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The structure, vibrational spectra and nonlinear optical properties of neutral melamine and singly, doubly and triply protonated melaminium cations—theoretical studies

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Abstract

The melaminium cation can occur in three form: singly, doubly or triply protonated. The geometry and nonlinear optical properties (NLO) for all forms were computed by ab initio method. The restricted open Hartree–Fock (ROHF) computational method with 6-311 + G basis set was used. Comprehensive studies of electronic and molecular structures have been performed.

The theoretical vibrational frequencies and potential energy distribution (PED) of melaminium cations were calculated by B3LYP method. The calculated frequencies were compared with measured one for newly obtained compounds where melaminium cations are common component. The assignment of the bands has been made on the basis of the calculated PED.

The restricted Hartree–Fock (RHF) methods were used for calculation of the hyperpolarizability for each ion. For comparison, analogous calculations were carried out for the closed-shell neutral melamine. The theoretical results can be used in design of new molecular compounds with nonlinear optical properties.

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1. Introduction

Organic molecules with delocalized electron systems are of particular interest because of their potentially large nonlinear optical response. Traditionally, the large value of the second-order NLO coefficient β of an organic molecule has been associated with the intramolecular charge transfer (CT), resulting from the electron donor and acceptor groups communicating through a π-conjugated molecular framework [1–3]. This charge transfer from the donor to the acceptor group in the ground state of the molecule manifests itself in a redistribution of the electron cloud, which, on interaction with an external optical field, yields large change in a molecular dipole moment and leads to enhanced second-order nonlinear optical response.

Molecules with symmetry close to threefold rotational (octupolar molecules) can exhibit non-zero β, despite being non-polar [4]. A number of molecules as well as molecular ions of D_{3h} (or C_3 or D_3) symmetry have been shown to display promising properties. In addition to molecules with a two-dimensional (2D) character of β, a few 3D octupolar molecules have been investigated, also.

Contemporary trends in investigation of new compounds with NLO properties focus attention on designing of new crystals with two parts: organic cations and inorganic ions. The crystals display interesting physical and chemical properties, exhibiting transitions with ferroelectric, antiferroelectric and ferroelastic behavior as well as phases with commensurate and incommensurate superstructures [5,6]. The most important role in construction of new crystals seems to be reserved for weak intermolecular interactions such as hydrogen bonds [7,8]. Usually, these complexes are very stable and have good NLO properties [9]. Good chemical and physical stability is connected with existence

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of inorganic part in investigated compounds, whereas the organic part is responsible for nonlinear optical properties.

The melamine molecule could be used as organic part of investigated crystals. This molecule and its polymers found application in a wide variety of technological fields. In newly designed crystals, the melamine could occur in three forms: singly, doubly and triply protonated cations.

In this paper, we report the results of theoretical calculations for all melamine forms and for neutral molecule, also. These studies are focused on theoretical approximation of geometry and on infrared spectra as very important in designing of new complexes. The full PED analysis and assignment for all characteristic bands of each forms was performed. Comparison with experimental spectra of adequate crystal was made. Furthermore, the time dependent Hartree–Fock calculations of NLO properties and dipole moments of the molecules under investigation are performed and discussed.

2. Experimental

The optimized equilibrium structure for melamine has been calculated by the DFT/B3LYP RHF method. The structures of three melaminium cations were calculated by the ROHF method. The $6-311++G(d,p)$ basis set have been employed.

The harmonic frequencies and infrared intensities were calculated by the density functional triply parameter hybrid model (DFT/B3LYP). The $6-311++G(d,p)$ basis set was used.

The normal coordinate analyses have been carried out for melamine and its cations according to the procedure described and recommended by Fogarasi and Pulay [10]. The frequencies of NH stretching and bending vibrations involved in hydrogen bond network were scaled by 0.92. This scaling factor is smaller than that recently reported for the A–H stretching force constants [11]. The other harmonic frequencies were scaled by the factor of 0.983 determined in previous studies of similar organic systems [12]. The calculated potential energy distribution for melaminium cations has enabled us to make detailed band assignment in infrared spectra of these basic 'bricks' of investigated structure.

The nonlinear optical response of an isolated molecule in an electric field $E_i(\omega)$ can be presented as a Taylor series expansion of the total dipole moment, μ_t, induced by the field

$$\mu_t = \mu_0 + \alpha_{ij}E_i + \beta_{ijk}E_iE_j + \cdots$$

where α is a linear polarizability, μ_0 is permanent dipole moment, and β_{ijk} are the first hyperpolarizability tensor components. The NLO response of the material in molecular state can be determined by computation and by measuring it experimentally. The values obtained by different methods may be different, therefore it is necessary to give an exact definition [13]. In this paper, we will consider only the frequency doubling process, i.e. $\beta = \beta(-2\omega, \omega, \omega)$, and define in a molecule fixed coordinates

$$\beta_i = \beta_{iii}\frac{1}{3}\sum_{ki\_k}(\beta_{ikk} + \beta_{kik} + \beta_{kki})$$

where $I = x, y$ or z

$$\beta_V = \sqrt{(\beta_x^2 + \beta_y^2 + \beta_z^2)}$$

For calculation of the first hyperpolarizability by quantum chemical methods at RHF ab initio level of theory with $6-311++G(d,p)$ basis set was chosen.

All calculation was performed with the GAMESS [14] program, version from 12 December 2003 (R2) compiled under Linux operating system. This job was executed on PC Cluster consists of one server node with two 32-bit Intel Xeon processors running at 1.8 GHz and 3 GB RAM, 20 computing nodes with dual 32-bit Intel Xeon processors running at 2.8 GHz and 2 GB RAM, nine computing nodes with dual 32-bit Intel Xeon processors running at 1.7 GHz and 1 GB RAM.

3. Results

The numbering of atoms, optimized geometrical parameters of melamine and their cations are collected in Fig. 1. The theoretical and experimental studies indicate that melamine molecule in ground state is planar and very close to D_{3h} symmetry. These results are in good agreement with previous data published by Paz Fernandez-Liencres et al. [15]. In this paper, the detailed theoretical study was performed, but the geometrical parameters were not published. The molecular structure of melamine has already been studied theoretically by semi-empirical and Hartree–Fock methods some years ago [16,17]. Recently, a new and more accurate study has been carried out by Wang et al. [18] at ab initio (MP2) and several density functional theory (DFT) schemes, with different basis sets. The geometric parameters at either MP2 or DFT are close to the X-ray experimental data, showing that the most stable form of melamine has non-planar geometry of C_s symmetry where the triazine ring is planar and the amino groups have pyramidal structure. However, due to the calculated conformers (C_s and C_{3v}) and the D_{3h} transition state, the authors conclude that the melamine is a floppy molecule with an effective (average) structure of D_{3h} symmetry.

According to our calculation performed with better basis set the melamine molecule is flat. All C–N bonds in the ring are practically equal to 1.3257 Å. All amino groups are coplanar with the ring. The length of C–N bonds between amino groups and triazine ring is equal to 1.3417 Å. All N–H bonds in amino groups are equal to 0.9906 Å. Very interesting seems to be studies of the angles relationship in