

IRRADIATION-INDUCED CHANGES IN VIBRATION STRUCTURE OF FILMS OF SQUARINE DYE

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Influence of high energetic electron irradiation ($E_e = 1.8$ MeV) on the vibration properties of the squaraine dye film was studied. Quantum-chemical calculations were applied for determination of vibration bands in Raman spectra of the squaraine dye molecule. Results of Raman scattering of the film showed that its irradiation with dose of 1 MGy leads to shift of vibration bands positions by 2...6 cm^{-1} , appearance of background due to knocking of the atoms from the squaraine dye molecules. But all vibration modes at this dose are still present that points on possibility of functioning of the squaraine film in solar elements at this dose.

INTRODUCTION

Squaraine dyes are organic molecular compounds, optical and nonlinear properties of which are widely used in different applications: sensors, sensitizers, molecular electronics. Sensitization of wide band-gap semiconductors with organic and inorganic dyes is currently of great interest in different conversion systems like self-powered electrochromic windows, light-emitting diodes, lasers, xerographic photoreceptors, cation detectors, long-wavelength fluorescence reporters etc. [1–4] what have potential to be used in the atomic energetics systems.

The dyes are also perspective in the solar elements as donors of the electrons due to sharp absorption bands in the visible region, chemical stability and chipness of technology of synthesis and creation of thin films by vacuum evaporation and coating from solutions on the nanostructured surfaces [5]. The acceptors of the electrons in such elements can be fullerenes C_{60} [5]. Functioning of organic solar elements in critical conditions such as high-energetic irradiation is very important and depends on stability of the constituents. It is known that fullerenes C_{60} are stable for relatively high doses of irradiation (up to 20 MGy) [6–10]. At dose of 1 MGy structural properties of the C_{60} leave the same as in the initial state [6–10]. But the behavior of organic squaraine dyes under influence of irradiation was not studied. Raman spectroscopy is very useful and informational tool due to its high sensitivity for determination of structural molecular characteristics.

The work presents investigation of vibrational properties of film of new-synthesized squaraine-dye $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_2$ under high energetic electron bombardment comparing to its initial state.

MATERIALS AND METHODS

Films of squaraine dye $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_2$ with thickness of 500 nm were prepared by vacuum evaporation of dye powder on silicon substrates. Raman spectra were recorded on Raman microspectrometer system, excitation wavelength was 535 nm. After measurements of the properties in the initial state the film was irradiated with electrons, energy of which was $E_e = 1.8$ MeV; dose of the irradiation was 1 MGy.

A theoretical study using density functional theory (DFT), (Gaussian 09) was undertaken to further understand the appearance of the spectrum. Initial geometry optimisation calculations were performed. Frequency calculations were then performed using density functional theory DFT/B3LYP with 6-31G, d, p basis set. Typically there is not strict coincidence of theoretical and experimental data for the intensities of the bands [11, 12] but the calculations are useful for correct analysis of the forms and positions of vibration bands. The chosen method gives the best agreement with the experimentally observed carbonyl band at 1740 cm^{-1} [13].

RESULTS AND DISCUSSION

“Squaraine dyes” are cyanine derivatives that have quadrupolar donor – π -acceptor – π -donor structure what is characterised by the central C_4O_2 cyclobutadione bridge comprising an electron-deficient Hückel ring. The main chromophore consists of an extended chain of methine groups (the polymethine chain) capped by two terminal groups with their own branched conjugated systems. The charge is considered to be largely delocalised over the molecule. Optimized molecular structure of synthesised squaraine dye $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_2$ that is donor of electrons is presented on Fig. 1.

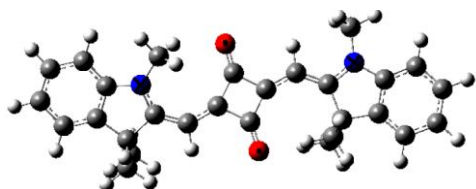


Fig. 1. Structure of squaraine dye molecule $C_{28}H_{28}N_2O_2$. Gray atoms denote Carbon, little gray ones – Hydrogens, marked with crosses – Nitrogen, dotted ones correspond to Oxygen

It is a polymethine dye based on square acid with Oxygen substituents (denoted with dots) and indolinine groups with Nitrogen atoms depicted by crosses.

