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Optical nonlinearity and electric conductivity origin study on sucrose crystal by using IR, Raman, INS, NMR, and EPR spectroscopies

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ABSTRACT

The supposed importance of hydrogen bonds toward the origin of second harmonic generation (SHG) and electric conductivity in crystalline sucrose was investigated by IR (4000–10 cm^{-1}), INS (2000–10 cm^{-1}, at 35 K), polarized Raman (3600–50 cm^{-1}) spectra, and ^1H NMR second moment line records in the temperature range 450–80 K. The temperature dependence of NIR (7000–5500 cm^{-1}) polarized spectra gave information about –CH_2 motions complementary to NMR results concerning –CH_2OH group rearrangements. The EPR spectra were applied to study the generation of radical ions by exposure to NIR radiation. Density functional theory quantum chemical calculations were performed to reproduce the vibrational spectra in order to complete as far as possible the assignments of bands observed by us and in the literature in sucrose crystals, and to throw more light on the possible reasons of sucrose electric conductivity and optical nonlinearity by the knowledge of theoretical values of dipole moments, polarizabilities, first order hyperpolarizabilities of sucrose molecule and clusters as well as ionization energy and electron affinity. The proton transfer in one specific hydrogen bond parallel to the helical axis *b* is proposed to be the most important in SHG and conductivity origin.

1. Introduction

Intense interest in sucrose (α-D-glucopyranosyl-β-D-fructofuranoside, saccharose, table sugar, $C_{12}H_{22}O_{11}$, Scheme 1) is observed in the current literature: complete characterization of the molecular vibrational spectra,[1,2] assignments of vibrational modes and optical activity of sucrose crystal in the terahertz region,[3–5] birefringence and anisotropy of the crystal,[6] variable temperature[7] and pressure,[8] infrared spectra, and the discovery of new, high-pressure sucrose polymorph,[9] have appeared in the last 6 years. Also many articles concerning dosimetric[10–12] and bioprotective[13] properties of sucrose have lately been published. In contrast with the above mentioned subjects the second harmonic generation (SHG) and nonlinear optical (NLO) property, of the sucrose crystal found in the eighties of XX century[14] and the first approaches to explain its origin by spectroscopic methods[15,16] have passed into silence. Meanwhile the SHG origin in many organic materials has been elucidated. The two-state model with intramolecular charge transfer (ICT) was one of the first applied to disubstituted benzenes, electron donor–acceptor (push–pull) molecules.[17] The extensive development of quantum chemistry and computational methods enabled us to take into account the weak intermolecular interactions and to calculate the NLO properties in solid state.[18–20] In *meta*-nitroaniline (*m*NA)[21,22] and 2-methyl-4-nitroaniline (MNA)[23] crystals with hydrogen bonds (HBs), the ICT, the intermolecular CT along HBs, helical crystal packing and radical anions (polarons) presence were found to be essential toward optical nonlinearity generation. In the 3-dinitrobenzene (*m*DNB) crystal the through-space CT between oxygen atoms coupled with the nitro group large amplitude motions as well as polarons presence are reasons for the origin of its NLO properties.[24–27] In the *N*-benzyl-2-methyl-4-nitroaniline (BNA) stable orthorhombic crystal the suitable L-shaped molecular arrangement that enables ICT and intermolecular CT along HBs and the prominent electrical anharmonicity resulting from CT's vibronic couplings with relevant vibrations are the reasons for the origin NLO properties.[28] Our hypothesis concerning sucrose optical nonlinearity origin is as follows: five intermolecular and two intramolecular hydrogen bonds, some of them bifurcated, existing in the crystal lead to helical

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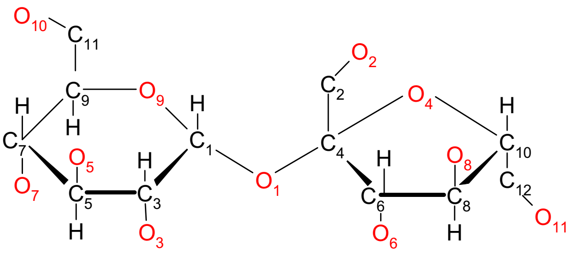

Scheme 1. Structural formula of sucrose molecule and numbering of atoms according to IUCr A09963 from Cambridge Crystal Data Centre.

arrangement of molecules along the crystallographic *b* axis and the magnetic dipole–electric dipole interactions in the helix cause natural optical activity (gyrotropy) and optical nonlinearity.[15,16]

Many years after the appearance of Refs. 15,16, taking into account the knowledge accumulated about molecular motions in sucrose,[29–31] we would like to enhance the hypothesis by the spectroscopic studies on all HB vibrational features, on the whole molecule and its part motions, as well as to check whether the NIR radiation generates radical ions in solid sucrose like in *m*NA,[21] MNA,[23] and *m*DNB.[27] The destruction of sucrose caused by X-ray, ionic, and particle irradiation is very well known[32–39] and constitutes the basis for its use as a dosimeter of this radiation.[10–12,39,40] The sucrose crystal exhibits electric conductance $\sim 10^{-7}$ S/m[41] similar to that found in *m*NA $\sim 10^{-8}$ S/m[21] and 4-isopropylphenol (4-IP) $\sim 10^{-6}$ S/m[42] crystals; in the sucrose crystal[41] as well as in *m*NA and 4-IP the conductivity is supposed to be protonic in nature, connected with a cooperative proton hopping along N–H···O (*m*NA) and O–H···O (4-IP) intermolecular HBs. In the *m*NA crystal the proton transfer (PT) is coupled with 180° jumps of the $-NH_2$ group[21] while in the 4-IP with the whole isopropyl and/or phenyl ring librations.[42] These motions in both crystals were recognized by the temperature dependencies of ^1H NMR relaxation time T_1 and of second moment of line M_2,[21,42] and in the case of the *m*NA crystal they became the basis for the model (hop and turn model) explaining its optical nonlinearity origin.[21,22] In past reports of dependence of ^1H NMR T_1 on temperature in solid sucrose two groups of proton motions with different activation energies, below and above 250 K, were found.[43] The motions of the $-CH_2OH$ groups in hydrated sucrose cause its conformational polymorphism.[31]

