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The influence of an external electric field on the X-ray scattering of 2-methyl-4-nitroaniline, an organic crystal with nonlinear optical properties

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Abstract. The influence of an electric field on the X-ray scattering of the nonlinear optical organic crystal MNA (2-methyl-4-nitroaniline) has been studied, using a three-step pulsed alternating electric field. The field changes are synchronized with the gating to three different counting chains (the three-step modulation method). A field strength of 39 kV cm^{-1} induces 0.2% maximum variation in the integrated intensity and a small shift in Bragg angles (an inverse piezoelectric effect). A special electron density refinement method, which uses the differences between the zero- and applied-field intensities as observations, has been developed and applied in the interpretation of the results.

Introduction. With the advent of high-intensity X-ray sources the effect of external perturbations on the X-ray scattering of crystals has attracted renewed interest. The analysis of the perturbation of the scattering by an external electric field can lead to the determination of the polarizability of molecules or groups of atoms on an atomic scale and a better understanding of the optical properties of solids. Several inorganic crystals have been studied: TiO_2 (Puget & Godefroy, 1975), $LiNbO_3$ (Fujimoto, 1982; Kvick, Chen, Ståhl & Abrahams, 1986), $LiTaO_3$ (Fujimoto, 1982), KTiOPO4 (Eddy, Stucky, Bierlein & Kvick, 1987), but no such work has been reported for organic solids, which sometimes show very large nonlinear optical effects (Chemla & Zyss, 1987). We report here the first such study on a crystal of the nonlinear optical material MNA, 2-methyl-4-nitroaniline (Levine, Bethea, Thurmond, Lynch & Bernstein, 1979; Lipscomb, Garito & Narang, 1981) using a rotating-anode generator. The study of the response of an organic crystal to an external field is an extension of electron density studies by diffraction methods. We have modified some of the techniques developed in this field and applied them in the present study.

Experimental. The 'three-step' modulation method. The variations in the scattered intensities generated by the applied electric field are typically 0.1% of the integrated intensity. As such small changes can be easily created by any experimental instabilities (like fluctuations in the incident X-ray beam intensity, in the temperature of the experiment) special methods are required.

The modulation method virtually eliminates these long-run fluctuations. It is a differential

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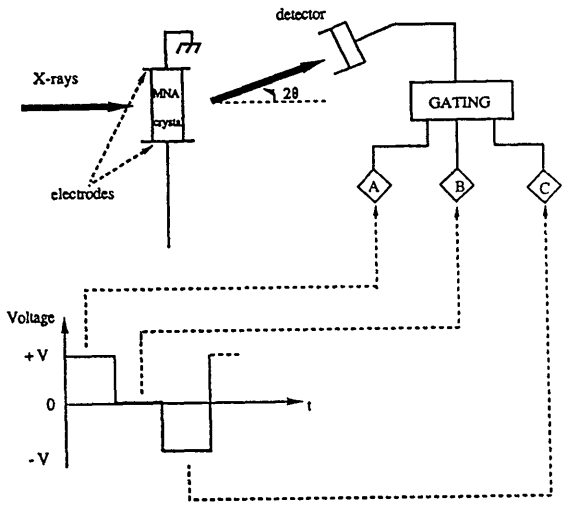

Fig. 1. The three-step modulation method.

method, in which counting in different chains is synchronized with the variations in the electric field. It was first applied by Godefroy (1963) (Puget & Godefroy, 1975) and improved by Fujimoto (1982). We further modified the method by including a zero-field step in the sequence.

A voltage of 2.9 kV is applied along the polar axis of the crystal, in a square waveform at the frequency 55 Hz (Fig. 1). The detector output is gated and accumulated to the counter A when the field is up, B when it is zero and C when it is down. A 0.7 ms delay was built in for every step to account for the pulse rise time. Three intensities I_+, I_0, I_- are thus measured. From their differences the small intensity variations can be deduced. The addition of the 0 V measurement allows the investigation of asymmetric effects as the field is reversed.

Preparation of the sample. Crystals of MNA were grown by the thermal-gradient vapor technique (Levine *et al.*, 1979), using commercially available MNA powder purified by sublimation.

MNA crystallizes in the monoclinic space group *Ia* (non-standard for *Cc*) with the cell parameters (determined from the positions of 20 reflections with $80<2\theta<148°$ on a CAD-4 automatic diffractometer, using Cu $K\alpha$ radiation, $\lambda=1.5417$ Å): $a=8.2229(15)$, $b=11.6199(9)$, $c=7.5879(17)$ Å, $\beta=94.167(26)°$.

