

Fluorescence Excitation Spectroscopy of Glucose Molecules

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ABSTRACT

The measurement technique and the results obtained by optical spectroscopy during excitation of glucose molecules by photons are described. For the first time, the photoluminescence spectra of glucose were studied in the wavelength range 400-700 nm upon excitation by photons of different energies 3.26-4.51 eV. Peculiarities were found in the luminescence spectra (radiation intensity, positions of maxima), indicating the excitation of the OH hydroxyl radical and the COH carbonyl group as fragments of the glucose molecule by photon impact. X-ray diffraction spectra were measured, which confirmed the presence of glucose hydrate in the studied samples and certain structural changes after interaction with photons. It has been shown that photon irradiation results in modification of glucose molecular crystals both at the macro and micro levels.

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Introduction

Interest in studying the processes of interaction of electrons and photons with monosaccharide molecules is caused, first of all, by their biological and industrial importance, as well as by the discovery of such molecules in interstellar space and in the atmospheres of planets [1-3]. Spectroscopic studies of elementary processes of electrons and photons interaction with complex organic compounds are determined by the exceptional importance of these compounds in the processes occurring in living organisms. In the region of threshold energies of collisions with electrons, features of their atomic and molecular structure appear. Studies of the processes of interaction with photons greatly complement the overall picture of the elementary processes of excitation and ionization of both organic molecules themselves and the structure of different molecular complexes. Such studies are especially important for understanding the processes that occur during radiation damage of biological systems [4-6]. It should be noted that electrons with energies well below the ionization threshold can induce significant damage in biological molecules due to dissociative electron attachment (DEA). The DEA process is capable of causing severe DNA damage such as single and double strand breaks that can lead to cancer [7,8]. The excitation of molecules is accompanied by the transition of one or more electrons of the initial molecule to higher electronic states, and subsequent de-excitation leads to the appearance in the emission spectra of both spectral molecular bands and lines of individual atoms in the wavelength range from infrared to visible and ultraviolet radiation [9-11].

A detailed study of the fragmentation of monosaccharide's is carried out with mass spectrometric and spectroscopic instruments

[12-22]. For example, it was found in that fragmentation is characterized by a pronounced site selectivity, i.e., neutral fragments contain C6, while the negative charge remains on the fragment containing the anomeric center C2. Using the density functional theory (DFT), dynamic modeling was performed, which made it possible to predict the formation of fragment ions and compare with experiment and obtain detailed information about the fragmentation channels. Theoretical and experimental studies of the ionization of complex organic compounds, including monosaccharide's, are the subject of a significant number of works, which focus on determining the ionization potential (IP) of the parent molecule and the appearance energy (AE) of dissociative ionization [19-22]. As for the study and analysis of the threshold behavior of fragment ions arising as a result of dissociative ionization, there are much fewer such data, and there are practically no data for alcohol molecules. Monosaccharides in the gas phase are cyclic molecules and retain their crystal structure in the form of pyranose throughout the evaporation process [20]. The density functional theory calculation (B3LYP/6-311++G(d,p)) showed that the pyranose form is probably the dominant monosaccharide form in the gas phase.

Interest in the fragmentation of monosaccharide's is also motivated by the influence of secondary low-energy electrons during radiation damage to DNA, where the sugar fragment is the main building block [8]. Thus, the stability of the sugar unit can play a decisive role when biological molecules are exposed to high-energy radiation, due to which low-energy electrons are formed in large quantities [14]. At the same time, a specific feature of the fragmentation of monosaccharide's is the loss of various amounts of H₂O molecules and the release of carbon-containing fragments consisting of CH₂O units [14].

It was shown in [23] by mass spectrometric analysis that the replacement of amino acids with their binary metal complexes can initiate various processes, including the oxidative degradation of their glucose conjugates, generating 1-amino-1-deoxyfructose and its derivatives. It was found that relatively intense ions with $m/z = 180$ ($C_6H_{14}NO_5$) appear. Moreover, ions originating from ketohexoses showed fragmentation identical to glucosamine, and ions identical to fructosamine were produced from aldohexoses.

In this work, we studied the photoluminescence spectra of glucose in the wavelength range 400- 700 nm. The range of luminescence excitation wavelengths was 250-400 nm (photon energies 3.26-4.51 eV). In the same wavelength range, the luminescence excitation function was measured at $\lambda = 535$ nm (photon energy 2.32 eV) and the observed features were identified. Differences were found in the photoluminescence spectra of microcrystalline and caramelized glucose, and the X-ray diffraction spectra were measured for them. The change in the microstructure of the surface of glucose after interaction with photons was studied.

Features of the Structure of the Glucose Molecule

Glucose $C_6H_{12}O_6$ is a structural component of all living organisms, performs a detoxifying function, participates in the neutralization of toxic metabolites and xenobiotics. Glucose is a polyhydroxyaldehyde from the aldohexose class containing six carbon atoms, an aldehyde group and five hydroxyl groups (Fig: 1a), the position of which has a significant effect on the chemical and physical properties of glucose molecules [24].