The mechanism of pressure that induced (4.80 GPa at 295 K) phase transition in the sucrose crystal is connected with the breakage of all HBs existing in the ambient pressure phase and the formation of new HBs, and with the polarity reversal of three O–H···O to O···H–O bonds in the high pressure polymorph.[9]

As the characteristics of vibrations and interactions in the sucrose crystal are rather scarce in the literature (in contrast with its water solution) we intend to fill up the vacant band assignments as far as possible. The purpose of this work is also to gain information about reorientations and motions in the sucrose crystal by the temperature dependency studies of ^1H NMR M_2 and of slope line width δ_H as well as of full width of half maximum (FWHM) of the chosen bands in sucrose single crystal polarized NIR spectra. The EPR spectroscopy is used to measure the paramagnetic species concentration in sucrose powder and the influence of NIR laser diode beams 980 nm and 1550 nm is checked by EPR spectral records before and after the exposure to NIR. The ab initio calculation results of polarizability (α) and first order hyperpolarizability (β) of the sucrose molecule and clusters (up to pentamer), and electron affinities (EAs), ionization energies (IEs), and dipole moments (μ) of one molecule are the basis for discussion of the conductivity and its plausible relation with the optical nonlinearity of the sucrose crystal.

1.1. Crystal structure, optical and other properties of sucrose crystal

At room temperature (RT) sucrose crystallizes in the $P2_1$ (C_2) symmetry group of the monoclinic system with two molecules ($z = 2$) in the unit cell and the binary axis *b*.[9,44] The cell parameters are: $a = 10.8633(5)$ Å, $b = 8.7050(4)$ Å, $c = 7.7585(4)$ Å, and $\beta = 102.945°$. Cleavage plane is parallel to (1 0 0) plane.[44] The crystal is biaxial negative with 2 V = 48° angle between the axes where the principal dielectric (indicatrix) axis *X* forms a 66.5° angle with the *c* axis, the *Z* axis forms 36.5° with the *a* axis, while $Y = b$ for symmetry reasons. Refractive indices at 1064 nm (532 nm) are equal $n_X = 1.5278$ (1.5404), $n_Y = 1.552$ (1.5681), and $n_Z = 1.5592$ (1.5737). SHG efficiency amounts to 0.2 times that of ammonium dihydrogen phosphate (ADP) crystal.[14] The maximal birefringence $n_Z - n_X = 0.033$ (532 nm) is small but in disagreement with the Singh et al. statement, that 'there is not birefringence in sucrose crystal'.[6] Sucrose crystal does exhibit small natural optical activity: 22°/cm rotation of the plane of polarization for the visible range along the *a* axis due to the helical alignment in the crystal.[5] Sucrose melts at about 185 °C, this temperature depends on many factors and at a low heating rate is often accompanied by decomposition (caramelization).[45] The sucrose molecule is polar. Its dipole moment in water/pyridine solution equals 2.2/2.8 D.[46] The sucrose crystal retains polarity due to the lack of an inversion center and exhibits at low temperature weak pyroelectricity.[47]

2. Experimental and Calculational methods

2.1. Preparation of samples

Sucrose pure p.a. was purchased from POCH S. A. and purified by recrystallization from water/ethanol (1:5, V/V ratio) solution (distilled water/ethyl alcohol absolute 99.8% pure, POCH S. A.). The transparent, colorless crystals were grown at RT after a few days. Large single crystals for temperature dependent NIR measurements were grown by slow evaporation of the solvent from water/methanol (1:1, V/V) solution. The fine ground powder of sucrose for the other spectroscopic measurements was obtained by grinding in an agate mortar.

2.2. MIR and NIR spectra

The FT-MIR–NIR spectrum of sucrose powder in KBr pellet (5:300 w/w) at RT was measured on a Vertex70v spectrometer, Bruker, under vacuum in the 7500–400 cm^{-1} range and the Attenuated Total Reflection (ATR) spectrum of sucrose powder fixed on the diamond crystal surface in the 4000–50 cm^{-1} range was measured also under vacuum on the same spectrometer. 128 scans with the spectral resolution 4 cm^{-1} were accumulated. The ATR spectrum was transformed into an absorbance spectrum. The FT-NIR spectra of crystalline and amorphous sucrose were measured on a Thermo Nicolet Nexus spectrometer with 4 cm^{-1} resolution and 64 scans in the 10000–4000 cm^{-1} range. The amorphous sucrose sample was placed on a KBr window. Variable temperature polarized NIR spectra in the 7300–5300 cm^{-1} range were measured on the apparatus described in Ref. 15. Crystals were cut and oriented under a polarizing microscope along the *XYZ* axes and 1.5 mm thick plate was placed into a laboratory-made cryostat operating from 370 to 80 K.

2.3. Polarized Raman spectra

The polarized FT-Raman spectra of the sucrose single crystal in backscattering geometry were recorded at RT on a FT-Raman