A good-quality single crystal, with high transparency and sharp extinctions under the polarized microscope, was cut to a parallel-epipedal shape (0.75×0.50×0.40 mm). Copper–tin alloy wires (Ø=0.8 mm) with polished tips were used as electrodes. They were aligned in a Lindeman capillary. The sample was glued to the electrodes with silver epoxy, with its polar axis (*i.e.* [201], which is the direction of the unit-cell dipole moment) parallel to the capillary axis.

Method of measurement. The response of the crystal to the applied electric field was expressed as the 'response ratios' η_+, η_-, η_{+-}, defined as follows:

$$\eta_{+0}=\Delta I_+/I_0=(I_+-I_0)/I_0$$
$$\eta_{-0}=\Delta I_-/I_0=(I_--I_0)/I_0$$
$$\eta_{+-}=\Delta I_{+-}/I_0=(I_+-I_-)/I_0.$$

Since the standard deviation of these ratios is approximately $(2/I_0)^{1/2}$, 10^8–10^9 counts have to be collected to get statistically meaningful values. Therefore, each reflection was measured as many times as necessary to obtain statistical accuracy, with counts being accumulated as the experiment proceeded. The evolution of the response ratios was monitored in real time (Fig. 2). The measurement was discontinued when the desired convergence was achieved.

All reflections were collected using a 12 kW Rigaku rotating-anode generator (Mo target, 60 kV, 90 mA, which is the maximum setting for the filament used). The accuracy of the electronics was checked with a three-step 0 V measurement of the strongest reflection $11\bar{2}$. This gave response-ratio corrections $\eta_+=-1.5(4)\times10^{-4}$ and $\eta_-=-4.9(4)\times10^{-4}$, which were applied to all other three-step measurements.

Scaling. For further treatment, the variations $\Delta_{+-}(F^2)$ need to be put on an absolute scale. For

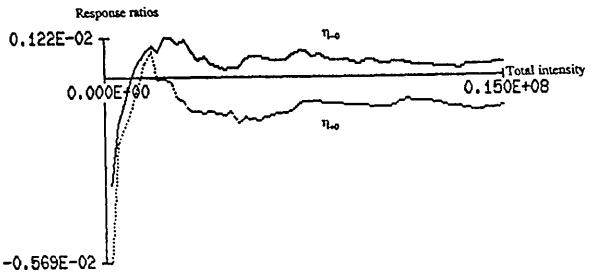

Fig. 2. Convergence of the response ratios η_{+0} (dotted line) and η_{-0} (solid line) for the 602 reflection.

this purpose, a set of 0 V structure factors was obtained by a conventional full-data collection at room temperature with a CAD-4 diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å). 616 unique reflections ranging from $\sin\theta/\lambda = 0.075$ to 0.660 Å^{-1} were obtained after averaging over symmetry-equivalent reflections with $\pm k$ ($R_{symm} = 0.03\%$). Lorentz–polarization and isotropic extinction corrections were applied. Atomic coordinates and temperature factors and the scale factor (131 parameters) were refined to give $wR(F) = 2.80\%$ [$R(F) = 3.40\%$, $w = 1/\sigma^2$, $\sigma(F) = \sigma(F^2)/2F$, $\sigma^2(F^2) = (\sigma_{stat})^2 + (0.02F^2)^2$] and a goodness of fit 1.11. The absolute scale obtained was used to scale the ΔF^2 values from the electric field experiment with the expression $\Delta_{+-}(F^2)_{abs} = \Delta_{+-}(F^2)(F_{abs,obs})^2/F^2$.

Results and data treatment. The main goal of the experiment was to prove the feasibility of the method and its application to MNA. Owing to the slowness of the data collection (typically 1–2 days per reflection), only six significant reflections were measured (Table 1). As expected, the response ratios vary in sign and magnitude depending upon the indices of the reflection. The effect of the field is found to be typically 0.1% of the integrated intensity, a value comparable to Fujimoto's results on $LiNbO_3$ and $LiTaO_3$, obtained with an even stronger field (Fujimoto, 1982). Most of the reflections show a symmetrical opposite response ($\eta_{+0} = -\eta_{-0}$) as the field changes direction (Fig. 2) with the possible exception of the 020 reflection. A significant shift of the Bragg angle is also observed from the peak profiles of $I_+ - I_0$, $I_- - I_0$ and $I_+ - I_-$ for reflections $7\bar{1}0$ and 602 (Fig. 3). The shifts are attributed to the inverse piezoelectric effect.