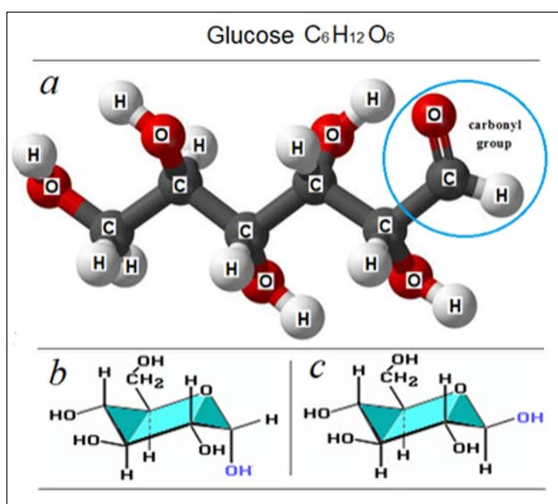


Figure 1: 3D Structural Formula of Glucose (a) Spatial Structure of Cyclic Isomers of α - and β -glucose (b, c)

It is important to note that the glucose molecule can exist in three isomeric forms: two of them α - and β - are cyclic and one is linear, and all of them are in dynamic equilibrium with each other. In the structure of glucose, cyclic α - and β -forms are distinguished (Fig: 1b, c), since they are spatial isomers that differ in position relative to the plane of the OH hemiacetal hydroxyl ring, which is highly reactive [25]. In α -glucose, this hydroxyl is in the trans-position, and in β -glucose, it is in the cis-position to the hydroxymethyl group CH_2OH (see Fig: 1c). In the crystalline state, glucose is in the α -form, it is characterized by optical isomerism (D- and L-isomers), and only the D-isomer occurs in nature.

Note that when a glucose molecule is ionized by electron impact, the charge is preferentially localized on the oxygen of the carbonyl group $-CHO$ (Fig: 1a). This leads to cleavage of the tetrahydropyranose ring, followed by fragmentation upon cleavage

of single bonds of the open oxo structure [25].

Experimental Setup

The experimental setup is described in detail in [26, 27], so here we briefly dwell on the measurement technique [26, 27]. The experiment on the study of luminescence spectra was carried out on the Spectrofluorophotometer RF-6000, which has a high sensitivity, a wide spectral range and allows measurements of the spectra of fluorescence, bioluminescence, chemiluminescence, electroluminescence of samples of various nature: liquids, powders, films and plates [28]. Measurements, control, and processing of the useful signal were performed automatically by a personal computer in the search mode for the optimal excitation/emission wavelength using the LabSolutions RF program [28]. Within the framework of this program, the measured signal is also corrected for the spectral sensitivity of the spectrofluorophotometer. The samples were made in the form of tablets with a diameter of 25 mm and a substance thickness of 1 mm by pressing from powdered glucose.

The experimental technique consisted in excitation of glucose luminescence by radiation from a xenon lamp, followed by analysis of the luminescence spectra at different excitation energies. Before the start of measurements, the background signal was recorded, i.e., a black matte surface was placed in place of the sample. The dependence thus obtained was subtracted from the luminescence spectrum. The ultraviolet region of the photon source spectrum was separated using an UFS-5 filter (bandwidth 200-400 nm, transmittance 45% at a wavelength of 275 nm), and a ZhS-11 light filter was installed in front of the entrance slit of the monochromator (transmission region ≥ 400 nm, transmittance $\geq 92\%$). Irradiation with photons that excite luminescence was carried out at an angle of 15° to the sample surface, and luminescence emission was observed at an angle of 75° to the surface. This geometry ensured minimal influence on the useful signal of reflected and scattered photons from the sample surface.

The sample was installed strictly vertically in a specially made holder, the area of the illuminated part of the sample surface was 5×10 mm². The slit widths were chosen so that the spectral transmission interval was 5 nm for both the radiation source and the monochromator. The studied luminescence spectra were recorded with a step of 1 nm at a scanning rate of 200 nm/min.

To select the wavelengths (energies) of excitation of the luminescence of microcrystalline glucose, the spectrum with the shortest excitation wavelength of 275 ± 2.5 nm (4.52 eV) was measured. In the obtained spectrum, the maximum at $\lambda = 535$ nm turned out to be dominant, at which the excitation function was measured. On Fig: 2 shows the luminescence excitation function of microcrystalline glucose under photon irradiation measured at a wavelength $\lambda_{max} = 535$ nm. Using the Levenberg-Marquardt algorithm, the positions of singularities on the excitation function are determined from the wavelengths of the maxima of the Gaussian distributions. Shown in Fig: 2 the dependency was processed by Fityk 1.3.1 according to the original formula [29]:

$$f(x) = a_0 e^{-\ln 2 \left(\frac{x-a_1}{a_2} \right)^2} \quad (1)$$

The following coefficients are used here: a_0 is the height of the maximum of the distribution function, a_1 is the position of the maximum (nm), a_2 is FWHM/2. This made it possible to identify 11 features, of which 4 most intense at wavelengths $\lambda_{exc} = 275$,

323, 354, and 380 nm (a, b, c, d in Fig. 2) were chosen by us for luminescence excitation. In addition, the choice of these λ_{exc} is also determined by the binding energies of the diatomic fragments (see Table 1) that make up the glucose molecule (Fig. 1c).

