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# Capability of X-ray diffraction to the determination of the macroscopic linear susceptibility in a crystalline environment: the case of 3-Methyl 4-Nitropyridine N-oxide (POM)

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## Abstract

In a recent work we have reported an investigation of the applicability of ground state electron density inferred from X-ray diffraction to the determination of the linear polarizability of an 'in situ' conjugated molecule labelled POM and corresponding to a nonlinear optical organic compound (F. Hamzaoui, A. Zanoun, G. Vergoten, *J. Mol. Struct.* 397 (1–3) (2004) 17–22). In this work and using the Unsöld approximation one can connect the susceptibility tensor of rank  $n$  to the multipolar charge distribution (in the fundamental state) of order  $2^n$ . Thus, the linear polarizability is associated to the quadrupole moment, whereas the first order hyperpolarizability is linked to the octupolar moment of the charge distribution. Using an approach similar to the one used for the determination of the linear polarizability, we present here the estimated values of the tensor  $\beta$  derived from the X-ray experiment. However more surprising is the good agreement between the calculation of the lowest order macroscopic optical nonlinearity as a tensor sum of molecular polarizabilities of the free molecule and the macroscopic non linear measurements, the generalization of this remark means that the crystalline effects are negligible in the estimation of nonlinear optical properties.

However, it seems difficult to infer from the Unsöld approximation a faithful description of the molecular optical properties, whereas an estimation of the first order hyperpolarizability components of  $\beta$  seems out of reach.

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**Keywords:** Electron charge density; Linear polarizability; Macroscopic linear susceptibility; Nonlinear optical compound (NLO)

## 1. Introduction

Considerable progress has been made in recent years towards understanding the nature of physical properties in terms of the underlying structures. In a previous lead article by Abrahams, the main relations between properties of molecules embedded in the crystalline structures and corresponding physical properties have been extensively discussed [2]. For example the second harmonic generation (SHG) tensor coefficients of POM (Fig. 1) are two order of magnitude larger than in KDP, a 'state of the art' inorganic nonlinear crystal [3,4]. The linear macroscopic susceptibility of the crystal can be inferred from the molecular

polarizability, based on oriented gas description model [5] and on the X-ray determination of the molecular structure and crystalline packing.

We have already reported the results on the linear polarizability obtained from X-ray diffraction study [1]. This connection is based on the application of a model due to Robinson [6,7] which allows to average the summation over excited states in the quantum expression of the polarizability to a single effective excited state [8], thereby reducing the expression of the polarizability to a compact formulation proportional to the average value of the electrostatic quadrupole tensor in the ground state. Assuming validity of this approach, the determination of the linear polarizability of the molecule should then be amenable to the knowledge of the ground state electronic charge distribution as inferred either from X-ray diffraction

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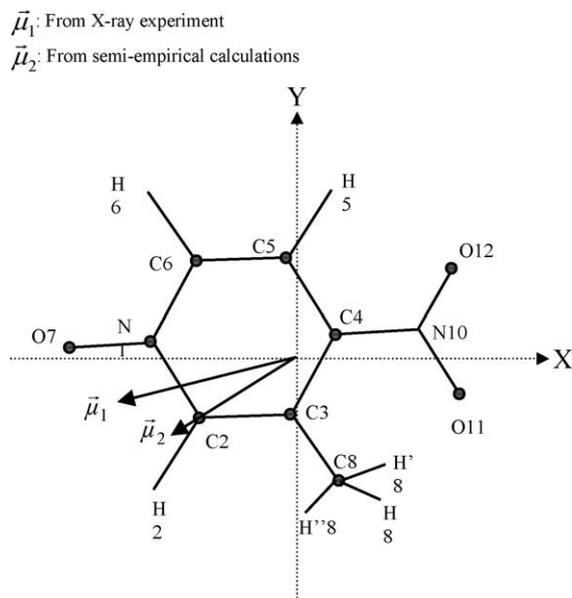


Fig. 1. Orientation of the molecular dipole moment. The positive sense from (charge excess) – to + (charge vacancy).  $\vec{\mu}_1$ : from X-ray experiment;  $\vec{\mu}_2$ : from semi-empirical calculations.

experiments, or from quantum calculations. We have demonstrated the applicability of this approach by using both X-ray diffraction and quantum chemical calculations and checking the consistency of both approaches with the Robinson quadrupolar model. Also, we have pointed out the limitations of this method along the polar directions which may be more sensitive to crystal field contributions.

