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Third Order Nonlinear Optical Properties of Hybrid Mono Crystals with π -Conjugated Systems

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ABSTRACT

In this work present an experimental study of third-order optical properties using the degenerate four wave mixing (DFWM) method, we have measured and calculate the third-order susceptibility $\chi^{(3)}$ at 532 nm of organic-inorganic hybrid compounds [a) Tryptophan nitrate ($C_{11}H_{13}N_3O_5$), b) Adeninium dinitrate ($C_5H_6N_7O_6$), c) Pyridinium nitrate ($C_5H_6N_2O_3$), d) D-Phenylglycinium nitrate ($C_8H_{10}N_2O_5$), e) m-Carboxyphenyl ammonium dihydrogenomonophosphate ($C_7H_{10}O_6NP$), f) Cytosinium nitrate ($C_4H_6O_4N_4$) and g) m-Carboxyphenyl ammonium dihydrogenomonophosphate ($C_7H_{10}O_5NP$)] witch have been prepared and characterized by spectroscopic analysis and crystallographic method. We have showed that there is a good agreement between the used theoretical model and the experimental results. We found that the studied compounds exhibit large second order hyperpolarisability (γ) values larger than CS_2 which is a reference material for DFWM.

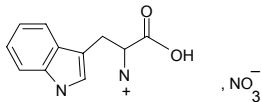
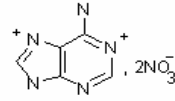
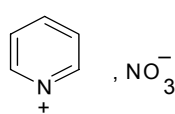
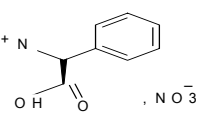
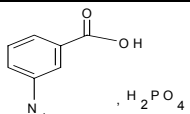
Keywords: nonlinear optics, hybrid material, DFWM.

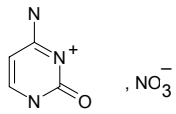
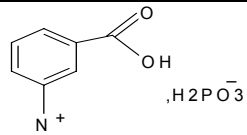
1. INTRODUCTION

The number of hybrid materials has been rapidly growing to their applications in medicine and material science. Organic-inorganic hybrid compounds are of intensive interest in the field of new materials chemistry. As these materials exhibit synergetic properties such as electrical, magnetic and optical properties [1]. Due to their efficiency, chemical flexibility and high conjugated framework, organic-inorganic compounds have received considerable attention as a possible material for non-linear optics. [2].

In this report, we analyse a systematic study of the third order nonlinear optical properties of 7 hybrid compounds: D-Phenylglycinium nitrate [3], Cytosinium nitrate[4], m-Carboxyphenyl ammonium dihydrogenomonophosphate, m-Carboxyphenyl ammonium dihydrogenomonophosphate[5], Pyridinium nitrate [6], Adeninium dinitrate[7] and Tryptophan nitrate as part of a series of investigations of interactions between amino acids and various nitric acids or phosphoric acid. The chemical structure and crystal data of the studied compounds are presented in table 1.

Table 1. Crystal data and chemical structure.

a-Tryptophan Nitrate	$C_{11}H_{13}N_3O_5$, Mr = 267.23 This compound wasn't studied by the X-ray diffraction	
b- Adeninium Dinitrate	$C_5H_6N_7O_6$, a = 4.995(4)Å Mr = 260.14, b = 9.948(3)Å Orthorhombic, P 2 ₁ 2 ₁ 2 ₁ , c = 19.793(3)Å V = 983.5(2)Å ³ , Z = 4	
c- Pyridinium Nitrate	$C_5H_6N_2O_3$, a = 3.9085(10)Å Mr = 142.11, b = 12.353(4)Å Monoclinic, P2 ₁ /c, c = 13.532(4)Å β = 90.500(19)°, V = 653.3(3)Å ³ , Z = 4.	
d- Phenylglycinium Nitrate	$C_8H_{10}N_2O_5$, a = 10.4320(3) Å Mr = 214.18, b = 5.6450(2) Å Monoclinic, P2 ₁ , c = 16.7830(2)Å β = 94.943(3), V = 984.65(5)Å ³ , Z = 4.	
e-m-Carboxyphenyl ammonium dihydrogenomonophosphate	$C_7H_{10}O_6NP$, a = 6.578 (5)Å Mr= 235.13, b = 11.780(9)Å Monoclinic P2 ₁ /c, c = 12.928(3)Å β = 102.673 (3)°, V = 977.5 (4)Å ³ , Z = 4	