Table 1 lists the photon energy intervals and the corresponding λ_{exc} for measuring the luminescence spectra. Note that the given energy ranges of photons that excite luminescence are determined by the spectral transmission range of the device. As for the binding energy of the C-N fragment (the nitrogen atom is not part of the glucose molecule), however, the possibility of its appearance may be associated with the process of nitrogen chemisorptions from the atmosphere. For the same reason, the formation of glucose hydrate on the sample surface cannot be excluded.

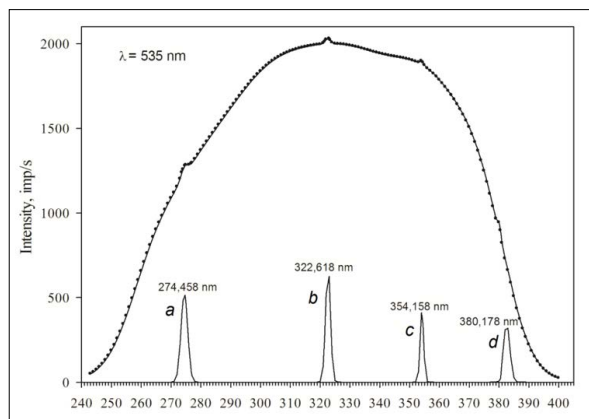


Figure 2: Function of Excitation (Excitation Spectra) of Microcrystalline Glucose and Gaussian Distribution Functions: a, b, c, d

Table 1: Binding Energies of atoms in diatomic molecules that make up glucose and energy intervals of photons that excite luminescence

Bond	Bond energy [30], eV	Photon energy intervals, eV and corresponding λ_{exc} , nm
H-O	4.52	4.47-4.55 ($\lambda_{exc} = 272.5-277.5$)
H-C	4.20	
C-C	3.61	3.81-3.87 ($\lambda_{exc} = 320.5-325.5$)
C-O	3.31	3.48-3.53 ($\lambda_{exc} = 351.5-356.5$)
C-N	2.89	3.242-3.28 ($\lambda_{exc} = 377.5-382.5$)

Results and Discussion

On the experimental setup described above, the photoluminescence spectra of microcrystalline glucose and its caramel were measured. To minimize the effect of exciting photons on the surface structure, the measurements were carried out with a successive increase in the photon energy. Then, microscopic studies of the degree of influence of exciting photons on the structure of the sample surface at the irradiation point were carried out. Also performed X-ray powder diffraction studies for both glucose and its caramel. Photoluminescence Spectra

On Fig. 3a shows the luminescence spectra of microcrystalline glucose. All the wavelengths used by us for excitation (275, 323, 354, and 380 nm) lead to the appearance of photoluminescence with a continuous spectrum in the region of 400-700 nm. The spectra exhibit two emission maxima, a more intense one near 535 nm and a less intense one at 449 nm. The highest luminescence intensity is observed upon excitation by photons with $\lambda_{exc} = 323$ nm and $\lambda_{exc} = 354$ nm. Photons with the lowest quantum energy ($\lambda_{exc} = 380$

nm) excite luminescence with the minimum quantum yield. The ratio of intensities in the luminescence maxima upon excitation by photons with $\lambda = 323$ nm and $\lambda = 354$ nm changes due to a significant increase in the contribution of the short-wavelength (449 nm) maximum. This means that the quantum yield of glucose luminescence depends on the wavelength of the exciting photons. The difference in the change in the luminescence intensity at the maxima with a change in the energy of exciting photons indicates the implementation of differences in the intermolecular and intermolecular transfer of excitation energy [30, 31].

The most intense emission upon excitation by photons with $\lambda = 323$ nm and $\lambda = 354$ nm suggests that the main contribution to the formation of the glucose luminescence spectrum is made by the processes of excitation of the CHO carbonyl group (see Fig. 1a and Table 1) (maximum 535 nm) and hydroxyl group OH (maximum 449 nm). An analysis of the position of features in the glucose luminescence spectrum (Fig. 2b) shows that, with a change in the energy of exciting photons, the maximum near 449 nm hardly shifts. A different picture is observed in the long-wavelength region of the spectrum. Excitation of luminescence with $\lambda_{exc} = 323$ nm leads to the longest wavelength position of the maximum, 537 nm. At $\lambda_{exc} = 323$ nm there is a noticeable shift up to 535 nm, at $\lambda_{exc} = 275$ nm it is 530.6 nm, and at $\lambda_{exc} = 380$ nm the shortest wavelength location of the maximum is 529 nm. Such a noticeable shift in the position of the maximum depending on the energy of photons that excite luminescence indicates a significant effect of intermolecular interaction on the transfer and transformation of electronic excitation [31]. Note that high hydration of glucose probably affects the photoluminescence spectra; therefore, the samples studied by us contain a significant portion of glucose hydrate.