Analysis. If $F = A + iB$ is the structure factor of a given hkl reflection without an applied field and $F_+ = F + \Delta F_+$, $F_- = F + \Delta F_-$, the structure factors with the field up and the field down, respectively, then the following expressions can be derived (neglecting second-order terms):

$$\begin{aligned} \Delta_+(F^2) &= F_+^2 - F_0^2 = 2(A\Delta A_+ + B\Delta B_+) \\ \Delta_-(F^2) &= F_-^2 - F_0^2 = 2(A\Delta A_- + B\Delta B_-) \end{aligned} \quad (1)$$

where $\Delta F_+ = \Delta A_+ + i\Delta B_+$ and $\Delta F_- = \Delta A_- + i\Delta B_-$.

Data were analyzed with a modification of the charge density refinement program *MOLLY* (Hansen & Coppens, 1978), in which expression (1) is used as the observational equation.

Though the current data set is too small for a refinement of the atomic multipole populations, a test refinement was made in which only the monopole populations of three atoms, N(1), N(2) and C(3) (Fig. 4), were varied. With field up net charges of 0.0065(31) e on N(1), 0.0006(11) e on

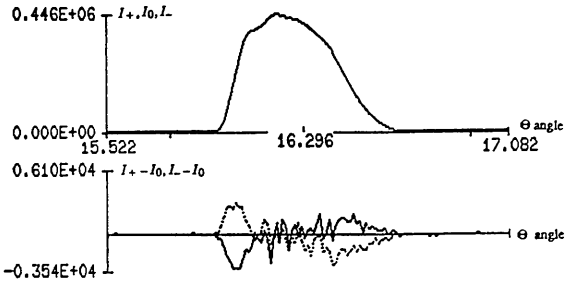

Fig. 3. Inverse piezoelectric effect for the reflection 602. The top plot shows the three total profiles I_+, I_0, I_-, the differences are too small to be seen in the figure. The bottom plot shows $I_+ - I_0$ (dotted line) and $I_- - I_0$ (solid line) for each step of the profile. The change of sign of the difference curves indicates a shift in Bragg angle as a result of the electric field.

Table 1. *Measured response ratios*

h	k	l	$\sin\theta/\lambda$(Å^{-1})	$F_{0,abs}$*	η_{+0} (10^{-3})	η_{-0} (10^{-3})	η_{+-} (10^{-3})
1	1	0	0.07463	37.06	0.68(23)	–0.96(23)	1.63(23)
0	2	0	0.08606	85.95	–0.22(6)	0.03(6)	–0.26(6)
0	0	2	0.13226	37.38	0.60(25)	–0.83(25)	1.43(25)
1	1	2	0.15560	38.96	1.06(41)	–0.19(41)	1.24(41)
6	0	2	0.39781	32.84	–0.97(37)	0.41(37)	–1.38(37)
7	–1	0	0.42904	27.69	–0.58(43)	1.23(43)	–1.81(43)

* Structure factors scaled with zero-volt measurements, see text.

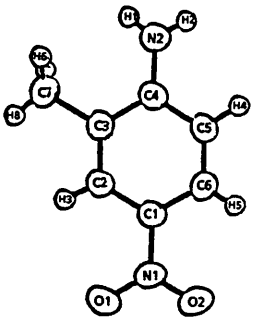

Fig. 4. The molecular structure of 2-methyl-4-nitroaniline (Lipscomb *et al.*, 1981).

N(2) and −0.0071(24) e on C(3) were obtained $\{R[\Delta(F^2)]=0.75,\ wR[\Delta(F^2)]=0.68,\ \mathrm{GOF}=1.63\}$. Corresponding values with the field down are −0.0047(40), 0.0004(14), 0.0043(31) e $\{R[\Delta(F^2)]=0.96,\ wR[\Delta(F^2)]=0.92,\ \mathrm{GOF}=2.06\}$. As may be expected, a change of sign in the electron shift is observed as the field is reversed in direction. A full treatment of the effect of the electric field must include the molecular reorientation contribution to the induced dipole moment. This reorientation is reflected in the small change in unit-cell dimensions, evident from the observed shifts in the Bragg angles.

Though this work is a preliminary to more extensive data collection using a synchrotron source, it establishes the feasibility of the study of electric field effects in molecular crystals.

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