f- Cytosinium Nitrate	$C_4H_6O_4N_4$, $Mr = 174.13$, Triclinic, P-1, $\alpha = 71.96 (2)^\circ$, $\gamma = 73.75 (3)^\circ$, $a = 6.5300 (2) \text{ \AA}$, $b = 6.7240 (2) \text{ \AA}$, $c = 9.2110 (3) \text{ \AA}$, $\beta = 72.84 (3)^\circ$, $V = 359.44 (7) \text{ \AA}^3$, $Z = 2$.	
g- m-Carboxyphenyl ammonium dihydrogenomonophosphite	$C_7H_{10}O_5NP$, $Mr = 219.14$, Monoclinic P2 ₁ /c, $\beta = 104.746 (3)^\circ$, $a = 12.982 (2) \text{ \AA}$, $b = 11.507 (1) \text{ \AA}$, $c = 6.623 (4) \text{ \AA}$, $V = 956.7(3) \text{ \AA}^3$, $Z = 4$.	

They were prepared by slow evaporation at room temperature of a diluted aqueous solutions containing m-amino benzoic with phosphoric or phosphorus acids and D-phenylglycine, Cytosine, Pyridine, Adenine, Tryptophan with nitric acid.

The configuration of tryptophan nitrate unit was established from NMR and IR spectra, and from X-ray others structures. X-ray studies reveal a good planarity conformation of a organic matrices, see Figure1.

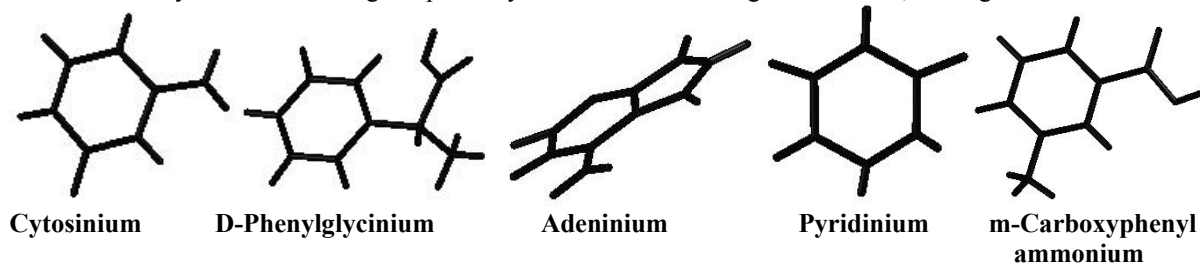


Figure 1. The planity conformation of the studies organic matrices.

The samples were prepared in the form of solutions from organic molecules dissolved in water with a little heating. The measurements of the third-order susceptibility $\chi^{(3)}$ of these compounds it has been than for solutions with concentration order ($\sim 10^{-2}$ mol/l). The optical spectra of the molecules are presented in table 2, were performed with a cell thickness of about 1 cm and very weak concentration ($\sim 10^{-5}$ mol/l). The spectra showed that all this compounds absorb in a weak zone inter 200 nm and 230 nm, with a maximum absorption (λ_{max}) at 220 nm for molecule a, 210 nm for b, 206 nm for c, 225 nm for d, 222 nm for e, 230 nm for f and 225 nm for g. Observe that all this compounds exhibit no measurable absorption at 532 nm.

Due to the observation that has been made, we would like to notice that the difference between each UV spectra and transmission spectra is due to the high concentration and the color of the studied compounds (a, e and g).