It is known that the absorption of low-energy photons by a substance mainly occurs due to photo excitation and the photoelectric effect [32]. These processes lead to the simultaneous passage of several processes at the macro and micro levels. On the one hand, the configuration of the solvate shell of a molecule is essentially determined by the energy state (ground or excited). On the other hand, optical excitation almost instantly stimulates the violation of some degrees of freedom of the vibration equilibrium between the molecule that absorbed the photon and its environment. Further, the environment of the molecule will inevitably be rearranged until a new equilibrium state is formed between the now excited molecule and its environment. Considering the photon energy (3.24-4.55 eV), which we used to excite luminescence, all these mechanisms can be realized.

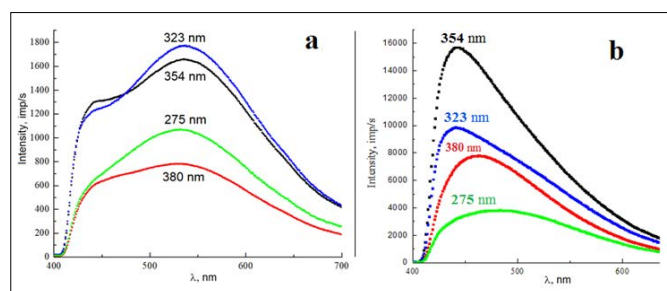


Figure 3: Photoluminescence Spectra of Glucose (a) and Caramel (b)

In order to elucidate the nature of intermolecular bonds in the formation of photoluminescence spectra, we compared the luminescence spectra of microcrystalline and caramelized glucose (see Fig. 3b). It is known [32] that caramelization of glucose

leads to the loss of the crystal structure and includes a number of processes, the most important of which is the transition of the anomeric and cyclic forms into chemical equilibrium, as well as dehydration and fragmentation reactions. Caramel was made by heating a container with glucose to a temperature of 419 K (the melting point of α -glucose is 419 K, β -glucose is 423 K), followed by cooling to room temperature [33]. As a result, a sample of white transparent caramel with no glucose hydrate was obtained, for which the properties are fundamentally different in the length and nature of intermolecular bonds, which is confirmed by X-ray powder diffraction studies.

As can be seen from Fig: 3b, the photoluminescence spectra of caramelized glucose are very different from the microscopic spectra. Firstly, the luminescence intensity increased up to ~ 10 times and, secondly, a significant transformation of the shape of the spectra is observed. Only in the case of $\lambda_{exc} = 323$ nm can we assume that the structure of the spectrum is due to the appearance of two maxima. In the other three spectra, there is a clearly pronounced one emission maximum. Depending on the energy of the exciting photons, its position on the wavelength scale changes more significantly. At $\lambda_{exc} = 380$ nm – 463.5 nm; $\lambda_{exc} = 351$ nm – 443 nm; $\lambda_{exc} = 323$ nm – 441.2 nm; $\lambda_{exc} = 275$ nm – 479 nm. Considering that the highest luminescence intensity is observed at $\lambda_{exc} = 354$ nm (quantum energy 3.5 eV, see Table 1), it can be assumed that the main contribution to the emission is made by the processes of relaxation of the excited states of the COH carbonyl group. Since caramel is dehydrated glucose, the absence of free OH radicals leads to more efficient excitation of the interatomic bonds of the carbonyl group.

Micrograph of Glucose

At a certain photon energy at the macro level, it is possible to change the structure of a molecular crystal, the “building blocks” of which are glucose molecules, and the emergence of a photonic crystal in which an additional “field” is artificially created, comparable to the wavelength of the exciting radiation. In our case, the photon energy range is 3.24-4.55 eV and includes both the range of binding energies of diatomic molecules (Table 1) and the energy values sufficient to change the structure of the glucose molecule. The possibility of changing the length of intermolecular bonds is also not ruled out.

To test this assumption, photographs of microcrystalline glucose samples were taken before and after measuring the photoluminescence spectra using a MICROMed XS-5520 microscope with a Web camera. Irradiation with photons leads to modification of its crystal structure (Fig: 4). It can be seen that the transparency at the edges decreases, the rod-like edging disappears, and a small fringe appears along the perimeter (see Fig: 4b), which is probably stimulated by the dissipation of the absorbed photon energy. Excitation by photons with energies > 3 eV inevitably leads to a change in the binding energies between glucose molecules, which are manifested by the modification of its crystal structure.

