profitable at this time. We are, therefore, reserving any such

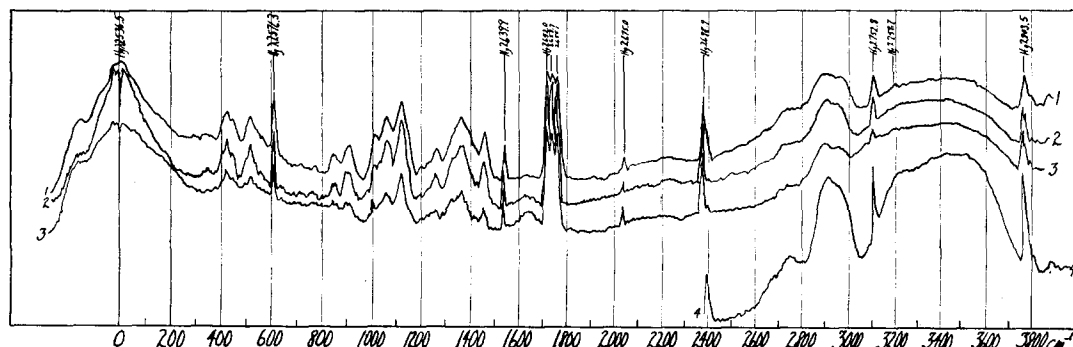


FIG. 3. Superposition of microphotometer tracings of: 1. 5 moles  $\text{H}_2\text{O}$ /mole glucose, 2. 15 moles  $\text{H}_2\text{O}$ /mole glucose, 3. 50 moles  $\text{H}_2\text{O}$ /mole glucose. 4. High  $\lambda$  part of plate with suitable exposure in this region but under-exposed in lower  $\lambda$  region. 5 moles  $\text{H}_2\text{O}$ /mole glucose.



comments until we have obtained much more data on the various sugars. A comparison of the Raman frequencies of anhydrous  $\alpha$ - and  $\beta$ -*d*-glucose is given in Fig. 2.

### Glucose Solutions

When the sugars are dissolved in water, allowed to come to equilibrium, and the Raman spectra of the solutions obtained, the frequencies are no longer sharp but are broadened considerably. Below  $1500\text{ cm}^{-1}$  there are 15 solution bands having no counterpart in the  $\alpha$ - or  $\beta$ -form. There are no  $\alpha$ -lines which are not covered by a solution band and only two  $\beta$ -lines ( $\Delta\nu$  825 and  $1507\text{ cm}^{-1}$ ). However, there are four  $\alpha$ -lines ( $\Delta\nu$  363, 887, 1057, and  $1345\text{ cm}^{-1}$ ) lying more than  $5\text{ cm}^{-1}$  from band maxima or shoulders in all three concentrations and five  $\beta$ -lines ( $\Delta\nu$  1051, 1118, 1312, 1363, and  $1452\text{ cm}^{-1}$ ) in this category. Unfortunately, the microphotometer available to us was not very satisfactory in that there was a certain amount of random drift in the intensity deflection. While this could be kept at a minimum in closely adjacent regions, absolute intensities or true shapes of lines were not to be depended on except as rough estimates. It is hoped that this microphotometer will be in first class shape in the future as soon as parts can be obtained. In Fig. 3 we have reproduced the microphotometer curves of the three solutions of different concentrations. Within the accuracy of our tracings, which we estimate to be of the order of magnitude of  $5\text{ cm}^{-1}$ , there are no systematic changes with dilution except for the frequency  $894\rightarrow 899\rightarrow 905$ . In order to obtain reasonable intensities for the frequencies below  $1500\text{ cm}^{-1}$  it is necessary to over-expose the  $2800\text{--}3600\text{ cm}^{-1}$  region. This has a tendency to flatten the tracing in that range. In curve 4 we have microphotometered a plate (5 moles  $\text{H}_2\text{O}$ /mole glucose) where the  $2800\text{--}3600\text{ cm}^{-1}$  region was not over-exposed.

We do not yet feel justified in drawing any conclusions from the curves as to the percentages of  $\alpha$ - and  $\beta$ - (or other) forms present in solution.

A careful study of how the frequencies and intensities of the lines shift in going from the anhydrous crystalline forms to the various crystalline hydrates (if they exist) should indicate how the frequencies are affected as the sugar-sugar association is replaced by the sugar-water association. More information should also be obtained by studying the changes in the shape and position of the line envelopes in the equilibrium sugar solutions as the concentration changes from a saturated solution (where considerable sugar-sugar association must still exist) to a very dilute solution (where only sugar-water association could be present). From the above work it can be seen that these shifts must be small, about the order of magnitude of our errors. The question as to whether the difference in the sugar-sugar sugar-water association can cause enough changes in the frequencies and intensities to permit the solution bands to be completely accounted for by the  $\alpha$ - and  $\beta$ -forms will have to wait until we have photographed more sugars and their hydrates and have obtained precise microphotometer tracings of their solutions.

### The Water Bands

These are located<sup>21</sup> at  $\sim 200$ ,  $320\text{--}1020$ ,  $1650$ ,  $2167$ ,  $3440$ , and  $\sim 4000\text{ cm}^{-1}$ . All of them but the last may be seen in the most dilute *d*-glucose solution (0.1 molar), reproduced in the fifth picture in Fig. 1. Although the water bands in this case cover almost every region except  $1000\text{--}1500\text{ cm}^{-1}$  it can be seen from this last picture that even in dilute solutions the Raman lines of the sugar can be seen superimposed upon the water bands.

### ACKNOWLEDGMENTS

We wish to thank Dr. R. M. Hixon for his interest in and support of this project and the Physics Department for allowing us to use their microphotometer.

<sup>21</sup> Cross, Burnham, and Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).