Due to charge alternation in the polymethine chains of two neighbor dyes they can form aggregates in the solutions and in the condensed state. Interaction of molecules is not significantly manifested in the Raman spectra [13, 14]. Results of Raman scattering for the film of squaraine dye $C_{28}H_{28}N_2O_2$ in the initial state are presented on Fig. 2, curve 1. In the region from 100 to 1800 cm^{-1} the rich spectrum of intensive bands is observed. But the region of the spectrum from 1650 to 2000 cm^{-1} is almost totally free of bands. Group vibrations with energies that correspond to this region are mainly those of carbonyl groups. The selection rules in infrared spectroscopy generally give strong absorbance bands for carbonyl groups due to the large change in permanent dipole during the vibration. Conversely, in Raman spectroscopy the carbonyl band is weak due to a small polarizability change during the vibration [14].

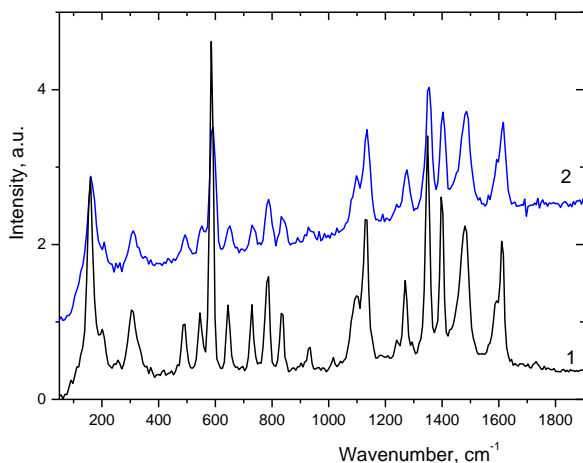


Fig. 2. Raman spectra of film of squaraine dye $C_{28}H_{28}N_2O_2$ in the initial state (1) and after irradiation with dose 1 MGy , $E_e = 1.8\text{ MeV}$ (2) ($\lambda_{exc} = 535\text{ nm}$, thickness is 500 nm , Si substrate)

Quantum-chemical calculations of single squaraine dye molecule $C_{28}H_{28}N_2O_2$ in vacuum were applied for determination of vibration bands in Raman spectra. The results of calculations are presented on the Fig. 3. Due to asymmetry of the molecule and its planar bending almost all 176 modes appear in the spectrum with high and low intensities. In the range up to 440 cm^{-1} different types of vibrations of methine $-CH_3$ groups are observed. At $500\text{--}600\text{ cm}^{-1}$ vibrations of modified

indolenine groups $-C_{11}H_{13}N$ can be seen. Fig. 4 shows some forms of molecular vibrations of dye $C_{28}H_{28}N_2O_2$.

The range at $1100\text{--}1450\text{ cm}^{-1}$ is characterised by symmetrical and assymetrical vibrations of benzene (phenol) ring (for example 1170 , 1340 cm^{-1}). “Breathing” mode of benzene ring in which shortening of pentagone happens is at 1670 cm^{-1} . Shift of carbon atoms of chromophore of the polymethine chain is at 1646 cm^{-1} .

Vibration of the squaraine functional group with Oxygen atoms is forbidden due to symmetry rules therefore it is not active in the experimental spectrum. The C_2O_2 group is highly delocalised. When this group vibrates both symmetrically and asymmetrically a band is not observed in the spectra. This effect is characteristic of squaraines and is often used to confirm that the dye has been synthesised successfully, as squaric acid has strong carbonyl lines in the infrared spectrum. In the Raman spectrum the totally asymmetric C_4O_2 mode is not observed. This form of vibration at 1825 cm^{-1} is shown on Fig. 4. In this computational study, the Raman intensity calculated for the vibration is relatively small comparing to the other “dye backbone” lines.