However, almost no changes are observed in the luminescence spectra during repeated measurements. The shapes of the spectra remain unchanged: both luminescence maxima are observed, while

the luminescence quantum yield somewhat decreases by $\sim 15\%$. The invariability of the shape of the luminescence spectra during repeated measurements indicates the absence of intermolecular defect formation, and a decrease in the quantum yield confirms the presence of violations of intermolecular bonds, i.e. some change in the structure of the substance we are studying.

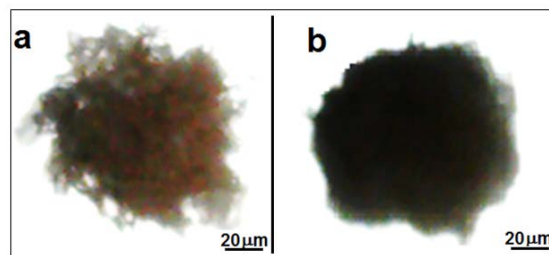


Figure 4: Photographs of Microcrystalline Glucose (64x magnification): before Photon Irradiation (a), after measurements of Photoluminescence Spectra (b).

X-Ray Structural Analysis

The structure of glucose and its caramel samples before and after photon irradiation was studied by X-ray powder diffraction. Experiments were carried out using a conventional Bragg–Brentano technique with a DRON-4 diffractometer (Cu K_{α} $\lambda = 1,54$ Å radiation, Ni filter, scan mode with the step of 0.02° , exposition time 10 s/step, room temperature, angles interval of $5^{\circ} \leq 2\theta \leq 60^{\circ}$).

Comparison with the characteristic spectra of pure glucose and glucose hydrate [34] shows that the spectra measured by us contain both peaks of α glucose ($2\theta = 11.89^{\circ}; 14.83^{\circ}; 17.05^{\circ}; 20.65^{\circ}$) and mainly glucose hydrate peaks. The diffraction spectrum measured after photon exposure (see Fig: 5) has some differences from the spectrum of non-irradiated sample. Moreover, changes occur both for the peaks of glucose hydrate ($2\theta = 12.7^{\circ}; 14.6^{\circ}$) and for the glucose peak $2\theta = 20.65^{\circ}$.

Note that the peak at 21.221° is dominant in intensity in the spectrum of α -glucose, and 19.732° in the spectrum of glucose hydrate. At 21.648° , glucose hydrate also has a fairly intense peak. However, in our spectra in this range of angles ($21^{\circ} \leq 2\theta \leq 22^{\circ}$), only rather broad weakly intense features are observed.

On Fig: 6 shows the selected sections of the spectra, which make it possible to evaluate changes both in the position of the peaks and in their width. An analysis of the presented X-Ray diffraction spectra shows that there are differences between them both in intensity and in the position of the peaks, as well as in their width. This indicates that the excitation of glucose luminescence by photons with an energy of 3.24-4.55 eV leads to microcrystalline changes in its structure. Note that most of the peaks in the diffraction spectra belong to glucose hydrate (see Table 2). The X-Ray diffraction spectra measured by us are in good agreement with the known spectra of glucose hydrate [34]. Some of the peaks are identified with α -glucose. This means that since all measurements were carried out in air, glucose hydrate is present on the surface of the samples.

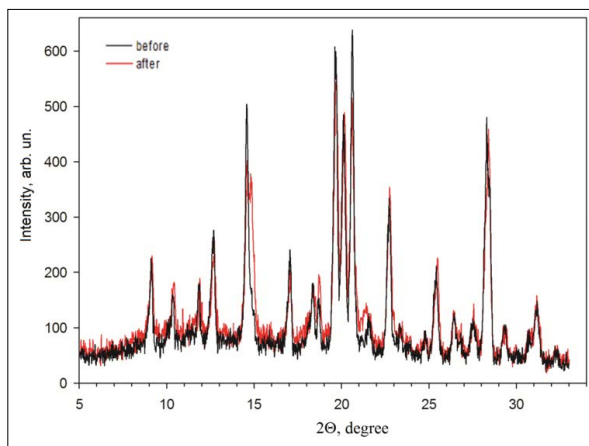


Figure 5: X-Ray Diffraction Spectra obtained before and after Luminescence Measurements