2. THEORETICAL APPROACH

This process measure the susceptibility of order 3, $\chi^{(3)}$ for a non linear medium [8].

Let us consider three coherent electromagnetic waves $E^{<1>}$, $E^{<2>}$, $E^{<3>}$: $E^{<1>}$ and $E^{<2>}$ are pump waves, that propagate in opposite directions along **oz** axis, and the wave $E^{<3>}$, the probe one, makes a small angle θ with the **z** axis. The three waves have the same frequency ω and they coincide temporally and spatially in the medium. The interaction of these three waves with the nonlinear materials creates a polarization of the third order, this polarization being the source of the fourth wave. We should notice here that the conditions of phase matching are satisfied by geometry of the experience see Fig. 2: $\vec{k}_4 = -\vec{k}_3$, $\vec{k}_1 = -\vec{k}_2$, $\omega_4 = \omega - \omega + \omega$. The DFWM efficiency (R) was calculated from Maxwell propagation equations of the coupled four beams by taking into account the linear and nonlinear absorption coefficients. The interacting waves are taken as plane waves:

$$\tilde{E}_i(\vec{r}, t) = \vec{E}_i(\vec{r}) e^{-i\omega t} + cc = \vec{A}_i(\vec{r}) e^{i(\vec{k}_i \vec{r} - \omega t)} + cc, \quad \text{for } i = 1, 2, 3 \quad (1)$$

The propagation equations of the interaction are deduced from the Maxwell equations using the slowly varying amplitude approximation and take into account linear and non linear absorption. In CGS units the propagation equations of four interacting waves are given by the system:

$$\begin{cases} \frac{\partial A_i^{<1>}}{\partial z} = -\frac{\alpha}{2} A_i^{<1>} + iH\chi_{ijkl}^{<3>} (A_k^{<1>} A_l^{<1>*} + 2A_k^{<2>} A_l^{<2>*}) A_j^{<1>} \\ \frac{\partial A_i^{<2>}}{\partial z} = \frac{\alpha}{2} A_i^{<2>} - iH\chi_{ijkl}^{<3>} (2A_k^{<1>} A_l^{<1>*} + A_k^{<2>} A_l^{<2>*}) A_j^{<2>} \\ \frac{\partial A_i^{<3>}}{\partial z} = -\frac{\alpha}{2} A_i^{<3>} + 2iH\chi_{ijkl}^{<3>} (A_j^{<1>} A_k^{<2>} A_l^{<4>*} + A_j^{<3>} A_k^{<1>} A_l^{<1>*} + A_j^{<3>} A_k^{<2>} A_l^{<2>*}) \\ \frac{\partial A_i^{<4>}}{\partial z} = \frac{\alpha}{2} A_i^{<4>} - 2iH\chi_{ijkl}^{<3>} (A_j^{<1>} A_k^{<2>} A_l^{<3>*} + A_j^{<4>} A_k^{<1>} A_l^{<1>*} + A_j^{<4>} A_k^{<2>} A_l^{<2>*}) \end{cases} \quad (2)$$

Where $H = \frac{12\pi^2}{n\lambda}$, n is the linear refractive index of the material, α is the linear absorption coefficient and $i, j, k, l = x, y, z$.

Let the propagation direction of the waves be on the z -direction and the polarisation state of the three incident beams be x , so $A_z^{<i>} = 0$ and $A_y^{<i>} = 0$. We now denote $A_x^{<i>} = A_i$ and $\chi_{xxxx}^{<3>} = \chi^{<3>}$. From system (2) we deduce:

$$\begin{cases} \frac{\partial A_1}{\partial z} = -\frac{\alpha}{2} A_1 + iH\chi^{<3>} (A_1 A_1^* + 2A_2 A_2^*) A_1 \\ \frac{\partial A_2}{\partial z} = \frac{\alpha}{2} A_2 - iH\chi^{<3>} (2A_1 A_1^* + A_2 A_2^*) A_2 \\ \frac{\partial A_3}{\partial z} = -\Phi A_3 + 2iH\chi^{<3>} A_1 A_2 A_4^* \\ \frac{\partial A_4}{\partial z} = \Phi A_4 - 2iH\chi^{<3>} A_1 A_2 A_3^* \end{cases} \quad (3)$$

Where $\chi^{<3>} = \chi' + i\chi''$ and $\Phi = \frac{\alpha}{2} - 2iH\chi^{<3>} (A_1 A_1^* + A_2 A_2^*)$.