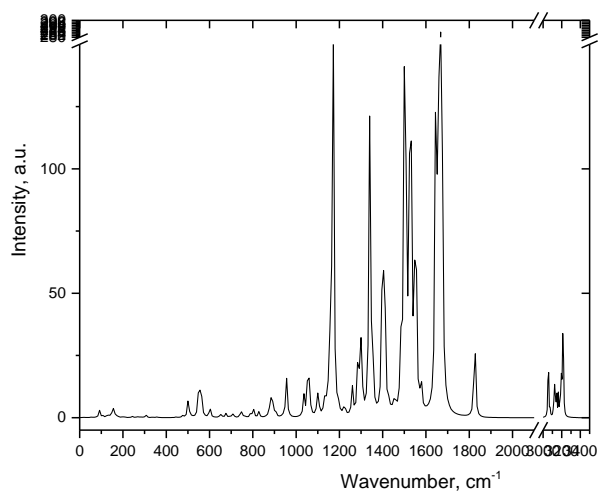


Fig. 3. Calculated Raman spectrum of molecule of squaraine dye $C_{28}H_{28}N_2O_2$

Vibrations are very sensitive to the irradiation that causes formation of different types of radicals: mono-, bi-radicals due to knocking of the electrons. Due to the π -conjugation of the squaraine dye absence or presence of one additional electron on the molecule, general characteristics of the polymethine molecules do not alter totally [15]. Knocking of the atoms from the molecular cages of squaraine dyes $C_{28}H_{28}N_2O_2$ destructs their chromophore, terminal and square groups. Therefore donor and acceptor functions of the damaged molecules will be worsening with the dose increase. Atomic knocking leads to fall of intensities of vibrational modes in the spectrum of the film, as it can be seen from Fig. 2, curve 2. Destruction of squaraine molecules is accompanied by appearance of the background, especially in the high-frequency region of $1000\text{--}1700\text{ cm}^{-1}$.