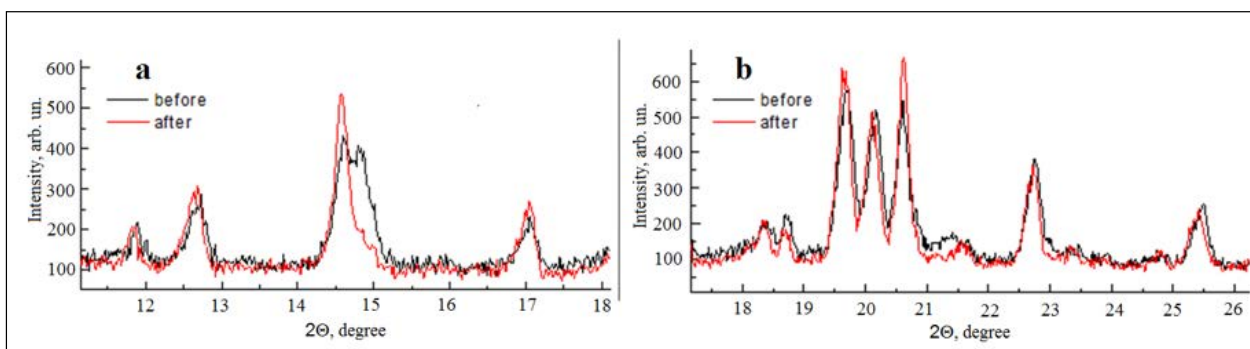


Figure 6: Fragments of X-Ray diffraction spectra $11^{\circ} \leq 2\theta \leq 18^{\circ}$ (a) and $17^{\circ} \leq 2\theta \leq 26^{\circ}$ (b) from Figure: 5.

To analyze the obtained X-ray diffraction spectra, it is more convenient to go to the tabular data. In Table 2 shows the HKL, 2θ values, relative peak intensities and their half-height widths (FWHM), for glucose samples before and after luminescence measurements.

Table 2: Peak positions (2θ), their relative intensities and peak widths at half maximum (FWHM)

H	K	L	Before luminescence			After luminescence			Source
			2θ	J/rel.	FWHM	2θ	J/rel.	FWHM	
0	0	1	9.157	45	0.462	9.104	38	0.258	Glucose hydrate
1	0	0	10.434	37	0.243	10.34	28	0.142	Glucose hydrate
0	2	0	11.89	38	0.132	11.86	31	0.126	α -Glucose
-1	0	1	12.735	50	0.237	12.684	46	0.227	Glucose hydrate
1	0	1	14.593	75	0.196*	14.574	80	0.172*	Glucose hydrate
1	2	0	14.83	70	**	14.8	30	**	α -Glucose
2	0	0	17.05	41	0.194	17.05	40	0.175	α -Glucose
2	1	0	18.41	36	0.305	18.382	210	0.19	α -Glucose
0	0	2	18.75	39	0.176	18.702	32	0.158	Glucose hydrate second order of peak 9.1
0	1	1	19.69	100	0.29	19.68	96	0.25	Glucose hydrate
1	1	0	20.15	89	0.26	20.135	75	0.24	Glucose hydrate
2	0	0	20.611	95	0.215	20.62	100	0.201	Glucose hydrate second order of peak 10.43
1	0	1				α -Glucose			
1	1	1	22.745	67	0.254	22.72	55	0.22	Glucose hydrate

*- Left margin evaluation

** - very broad

We can convert peak positions to spacing's values using the formula:

$$n\lambda = 2d\sin \theta, \quad (2)$$

where: n is the order in the spectrum; λ is the wavelength of the X-ray line $\text{Cu K}\alpha$ $\lambda = 1.54\text{\AA}$; d are the spacing's values in \AA ; θ is the diffraction angle measured in the experiment. Then the changes in the glucose spectra before and after photon irradiation are as follows. First, a noticeable change in the intensity of the peaks, in the range of spacing's values $d = 9.72\text{--}3.5\text{\AA}$ (range of diffraction angles $9.16^\circ \leq 2\theta \leq 25^\circ$) are observed. Second, the spacing's values of the sample not subjected to luminescence excitation are somewhat lower than after luminescence. The effect of photon irradiation in this range of d also manifests itself in a decrease in the FWHM peaks in X-Ray diffraction spectra (see Table 2). Third, in the region of smaller spacing's values of d ($\leq 3\text{\AA}$), one can notice the equality or decrease in the values for the sample subjected to interaction with photons. Most likely, photon irradiation leads to a change in the position of hydroxyl radicals, since the strongest changes are observed at large values of d and relate to the peaks of glucose hydrate. Large peak widths for non-irradiated glucose indicate a significant disorder in the structure of microcrystal's; however, their further studies and detailed analysis are required.

Similar X-Ray diffraction spectra were also measured for glucose caramel. As can be seen, in Fig: 7, a completely different picture is observed here: in the spectrum of caramel, the main structure of the peaks characteristic of glucose or glucose hydrate disappears (see Fig: 5). At the same time, a number of peaks appear at $2\theta = 16.8^\circ\text{--}17.3^\circ$; 21.9° ; 23.78° ; 24.71° ; 32° and 51.4° , which are absent in the X-Ray diffraction spectra of microcrystalline glucose, as well as monohydrate. Their appearance is most likely associated with the processes of glucose crystallization in caramel when it is cooled from the melting point $T=419\text{ K}$ to room temperature.