Using the obtained results on the molecular linear polarizability and by application of the oriented gas model, it is possible to derive the index of refraction along the principal dielectric axis of the POM crystal which are along the three two-fold axis of the crystal [5]. An estimation of the first non linear hyperpolarizability will also be proposed and discussed along this article.

## 2. Crystallographic investigation

The crystal data and results concerning the electron density distribution are published in previous papers [1,9,10]. Values and parameters of the Hansen and Coppens function [11]  $\rho(\vec{r})$  at convergence are summarized in Table 1. The different electrostatic moments of the charge distribution expressed by the property  $\langle O \rangle$  can be directly derived from the knowledge of the density function  $\rho(\vec{r})$  using the general equation:

$$\langle O \rangle = \int_V \hat{O}(\vec{r})\rho(\vec{r})d\vec{r} \quad (1)$$

where  $\langle O \rangle$  is the property associated to the average value of a quantum observable related to the density function,  $V$  is the molecular volume.

In a previous paper, we have described the molecular components of the electrostatic dipole and quadrupole moments [1,10]. These studies have clearly evidenced the connection between the molecular linear polarizability and the molecular electrostatic moment up the rank 2 of the charge distribution. In a similar fashion, the electrostatic octupolar moment can be deduced by replacing the operator  $\hat{O}$  by  $\vec{r}_\alpha A \vec{r}_\beta A \vec{r}_\gamma$  in Eq. (1), leading to:

$$\begin{aligned} O_{\alpha\beta\gamma} = & \sum_i O_{\alpha\beta\gamma}^i \sum_i (r_{i\alpha} Q_{i\beta\gamma} + r_{i\beta} Q_{i\alpha\gamma} + r_{i\gamma} Q_{i\alpha\beta}) \\ & + \sum_i (r_{i\beta} r_{i\gamma} d_{i\alpha} + r_{i\alpha} r_{i\gamma} d_{i\beta} + r_{i\alpha} r_{i\beta} d_{i\gamma}) \\ & + \sum_i r_{i\alpha} r_{i\beta} r_{i\gamma} q_i \end{aligned} \quad (2)$$

The octupolar moment is given by the contribution of the atomic octupoles (first term), quadrupoles (second term), dipoles (third term) and net charges (last term) respectively. The different components were also estimated by both multipolar and direct methods. In the case of the multipolar development was stopped at  $l=1$ ) while in the direct integration method all the terms have been taken into account. The corresponding expression after implementation of the direct integration method is:

$$\begin{aligned} O_{\alpha\beta\gamma} = & \sum_{\vec{H}} \Delta F(\vec{H}) \left[ \sum_i O_{\alpha\beta\gamma} + \sum_i (r_{i\alpha} Q_{i\beta\gamma} + r_{i\beta} Q_{i\alpha\gamma} \right. \\ & + r_{i\gamma} Q_{i\alpha\beta}) + \sum_i (r_{i\beta} r_{i\gamma} d_{i\alpha} + r_{i\alpha} r_{i\gamma} d_{i\beta} \\ & \left. + r_{i\alpha} r_{i\beta} d_{i\gamma}) + \sum_i r_{i\alpha} r_{i\beta} r_{i\gamma} q_i \right] \end{aligned} \quad (3)$$

where  $O_{\alpha\beta\gamma}^i = \int_{t_i} (r_\alpha - r_i)(r_\beta - r_i)(r_\gamma - r_i) e^{i2\pi\vec{H}(\vec{r}-\vec{r}_i)} d^3r$  is the octupolar moment of the subunit  $t_i$ . The last integrals are well documented and expressed in terms of Bessel functions. The different electrostatic moments were estimated in the first method by the DSIGMA program [11] in which we have implemented the molecular higher order moments. For the direct integration method we have used the updated BARBIE program [12]. The results of the different calculations are summarized in Table 2, where the corresponding components estimated from the ‘Point Charge Model’ have also been incorporated. One can note that the multipolar model and the direct integration methods lead to practically identical values. It is then confirmed that the atomic quadrupole and octupole moments do not contribute significantly to the molecular electrostatic moments. As for the  $Q_{xx}$  of the quadrupolar moment, we observe that the  $O_{xxx}$  component, is largely under-estimated with respect to the same component deduced from the Point Charge Model. Some more comments about those anomalies are being deferred to the next section.