In CGS units the intensity of a laser beam is $I_i = \frac{nc}{2\pi} A_i A_i^*$, $i = 1, 2, 3, 4$; where c is the velocity of light propagation

The imaginary part of $\chi^{<3>}$ is related to the nonlinear absorption coefficient:

$$\beta = 24 \frac{\omega\pi^2}{n^2 c^2} \chi'' \quad (4)$$

To solve the system (3) and to calculate the DFWM reflectivity $R = I_4(0)/I_1(0)$, we perform a change of variable:

$$A_3 = u \exp(-\Phi z), A_4 = v \exp(\Phi z) \quad (5)$$

Using Φ and $A_1 A_2$ are constant, which means that $I_1 + I_2$ and $I_1 I_2$ are considered as constants, the equations (3,3) and (3,4) lead to a second order differential equation:

$$u'' + \psi u' + K^2 u = 0 \quad (6)$$

where $\psi = -(\phi + \phi^*) = -\alpha - 2\beta(I_1(z) + I_2(z))$ and $K^2 = \left(\frac{4\pi H}{nc}\right)^2 (\chi'^2 + \chi''^2) I_1(z) I_2(z)$.

The equation (6) can be solved analytically. We obtain the DFWM reflectivity as follows :

$$R = \frac{I_4(0)}{I_1(0)} = \begin{cases} \frac{K^2}{[p(\cot(p\ell) - \psi - 2)]^2} & \psi^2 - 4K^2 \leq 0 \\ \frac{K^2}{[q(\coth(q\ell) - \psi - 2)]^2} & \psi^2 - 4K^2 > 0 \end{cases} \quad (7)$$

where $p^2 = K^2 - (\Psi/2)^2$ and $q = ip$.

In the absence of the linear and nonlinear absorption, that means α and β approach zero the system, (3) leads to the classical formula (1,2):

$$R = \text{tg}^2 |\zeta| \ell, \text{ where } p = \frac{48\pi^3}{n^2 c \lambda} \chi^{<3>} I_1(0)$$

we should notice here that when intensities are known experimentally α and β can be determined from the nonlinear transmission and UV spectra (Table. 2). Therefore the only parameter that remains to be determined is $\chi^{<3>}$ [9, 10].

In order to characterise the individual molecule we determine the second order hyperpolarisability using the following relation (8):

$$\chi^{<3>} = F^4 N \gamma_{\text{solution}} + \chi^{<3>}_{\text{solvent}} \quad (8)$$

where $F = (n^2 + 2)/3$ is the Lorentz field factor correction, $N = N_A$. C/M is number of solution molecules per, the unity of volume; N_A is Avogadro number. In our case $\chi^{<3>}_{\text{solvent}}$ is small, so it can be neglected.

Table 2. UV spectra of studied compounds.

Compounds	UV Spectre
a- Tryptophan Nitrate	$\lambda_{\max} = 220 \text{ nm}$
b- Adeninium Dinitrate	$\lambda_{\max} = 210 \text{ nm}$
c- Pyridinium Nitrate	$\lambda_{\max} = 206 \text{ nm}$
d- Phenylglycinium Nitrate	$\lambda_{\max} = 225 \text{ nm}$
e- m-Carboxyphenyl ammonium dihydrogenomonophosphate	$\lambda_{\max} = 222 \text{ nm}$
f- Cytosinium Nitrate	$\lambda_{\max} = 230 \text{ nm}$
g- m-Carboxyphenyl ammonium dihydrogenomonophosphite	$\lambda_{\max} = 225 \text{ nm}$