In the range of angles $9^\circ \leq 2\theta \leq 15^\circ$ in the spectrum of caramel, X-ray diffraction peaks are practically absent (or appear at the background level). This range of angles allows us to establish that spacing's in X-Ray diffraction spectra are significantly lower in caramel spectra. In other words, there are no bonds longer than 5.3\AA in the caramel structure. A possible explanation for this result could be the tighter packing of glucose molecules in caramel. Probably, a significant decrease in the presence of hydrates in caramel is also manifested, which, as a rule, are located on longer bonds. The formation of new crystalline structures other than ordinary microcrystalline glucose cannot be ruled out either. The latter assumption can also be used to explain the large difference in the luminescence spectra (Fig: 3) of microcrystalline glucose and its caramel. This difference manifests itself not only in a significant increase in the luminescence intensity, but also in a shorter wavelength position of the maxima on the wavelength scale.

Thus, in the process of measuring glucose luminescence using high-energy photons, changes in the microcrystalline structure occur on the surface of the sample. The differences found by us in X-Ray diffraction spectra: peak intensities, their position and half-width after irradiation with photons confirm this conclusion. We also note a significant difference in the X-Ray diffraction spectra measured for caramel.

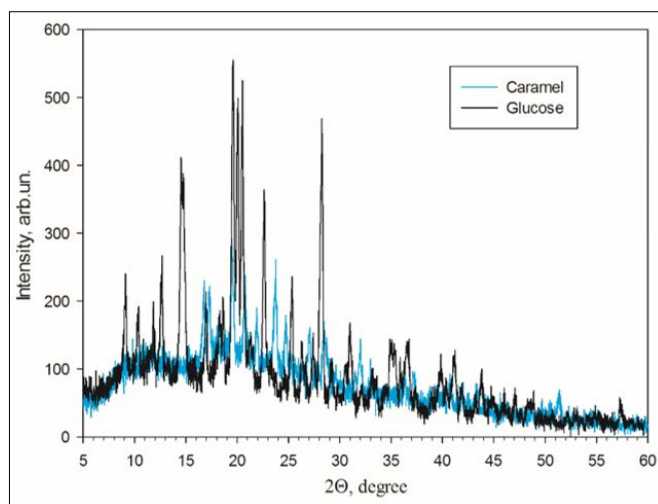


Figure 7: X-Ray diffraction spectra of glucose samples powder and caramel)

Conclusion

We have measured the photoluminescence spectra of samples of microcrystalline and caramelized glucose in the spectral range $400\text{--}700\text{ nm}$. The excitations in glucose molecules associated with processes in OH and COH fragments were found. The measured X-ray diffraction spectra showed the presence of glucose hydrate on the surface of powdered samples. X-Ray diffraction spectra of caramelized glucose showed that the diffraction spectra indicate the absence of glucose hydrate. The photoluminescence spectra of caramel are fundamentally different from the spectra of powdered glucose, and this may be not only due to dehydration, but also due to another structure of caramel. The process of measuring photoluminescence spectra leads to a change in the structure of powdered glucose samples, both at macro and micro levels.

We plan to use the obtained results on the study of glucose photoluminescence upon excitation by photons with energy of several eV to study the transformations of glucose molecules as a result of irradiation with high-energy electrons ($10\text{--}30\text{ meV}$) or neutrons.

In conclusion, we note that studies of monosaccharides by photon impact provide rich information about their unique properties, make it possible to determine the modification degree of the crystal structure, and to evaluate the parameters of intermolecular bonds. For a correct interpretation of our results, further studies are needed, including the study of the effect of optical excitation on the microstructure of molecular glucose crystals.

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References

1. Cline GW, Shulman GI (1995) "Mass and Positional Isotopomer Analysis of Glucose Metabolism in Periportal and Pericentral Hepatocytes" *J. Biological Chemistry* 270: 28062–28067.
2. Hannestad U, Lundblad A (1997) "Accurate and precise isotope dilution mass spectrometry method for determining glucose in whole blood", *Clinical Chemistry* 43: 794-800.
3. Billings L, Cameron V, Claire M, Dick GJ, Domagal-Goldman