Table 1  
The coefficients obtained from the multipolar refinement

Atoms	$l=0$	$l=1$			$l=2$				
	Pv	d1	d2	d3	Q1	Q2	Q3	Q4	Q5
N1	4.796	0	0.031	0.022	0.107	0	-0.023	-0.128	0
C2	4.337	0	-0.138	0.052	0.162	0	0.127	-0.124	0
C3	3.841	0	0.024	-0.003	0.095	0	-0.002	-0.165	0
C4	3.804	0	0.041	0.074	0.000	0	0.044	-0.140	0
C5	4.341	0	-0.046	-0.008	0.125	0	-0.028	-0.223	0
C6	4.273	0	-0.072	-0.057	0.118	0	0.094	-0.137	0
O7	6.221	0	0.007	-0.070	-0.157	0	-0.022	-0.060	0
C8	4.859	0	0.030	-0.121	-0.090	0	-0.001	0.011	0
N10	4.860	0	-0.001	0.076	0.039	0	-0.011	-0.148	0
O11	6.179	0	0.000	-0.033	-0.071	0	0.013	-0.110	0
O12	6.207	0	0.011	-0.017	-0.039	0	0.013	-0.093	0
HC2	0.660	0	0	0.072	0	0	0	0	0
HC4	0.712	0	0	0.085	0	0	0	0	0
HC5	0.593	0	0	0.077	0	0	0	0	0
HC8	0.753	0	0	0.072	0	0	0	0	0
HC8'	0.671	0	0	0.062	0	0	0	0	0
HC8''	0.694	0	0	0.052	0	0	0	0	0

Atoms	$l=3$						
	O1	O2	O3	O4	O5	O6	O7
N1	0.207	0	0.003	0.144	0	0	0.016
C2	0.280	0	-0.024	0.227	0	0	-0.015
C3	0.175	0	0.034	0.173	0	0	-0.021
C4	-0.237	0	-0.005	-0.126	0	0	-0.009
C5	0.261	0	-0.034	0.212	0	0	-0.017
C6	0.292	0	-0.009	0.267	0	0	0.006
O7	0.022	0	0.006	-0.012	0	0	0.010
C8	0.293	0	0.009	-0.037	0	0	-0.187
N10	0.261	0	0.004	0.166	0	0	0.021
O11	0.080	0	0.028	0.011	0	0	0.035
O12	0.071	0	0.047	-0.002	0	0	-0.002

As described in the model of Hansen and Coppens (1178) by the following equations:

$$\rho_k(\vec{r}) = P_{k,c} \rho_{k,c}(\vec{r}) + P_{k,v} \kappa^3 \rho^{k,v}(\kappa, \vec{r}) + \sum_{l=0}^4 \kappa^l 3R_{k,l}(\kappa', \vec{r}) \times \sum_{m=-l}^{+l} P_{k,lm\pm} Y_{lm\pm} \left( \frac{\vec{r}}{|\vec{r}|} \right)$$

where  $P_{k,c}$ ,  $P_{k,v}$  and  $P_{lm}$  are refinable population parameters,  $\kappa'$  and  $\kappa''$  are refinable parameters describing the contraction (or expansion) of the spherical and non spherical components of the valence electron density, respectively, and  $\rho_c$  and  $\rho_v$  are the core electron density and the spherical part of the valence electron density, respectively. The radial functions  $R_{j,l}(\vec{r})$  may be Slater-type functions or numerically defined functions based on the Hartree–Fock calculation of the spherically averaged valence density.

Table 2  
Components of the octupolar moment of the charge distribution ( $e \text{ \AA}^3$ ) from the point charge model (the net charges are estimated by PM3 Hamiltonian) are compared to the components derived from experimental electron density

	X-ray experiment			
	Semi-empirical Point charge Model	Multipolar refinement	Direct integration	Values from $\beta$
O <sub>xxx</sub>	4.641	0.35	-0.95	0.21
O <sub>xyy</sub>	-1.484	-1.85	-1.52	
O <sub>xxz</sub>	0.558	0.22	0.58	
O <sub>yyy</sub>	-3.662	-3.66	-3.50	
O <sub>yyz</sub>	-0.412	-0.17	-0.20	
O <sub>zzz</sub>	0.104	0.28	0.29	
O <sub>yyy</sub>	-2.163	-2.34	-1.90	0.009
O <sub>yyz</sub>	0.054	-0.01	0.44	
O <sub>yzz</sub>	-0.460	-0.78	-0.97	
O <sub>zzz</sub>	0.082	0.15	0.34	0.001

The origin coincides with the center of mass of the molecule, and the cartesian system is being referred to the inertial axis of the molecule.

