

05.2-4 SIMULTANEOUS MEASUREMENTS OF THE ELECTROGYRATION AND ELECTROOPTIC EFFECTS OF α -QUARTZ. By T.Asahi, S.Takahashi and M.Takada Department of Applied Physics, Waseda University, Japan.

Simultaneous measurements of the electrogyration and electrooptic coefficients of α -quartz were intended together with accurate measurements of the moduli of gyration tensors. The crystal symmetry of α -quartz does not allow the electrogyration effect to take place along the optic axis where gyrations can be readily measured. This fact makes measurements of the electrogyration effects of α -quartz extremely difficult; Rogers (Proc. R. Soc. Lond., 1977, A.353,177) measured the coefficients but with some approximations in the method. In order to measure the electrogyration effects along the directions deflected from the optic axis, one must separate the electrogyration from the electrooptic effects accurately. Therefore we applied the HAUP method (J.Kobayashi and Y.Uesu J. Appl. Cryst. 1983, 16, 204) to the present study. The results at 18°C are as follows,
 $|\mu_{11}|$ (linear electrogyration coefficient) $= (1.41 \pm 0.01) \times 10^{-12}$ m/v,
 $|\mu_{41}|$ (linear electrogyration coefficient) $= (1.44 \pm 0.01) \times 10^{-12}$ m/v,
 $|\nu_{21}|$ (quadratic electrogyration coefficient) $= (4.23 \pm 0.01) \times 10^{-18}$ m²/v²,
 $|r_{11}|$ (linear electrooptic coefficient) $= (4.9 \pm 0.1) \times 10^{-13}$ m/v,
 $|r_{41}|$ (linear electrooptic coefficient) $= (2.35 \pm 0.01) \times 10^{-13}$ m/v.

The electrooptic coefficients coincide closely with previous reports (e.g. U.N.Günther, Ann. der Phys. 1932, 5(13), 783). As compared with Rogers' results, $|\mu_{41}|$ is the same order of magnitude, but $|\mu_{11}|$ is two orders of magnitude less than his value. Temperature dependences of electrogyration coefficients and electrooptic coefficients are shown in Fig.1 (a) and (b). For measuring the accurate moduli of gyration tensors, an accurate measurement of $\gamma = p - q$, a systematic error due to the parasitic ellipticities p and q of the polarizer and analyzer respectively, was inevitable. A new method was developed for solving this problem. We successfully determined p and q of the present HAUP system separately by referring to other HAUP system containing an optically inactive gypsum test crystal.

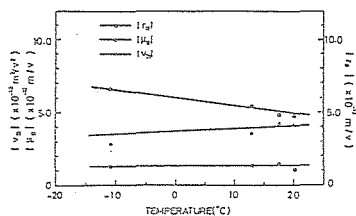


Fig.1(a)

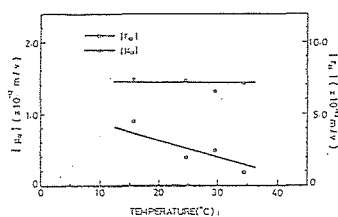


Fig.1(b)

05.2-5 STUDIES ON PUSH-PULL ETHYLENES AS NONLINEAR OPTICAL MATERIALS. By D. Kanagapushpam and K. Venkatesan, Department of Organic Chemistry, Indian Institute of Science, Bangalore, India.

Development of new organic materials exhibiting nonlinearities is important in the fields of nonlinear optics. The necessary conditions to be satisfied for nonlinear second-order optical properties of a material are (i) it must crystallize in an acentric space group (ii) the molecule should be conjugated and polarized (Williams, D.J., Angew. Chem. Int. Ed. Engl. 1984, 23, 690-703) and (iii) the difference between the ground state and excited state dipole moment $\Delta\mu$ must be large. Crystallographic studies carried out in our laboratory on push-pull ethylenes have shown that there is significant delocalization of π -electrons between the donor and acceptor groups across the ethylene bond suggesting that this class of molecules would be useful as nonlinear optical materials. As part of a programme of crystallographic studies aimed at correlating the nonlinear optical properties with the molecular packing, push-pull ethylenes with a chiral group, namely menthyl, attached to them have been examined. Compound (I); space group C2, $a=15.473$ (3), $b=6.963$ (2), $c=20.708$ (4)Å, $\beta=108.2$ (2)°, $Z=4$, R-factor 0.068 (II); P2₁2₁2₁, $a=7.634$ (1), $b=11.370$ (2), $c=34.166$ (3)Å, $Z=4$, R factor 0.060. The C=C bond length in compound I, is 1.447 (6)Å and 1.434 (9)Å in II, which are longer than in ethylene (1.336 (2))Å. The second harmonic generation (SHG) efficiency of compounds I and II in comparison with urea are measured to be 0.5 and 0.01 respectively (Eaton, D.F.; Wang, Y.; 1986). The charge transfer axis, namely the C=C bond, makes an angle of 43.5° with the crystallographic two-fold axis in I, whereas in II, the axis makes an angle of 86.9, 68.2 and 22.0° with a, b and c axes. From theoretical considerations the angle favourable for nonlinear interactions in crystals belonging to the point groups 2 and 222 is estimated to be 54.7° (Oudar, J.L. and Zyss, J.; Phys. Rev. 1982, A26, 2016-2027). The very low SHG efficiency of II is ascribed to the unfavourable molecular packing in which the charge transfer axis is almost perpendicular to a crystallographic axis. Although compound I shows slightly better SHG efficiency than II, the angle between the charge transfer axis and the two fold axis is not very different from the value of 54.7°, the SHG efficiency is not large. It is reasonable to conclude that the $\Delta\mu$ is unlikely to be very large. The SHG efficiency of the complexes of push-pull ethylenes I and II (without the chiral menthyl group) with β -CD turns out to be negligible. It is concluded that the alignment of push-pull ethylenes as guest molecules in the β -CD cavity is random as against the complexes formed with nitroanilines (Wang, Y. and Eaton, D.F.; Chem. Phys. Lett. 1985, 120, 441-444).