3. NONLINEAR TRANSMISSION

In the presence of linear and nonlinear absorption the variation of the intensity of the pump waves along the z axis is given by [7]:

$$\frac{dI}{dz} = -(\alpha + \beta I)I \quad (9)$$

where α is the linear absorption coefficient and β two photons absorption coefficient

$$I(\ell) = \frac{I(0) \cdot \alpha \exp(-\alpha \ell)}{\alpha + \beta I(0) (1 - \exp(-\alpha \ell))} \quad (10)$$

From intensity $I(1)$ and $I(0)$, one can easily deduced the expression of the transmission:

$$T = \frac{I(\ell)}{I(0)} = \frac{\alpha \exp(-\alpha \ell)}{\alpha + \beta I(0) (1 - \exp(-\alpha \ell))} \quad (11)$$

The best fit of the equation (11) to experimental data allows us to deduce α and β coefficients.

In the absence of the nonlinear absorption β , the variation of the intensity of the pump waves along the z axis is given by:

$$\frac{dI}{dz} = -\alpha I \quad (12)$$

where α is the linear absorption coefficient of the medium.

In the system of Gauss unity we have $I = (n_0 c / 2\pi) |E|^2$

the transmission relation is given by:

$$T = \frac{I(L)}{I(0)} = e^{-\alpha L} \quad (13)$$

4. RESULTS AND DISCUSSION

We have measured transmission T as a function of the incident beam intensity as shown in Fig. 2. Only one beam is sent to the studied medium.

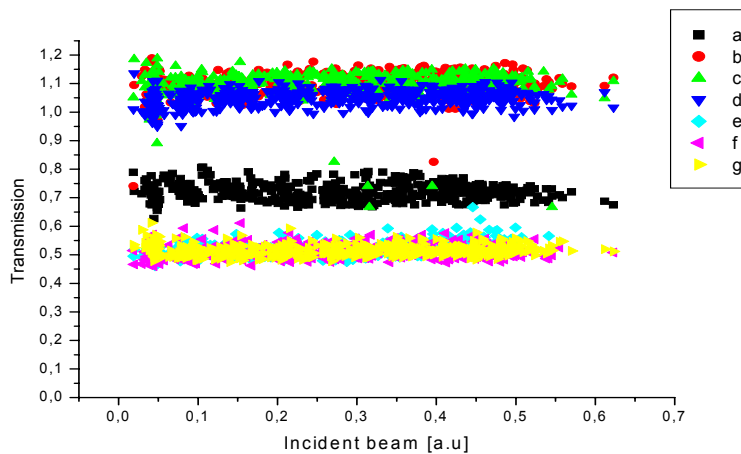


Figure 2. Transmission T versus intensity of the incident beam for studied molecules.

The observation is that linear dependence of transmission versus the incident pump beam. From these measurements, we deduce the values of absorption coefficients according to theoretical formula concerning the variation of the intensity of the pump exciting beam in the studied medium described in (10–11). Also obtained is a good agreement between the proposed theoretical model described by Eq. 3 and the experimental data of efficiency of degenerate four wave mixing. The best fit of the theoretical curve to experimental data (see Fig. 3) allows us to estimate values of susceptibilities $\chi^{<3>}$ for studied compounds. The obtained results are collected in, table 3: α and β are the linear and nonlinear coefficients of absorbance respectively, γ is the second nonlinear hyperpolarisability tensor and $\chi^{<3>}$ is the third nonlinear susceptibilities. The values $\chi^{<3>}$ obtained are of the same order as $\chi^{<3>}$ of CS₂ which is a material of reference for degenerate four wave mixing technique.