### 3. First order non linear hyperpolarizability

The energy of a molecule in an external field,  $\vec{F}$ , may be expanded in a power series as:

$$E(F) = E(0) - \mu_{i0}F_i - \frac{1}{2!}\alpha_{ij}F_iF_j - \frac{1}{3!}\beta_{ijk}F_iF_jF_k - \frac{1}{4!}\gamma_{ijkl}F_iF_jF_kF_l \dots \quad (4)$$

where summation over repeated indices is being assumed,  $\mu_{i0}$  is the  $i$  component of the permanent dipole moment,  $\alpha_{ij}$  is a tensor component of the linear polarizability and  $\beta_{ijk}$  is a component of the first order hyperpolarizability tensor. Since the nonlinear optical coefficients are functions of linear optical properties such as excitation energies and dipole matrix elements, the required electronic structure information can be conveniently obtained from spectroscopically based semi-empirical electronic structure description. The combination of semi-empirical molecular orbital methods and Finite Field perturbation technique [13–15], allows for the simultaneous calculations of all appropriate tensors components of the polarizability  $\alpha$  and of the first and second hyperpolarizabilities ( $\beta$  and  $\gamma$ ) for large organic molecules at the price of a moderate computational effort.

Values of  $\alpha$  and  $\beta$  calculated by this method using the PM3 Hamiltonian are reported in Tables 3 and 4. The ratios between the diagonal components of the polarizability tensor ( $10^{-24}$  esu) and those of the quadrupolar moment ( $e \text{ \AA}^2$ ) are of the order of 8 except for the smallest component  $\alpha_{zz}$  while for the hyperpolarizability and the octupolar moment the coefficients range from 0.1 to 1.8. The same type of relation between electrostatic moments and NLO properties has been evidenced recently for the large NPP molecule [16].

Concerning the moments estimated from the X-ray electronic density study the Unsöld approximation gives relatively good results for  $\alpha$  [17] but fails in the  $\beta$  estimate. The results reported here mimic very closely those published by Fkyrat et al. [16] on the *N*-(4-nitrophenyl)-(L)prolinol (NPP) another very efficient NLO compound.

Table 3

Values of the linear polarizability ( $10^{-24}$  esu) from the finite field method (column I) and point charge model (column II) are compared to components (column III) deduced from Eqs. (11) and (12)

	I	II	II	IV	V
	Finite Field method	Calculation P.C. model	X-ray experiment	Direct integration	Average values
			Multipolar refinement		
$\alpha_{xx}$	36.12	176.56	27.43	16.64	22.03
$\alpha_{yy}$	25.95	63.43	46.36	83.26	64.81
$\alpha_{zz}$	5.55	0.14	0.59	11.31	5.95
$\alpha_{xy}$	-0.865	8.18	-1.80	-1.47	-1.63
$\alpha_{xz}$	0.149	0.19	0.61	0.03	0.32
$\alpha_{yz}$	0.868	-2.52	-1.71	-2.85	-2.28
$\langle \alpha \rangle$	22.5	79.9	24.7	37.1	30.9

The profactor  $4m/\hbar^2$  is equal to 7.6 when the quadrupole moment is expressed in  $e \text{ \AA}^2$  and the linear polarizability in  $10^{-24}$  esu.

By extension of the approach used for the linear polarizability, the expression of the first non linear hyperpolarizability [18–20] is as follows:

$$\beta_{xyz} = \frac{e^3}{\hbar^2} \sum_P \sum_{a,b \neq g} \frac{\langle g|x|a\rangle\langle a|y|b\rangle\langle b|z|g\rangle}{(\omega_a - \omega_1 - \omega_2)(\omega_b - \omega_2)} \quad (5)$$

where  $a$  and  $b$  are two different excited states. The summation over  $P$  express the simultaneous permutations over indices and frequencies, a complete expression of this last equation being given in the references just cited before. As developed in Appendix B the diagonal and non-diagonal components of the first non linear hyperpolarizability can be expressed in terms corresponding electrostatic octupolar and quadrupolar moments. The corresponding expressions are respectively:

$$\beta_{xxx} = 3 \left( \frac{2m}{\hbar^2} \right)^2 Q_{xx}^2 O_{xxx} \quad (6)$$

$$\beta_{xxy} = \left( \frac{4m^2}{\hbar^2} \right) (Q_{xx}^2 + 2Q_{xx}Q_{yy}) O_{xxy} \quad (7)$$

Using these two last equations we are able to estimate the components of the first hyperpolarizability tensor, with results presented in Table 5, which provides also semi empirical values of the same components. The  $\beta$  tensor coefficients can be compared and analyzed along similar lines as previously proposed in the linear case. The ratio between the  $\beta_{iii}$  inferred from the Finite Field method and the components of the octupolar moment are ranging from 0.1 to 1.8.