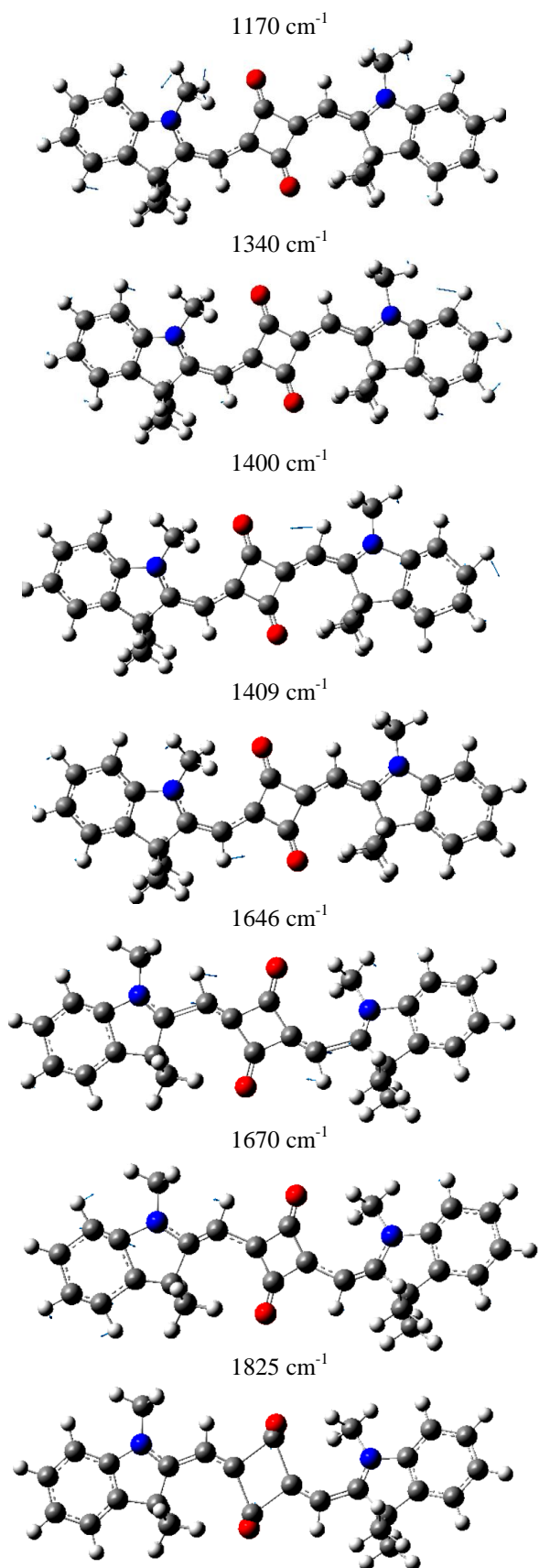


Fig. 4. Forms of some molecular vibrations of dye $C_{28}H_{28}N_2O_2$. Arrows show directions of atomic displacements

Low-intensity band at 1020 cm^{-1} totally disappears in the background. Irradiation with dose of 1 MGy leads to shift of vibration bands positions by $2\text{...}6\text{ cm}^{-1}$; mode

at 165 shifts to 171 cm^{-1} , 546 to 551 cm^{-1} , 592 to 592 cm^{-1} , 1480 to 1484 cm^{-1} , 1610 to 1612 cm^{-1} . But all vibration modes at this dose are still present that points on possibility of functioning of the squaraine film in solar elements at this dose. Further irradiation will cause full destruction of the molecules and their donor centers.

CONCLUSION

Vibration modes of the squaraine dye $C_{28}H_{28}N_2O_2$ film are sensitive to the high-energetic electron irradiation that causes knocking of the atoms from the molecular cages. Destruction of squaraine molecules is accompanied by fall of intensities of vibrational modes of the film, appearance of the background, especially in the high-frequency region of $1000\text{...}1700\text{ cm}^{-1}$ and shift of vibration bands positions by $2\text{...}6\text{ cm}^{-1}$. But all vibration modes at dose of 1 MGy are still present that points on possibility of functioning of the squaraine film in solar elements at this dose.

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РАДИАЦИОННО-ИНДУЦИРОВАННЫЕ ИЗМЕНЕНИЯ КОЛЕБАТЕЛЬНОЙ СТРУКТУРЫ ПЛЕНОК СКВАРАИНОВЫХ КРАСИТЕЛЕЙ

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Рассмотрено влияние высокоэнергетического электронного облучения ($E_e = 1,8$ МэВ) на колебательные свойства пленки из сквараинового красителя. С помощью квантово-химических расчетов определены колебательные полосы в спектре комбинационного рассеяния света молекулы сквараинового красителя. Результаты комбинационного рассеяния света пленки показали, что облучение с дозой 1 МГр приводит к смещению положений колебательных мод на $2...6$ см⁻¹, появлению радиационного фона вследствие выбивания атомов с каркаса молекул сквараиновых красителей. Но при данной дозе все колебания сохраняются, что указывает на возможность функционирования сквараиновых пленок в солнечных элементах.

РАДІАЦІЙНО-ІНДУКОВАНІ ЗМІНИ КОЛИВНОЇ СТРУКТУРИ ПЛІВОК СКВАРАЇНОВИХ БАРВНИКІВ

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Розглянуто вплив високоенергетичного електронного опромінення ($E_e = 1,8$ МеВ) на коливні властивості плівки зі сквараїнового барвника. За допомогою квантово-хімічних розрахунків встановлено коливні смуги у спектрі комбінаційного розсіяння світла молекули сквараїнового барвника. Результати комбінаційного розсіяння світла плівки показують, що її опромінення з дозою 1 МГр приводить до зсуву положень коливних мод на $2...6$ см⁻¹, появи радіаційного фону внаслідок вибивання атомів з каркасу молекул сквараїнових барвників. Проте, при цій дозі всі коливні моди зберігаються, що вказує на можливість функціонування сквараїнових плівок у сонячних елементах.