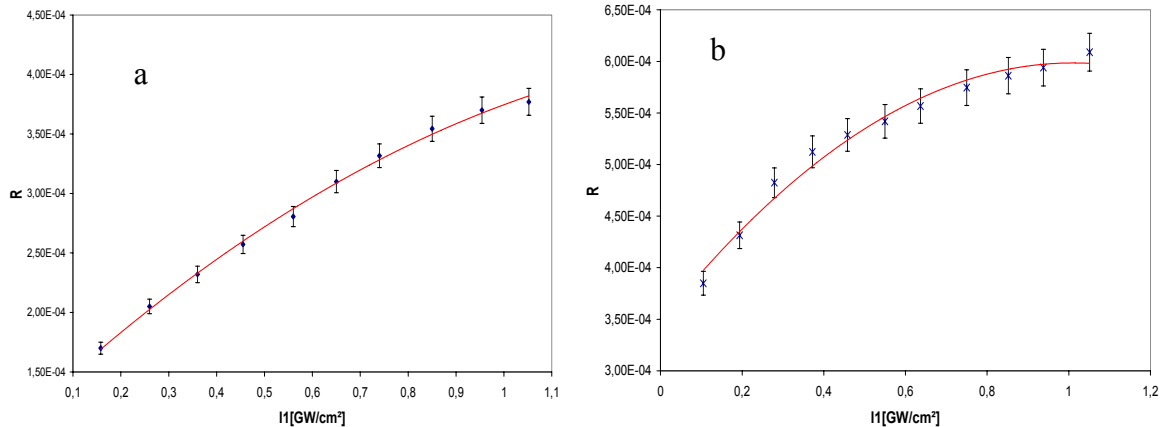


Fig.3. DFWM efficiency versus pump beam I_1 for the compound (a) and (b).

Table 3. Values of calculated and measured γ and $\chi^{<3>}$.

Molecule	M [g]	C [g/l]	α [cm ⁻¹]	$\chi_{exp.}^{<xxx>}$ [V ² m ⁻²]	$\gamma_{exp.}$ [m ⁵ V ⁻²] 10^{-45}	$\chi_{exp.}^{<xxx>} / \alpha$
a-C ₁₁ H ₁₃ N ₃ O ₅	267.23	5	11,1	8.01 10⁻²¹	0.28	7.21 10 ⁻²²
b-C ₅ H ₆ N ₇ O ₆	260.14	5	~ 0.1	4.93 10⁻²²	0.017	4.93 10 ⁻²⁰
c-C ₅ H ₆ N ₂ O ₃	142.11	5	~ 0.1	2.88 10⁻²¹	0.054	2.88 10 ⁻²⁰
d-C ₈ H ₁₀ N ₂ O ₅	214.18	5	~ 0.1	7.3 10⁻²²	0.021	7.3 10 ⁻²⁰
e-C ₇ H ₁₀ O ₆ NP	235.13	5	24,5	5.84 10⁻²⁰	1.81	2.38 10 ⁻²¹
f-C ₄ H ₆ O ₄ N ₄	174.13	5	~ 0.1	7. 21 10⁻²²	0.025	7.21 10 ⁻²¹
g-C ₇ H ₁₀ O ₅ NP	219.14	5	51,7	8. 21 10⁻¹⁹	23.77	1.58 10 ⁻²⁰
CS ₂	76.1	-	~ 0	1,94 10⁻²⁰	4,71 10⁻⁴³	1.94 10 ⁻²⁰

5. CONCLUSIONS

In conclusion the work we have presented as an experimental study of a third-order optical properties of 7 organic-inorganic hybrid compounds comparing with a reference material CS₂, by using the Degenerate Four Wave Mixing method. Measured and calculated is the third -order susceptibility $\chi^{<3>}$ for these compounds. The values $\chi^{<3>}$ obtained have the same order as $\chi^{<3>}$ of CS₂ which is a material of reference for degenerate four wave mixing technique. We can Concluded that the studied compounds have a large nonlinearities.

Due to the observation that has been made, we would notice that the difference between each UV spectra and transmission spectra is due to the high concentration and to the color of the studied compounds (a, e and g).

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