Following the same approach as in the linear case we consider the diagonal components of the  $\beta$  tensor calculated from Finite Field Method as experimental observations. Using  $Q_{ii}$  previously determined we obtain the  $O_{iii}$  from Eq. (6). The values thus deduced listed in column V of Table 4 fall off by one or two order of magnitude with respect to those found by the point charge model and the schemes using the X-ray electronic density study, with no coherence at all between the magnitude and the signs in the components of the  $\beta$  tensor except for  $\beta_{xxx}$  the strongest

Table 4

Values of the molecular first hyperpolarizability ( $10^{-30}$  esu.) from Finite Field method (Column I) and Point Charge model (Column II) are compared to components from Eqs. (4) and (5) corresponding to the X-ray experiment (Column III)

	I (F.F. Method)	II (P.C. Model)	III (X-ray)
	8.46	973.63	−3.96
$\beta_{xxy}$	0.72	60.62	33.48
$\beta_{xxz}$	0.11	36.78	−0.37
$\beta_{yyy}$	−2.6	214.98	1.03
$\beta_{xzz}$	0.2	−0.41	0.08
$\beta_{yyy}$	0.26	−163.02	−158.42
$\beta_{yyz}$	−0.09	1.48	4.47
$\beta_{yzz}$	0.02	−1.13	−15.67
$\beta_{zzz}$	0.01	0.01	2.33

The profactor  $4m^2/h^2$  is equal to 3.01 when the electrostatic octupole moment is expressed in  $10^{-30}$  esu.

components along the charge transfer axis (Table 4). As already mentioned in the linear case values from the point charge model (Table 4, column II) are greater by two order of magnitude with respect to those deduced from the Finite Field method (Table 4, column I), the most striking feature very much like in the case of the Alpha tensor, being an overestimate of  $\beta_{xxx}$  related certainly to a depolarizing field not taken into account in the point charge model.

The dispersion between the values of the Finite Field method and those from the experimental measurements show that it is difficult to infer from the Unsold approximation a faithful description of the molecular optical properties, this is in agreement with the statement of Flytzanis [21] who predicted from theoretical basis an error by one to two order of magnitude in the estimation of  $\beta$  from the Unsold approximation. In the study of the *N*(4-Nitrophenyl)-(L)-prolinol (NPP) [16] the authors have also observed more than one order magnitude discrepancy between  $\beta$  values derived from Finite Field method and P.C. model.

From the equation developed in appendix B the Robinson model shows how the charge asymmetry ( $\hat{x}^3$ ) and the charge expansion ( $\hat{x}^2$ ) intervene in the evaluation of  $\beta$ . Clearly as the system is getting larger, errors on the quadrupolar and octupolar molecular moments due to a crude estimation of  $\Delta\rho$  or to defaults of the model, will increase like cube and the square of the size of the molecule, so it would not be surprising that the Robinson model failed for very large molecules and specially for the evaluation

Table 5

Values of refractive indices calculated from polarizability tensor components inferred from the different methods (semi-empirical and experiment)

	I (F.F. Method)	II (P.C. Model)	III (X-ray Experiment)	IV (Measured at 1.0632 $\mu\text{m}$ )
	1.574	2.423	1.715	1.663
$n_b$	1.784	3.302	1.609	1.829
$n_c$	1.550	2.053	1.743	1.625

In column IV the measured refractive indices at 1.0632  $\mu\text{m}$  according to Zyss, Chemla and Nicoud [3].

of  $\beta$ . The assumption included in the Unsold approximation that the same energies should be used to evaluate  $\beta$ , remain also a questionable one.

#### 4. Macroscopic linear and non linear susceptibilities

In a molecular crystal the ‘oriented gas’ description [5] of the medium allows for straightforward connection of microscopic and macroscopic non linearities,  $\chi^1$  are related to  $\alpha$ ,  $\chi^2$  to  $\beta$  and  $\chi^3$  to  $\gamma$ .