- SD, et al. (2006) "The astrobiology primer: an outline of general knowledge--version 1", *Astrobiology* 6:735-813.
- Hanson KP, Komar VE (1985) "Molecular mechanisms of radiation cell death", *Energoatomizdat*, Moscow 141.
 - J. Kogl. "Biological effects of radiation", Mir, Moscow (1986).
 - Monteiro WA (2016) "Radiation Effects in Materials" doi: 10.5772/61498
 - Dawley MM, Tanzer K, Carmichael I, Denifl S, Ptasinska S (2015) "Dissociative electron attachment to the gas-phase nucleobase hypoxanthine" *J. Chem. Phys.* 142: 215101-215108.
 - Baccarelli I, Bald I, Gianturco FA, Illenberger E, Kopyra J (2011) "Electron-induced damage of DNA and its components: Experiments and theoretical models", *Physics Reports* 508: 1-44.
 - Heller JM, Birkhoff RD, Williams MW, Painter LR (1972) "Optical Properties of Liquid Glycerol in the Vacuum Ultraviolet", *Radiation Research* 52: 25-31.
 - Yongjun Hu, Elliot R Bernstein (2008) "Vibrational and photoionization spectroscopy of biomolecules: Aliphatic amino acid structures", *J. Chem. Phys.* 128: 164311.
 - M Inokuti (1995) "Atomic and Molecular Data Needed for Radiotherapy and Radiation Research". TECDOC-799 IAEA Press, Vienna.
 - Flosadottir HD, Bald I, Ingolfsson O (2011) "Fast and metastable fragmentation of deprotonated d-fructose – A combined experimental and computational study", *International Journal of Mass Spectrometry* 305: 50-57.
 - Sanche L (2016) "Interaction of low energy electrons with DNA: Applications to cancer radiation therapy", *Radiation Physics and Chemistry* 128: 36-43.
 - Sulzer Ph, Ptasinska S, Zappa F, Mielewska B, Milosavljevic AR, et al. (2006) "Dissociative electron attachment to furan, tetrahydrofuran, and fructose", *J. Chem. Phys.* 125: 044304-044306.
 - Taylor VF, March RE, Longerich HP, Stadey SJ (2005) "A mass spectrometric study of glucose, sucrose, and fructose using an inductively coupled plasma and electrospray ionization", *International Journal of Mass Spectrometry* 243: 71-84.
 - Bouvier C, S Van Nuffel, Walter P, Brunelle A (2022) "Time-of-flight secondary ion mass spectrometry imaging in cultural heritage: A focus on old paintings", *Journal of Mass Spectrometry* 57: 1.
 - Lebedev AT (2003) "Mass Spectrometry in Organic Chemistry", Binom., Moscow 493.
 - J Laskin, H Lifshitz (2012) "Principles of mass spectrometry applied to biomolecules", Technosphere, Moscow 608, 701. ISBN: 978-0-471-72184-0
 - Guler LP, Yu YQ, HI Kenttämaa (2002) "An Experimental and Computational Study of the Gas-Phase Structures of Five-Carbon Monosaccharides", *J. Phys. Chem.* 106: 6754-6764.
 - Sommerfeld T (2007) "Doorway mechanism for dissociative electron attachment to fructose", *J. Chem. Phys.* 126: 124301-124305.
 - Szarek WA, Korppi-Tommola SL, Martin OR, Smith VH Jr (1984) "Examination of the molecular properties of D-fructose and L-sorbose by abinitio LCAO-MO calculations", *Canadian Journal of Chemistry* 62: 1506-1511.
 - Gao Y, Bu J, Peng Zh, Yang B (2014) "Radical Reactions in the Gas Phase: Recent Development and Application in Biomolecules", *Journal of Spectroscopy* 2014: 570863.
 - Nashalian O, Yaylayan VA (2016) "In Situ formation of the amino sugars 1-amino-1-deoxy-fructose and 2-amino-2-deoxy-glucose under Maillard reaction conditions in the absence of ammonia", *Food Chemistry* 197: 489-495.
 - OB Shpenik, AN Zavilopulo, AS Agafonova, LG Romanova (2008) "Mass spectrometric studies of the glucose molecule", *Reports of the National Academy of Sciences of Ukraine* 5: 96-101.
 - Barton D, Ollis WD (1986) "General organic chemistry. Lipids, carbohydrates, macromolecules, biosynthesis", Chemistry, Moscow.
 - Yu A Bandurin, Zavilopulo AN, Molnar Sh, OB Shpenik (2022) "Excitation of L-valine molecules by electrons and photons", *Eur. Phys. J. D* 76: 9-14 (2022).
 - Yu A Bandurin, T Yu Popik, Zavilopulo AN (2022) "Interaction of photons with molecules of glucose and fructose" *Reports of the National Academy of Sciences of Ukraine* 1: 58-63.
 - Shimadzu Spectrofluorophotometer RF-6000. Instruction Manual. Shimadzu Corporation 86 (2015)
 - <https://www.top4download.com/fityk/download-xijutfns.html>
 - Huheey JE, Keiter EA, Keiter RL (1993) "Inorganic chemistry: Principles of structure and Reactivity". 4th edition. HarperCollins College Div; Subsequent edition.
 - NG Bakhshiev (1974) "Introduction to molecular spectroscopy", Leningrad State University, Leningrad.
 - Yariv, Yuh P (1987) "Optical waves in crystals", Mir, Moscow.
 - Caballero B, Finglas P, Toldrá F (2015) "Encyclopedia of Food and Health", Elsevier 4013. ISBN 978-0-12-384947-2
 - Mostad (1994) "X-Ray Crystallograph Study of α - Glucose at 140K". *Acta Chem. Scand* 48 276-278.

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