# SECOND HARMONIC GENERATION IN SQUARIC ACID

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From the temperature-dependent optical second harmonic generation in squaric acid we conclude that no local symmetry breaking occurs in the high temperature phase of this material.

In the last years squaric acid, $H_2SQ$, (3, 4-dihydroxy-3-cyclobutene-1, 2-dione) has found increasing interest, because, as is generally assumed, it shows quasi two-dimensional behaviour near a second order antiferro-distortive phase transition at about $T_{c,H} \approx 370$ K. The crystal is built of layers wherein $C_4O_4$ molecules are linked by hydrogen bonds to 4 neighbouring $C_4O_4$ groups. In the high temperature phase the crystal structure is body centered tetragonal with $I4/m\,(C_{4h}^5)$ symmetry [2,3]. The hydrogen atoms are supposed to be at the center of the O–H–O bonds on the average. In the low temperature phase, which has monoclinic structure with $P2_1/m\,(C_{2h}^2)$ symmetry, the hydrogen atoms are displaced from the center on the average, thereby producing a polarization proportional to the displacement. The planar ferroelectric layers are antiferroelectrically stacked. In deuterated crystals, $D_2SQ$, the transition temperature shifts to $T_{c,D} = 516$ K. This large shift in transition temperature indicates that an ordering process of the protons of the O–H–O bonds drives the phase transition, and that, possibly, the tunneling of the protons is important.

Recently, Nakashima and Balkanski [3] investigated the temperature dependence of Raman active modes. The increase in the band width of the external modes with temperature below $T_c$ was explained by disordering of hydrogen atoms. On the other hand Thackeray et al. [4] suggest that the results of the X-ray *and* the Raman scattering experiments obtained in the high temperature phase can be explained by orientational disorder, whereby the molecules, i.e. the direction of the C=C bonds, continuously change orientation.

In this note we report on temperature-dependent optical second harmonic generation (SHG) in $H_2SQ$. The experimental setup was described elsewhere [5]. The crystals used in the experiments were transparent and colorless platelets of about 5 × 5 × 1 (*b*-direction) $mm^3$. The samples were prepared by cleaving crystals which were grown from aqueous solution by the usual method described in ref. [6].

Fig. 1 shows the intensity of the SHG as function of temperature. The propagation of light was parallel to the crystal *b*-direction. No phase matching was achieved. Below the phase transition the intensity of the SHG increases approximately linearly with increasing temperature. Near $T_{c,H}$ there is a sharp drop in intensity with an inflection point at about 370 K. At higher temperatures the SHG signal vanishes within the accuracy of the measurements. As expected for a second order phase transition, no hysteresis was observed in the curvature for rising and falling temperatures.

Since the structure of $H_2SQ$ has inversion symmetry both in the high temperature and the low temperature phase, no SHG in lowest order is expected in

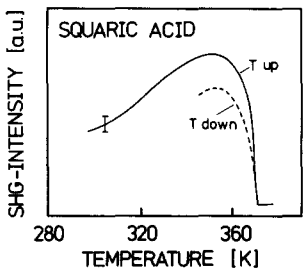


Fig. 1. Intensity of the second harmonic as function of temperature. The measurements were performed by using the photon counting system described in ref. [5]. The signal is divided by the square of the laser intensity.

both phases. Possible explanations for the observation of SHG in the low temperature phase are:

1. Higher order effects as for instance spatial gradient terms [7], like

$$P^{NL} = \chi^{N} : E^{(1)} \nabla E^{(1)} ,$$

or quadrupole terms, due to the fact that the antiferroelectrically stacked dipoles in the unit cell represent a quadrupole momentum. Well below the phase transition, both of these effects are expected to be temperature independent.

2. A dynamical distortion of the inversion symmetry due to a thermally activated motion of the H-atoms sitting in out-of-center positions of the O–H ... O bonds. The nonlinear polarization could then be written as

$$P^{NL} \propto \langle u^2 \rangle^{1/2} \propto (kT)^{1/2} ,$$

where $u$ is the displacement of the H-atom from its equilibrium position. In this case, SHG would be proportional to $kT$, because $I_{SHG} \propto (P^{NL})^2$.

Because the observed SHG intensity is "relatively strong" and seems to increase linearly with temperature below about 340 K, the second mechanism discussed seems to be dominating. From the absence of SHG intensity above the phase transition, we conclude that no symmetry breaking as discussed by Thackeray et al. [4] takes place. We therefore believe that the 245 $cm^{-1}$ Raman line should indeed be assigned to a $A_g$ bulk mode of the crystal, as suggested by Nakashima and Balkanski [3].

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*References*

[1] For a review see e.g. J. Feder, Ferroelectrics 12 (1976) 71.
[2] D. Semmingsen, Tetrahedron Lett. 1973 (1973) 807; Acta Chem. Scand. 27 (1973) 3961; G.D. Stucky, J. Williams and Y. Wang, J. Chem. Soc. Perkin II 1973 (1973) 35; D. Semmingsen, F.J. Hollander and T.F. Koetzle, J. Chem. Phys. 66 (1977) 4405; F.J. Hollander, D. Semmingsen and T.F. Koetzle, J. Chem. Phys. 67 (1977) 4825.
[3] S. Nakashima and M. Balkanski, Solid State Commun. 19 (1976) 1225.
[4] D.P.C. Thackeray, R. Shirley and B.C. Stace, Solid State Commun. 25 (1978) 1039.
[5] K. Betzler and D. Bäuerle, Appl. Phys. (1978).
[6] H.D. Maier, D. Müller and J. Petersson, Phys. Stat. Sol. (b) 89 (1978) 587.
[7] L. Ortmann and H. Vogt, Opt. Commun. 16 (1976) 234.