If,  $ij,k$ , are Cartesian indices related to molecular reference frame and  $I,J,K$  are Cartesian indices for the crystalline principal optical dielectric frame, we can write for  $\chi^1$  and  $\chi^2$  respectively:

$$\chi_{ij}^{(1)} = \frac{1}{V} F_I^\omega \sum_{i,j} \cos[I, i(s)] \cos[J, j(s)] \alpha_{ij}(s) \quad (8)$$

$$\chi_{ijk}^{(2)} = \frac{1}{V} F_I^{2\omega} F_J^\omega F_K^\omega \times \sum_{i,j,k} \cos[I, i(s)] \cos[J, j(s)] \cos[K, k(s)] \beta_{ijk}(s) \quad (9)$$

where  $F_I^{2\omega}$ ,  $F_J^\omega$ ,  $F_K^\omega$  are local field correction factors and  $V$  the volume of the unit cell. There are  $n$  molecules in the unit cell which are generated by the  $s$  elements of symmetry. The anisotropy correction of the local field is introduced through the refraction indices according the following equation:

$$F_I^\omega = \frac{n_I^2 + 2}{3} \quad (10)$$

The local field corrections according to Eq. (10) with the values of the refraction indices measured at 1.0632  $\mu\text{m}$  provide three indices  $n_b > n_a > n_c$  which could correspond to rather higher frequencies measurements (Table 5). We also observe that the point charge model over estimate strongly the values of the refractive indices, however, the proportionality between the different coefficients is nevertheless maintained.

As previously mentioned the Unsold approximation seems to provide good values for the linear polarization under the conditions of course that the moments of the charge distribution have been evaluated properly ( $Q_{xx}$  is certainly largely overestimated in the PC model).

Results from moments inferred from the X-ray electronic charge distribution inverse the values of  $n_b$  and  $n_c$  due here to an underestimation of the component of the moments along X. These weak values are already been observed in the *N*(4-Nitrophenyl)-(L)-prolinol (NPP) another NLO charge transfer compound [6].

The hypothesis of depolarizing fields to explain this anomaly observed in the ‘in situ’ molecule is particularly tempting, unfortunately the refractive indices calculated

from these in situ values are in worst agreement with those inferred from the free molecule and the experimental measurements.

Concerning the macroscopic nonlinear susceptibility  $\chi^2$  the one dimensional model of Zyss and Oudar [22] gives for  $\beta_{xxx}$  a value of  $(8.5 \pm 2) \times 10^{-30}$  esu which agrees perfectly with 8.46 obtained from the semi empirical calculation. About the  $\beta$ 's obtained from the experimental X-ray measurement using the Robinson model, the dispersion of the values shows that the model is clearly inadequate.

## 5. Conclusion

The comparison of the hyperpolarizabilities components inferred from the Finite Field method with the corresponding ones deduced from the Point Charge model show that the Unsöld approximation gives results far less reliable in the estimation of ( $\beta$ , in agreement with the statement of Flytzanis [21]).

Concerning the macroscopic susceptibility and the determination of the refractive indices from the molecular polarizability inferred from the Finite Field method the agreement with the experimental measurements is largely satisfactory and appeared not fortuitous.

In view of the good results obtained for the macroscopic properties from semi-empirical calculation it seems very difficult through a model and from experimental electronic density distribution to obtain better values of the  $\alpha$  tensor components and of the refractive indices. It is also puzzling to note that the crystal field effects are quite negligible regarding the determination of the NLO properties.

The main contribution of this work was to check the validity of the Robinson model (Unsöld approximation) and to follow the discrepancies which may appear when this model is applied both to a free molecule (Point Charge Model) and to the molecule in the crystal state. We have shown in this study that there is a reasonable agreement between electronic properties deduced from X-ray diffraction and those from semi-empirical calculations using the Point Charge Model. There is no doubt on some relations between the ground state molecular quadrupole

and octupole and the polarizabilities of the molecule, however, the Unsöld approximation in this study gives less reliable estimates of  $\beta$  than those claimed by O'Hare et al., Flytzanis et al. for smaller systems.

Of course it seems difficult to reach from the Unsöld approximation a very faithful description of the molecular optical properties, an estimation of the first order hyperpolarizability components of  $\beta$  seems to be out of question.

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