Second-Harmonic Generation in Centrosymmetric Crystals of Chiral Molecules

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We demonstrate that for centrosymmetric structures of chiral molecules the interaction with circularly polarized light gives rise to nonzero second-order susceptibilities. It is ascribed to transitions that are both magnetic and electric dipole allowed. Experimental demonstration is given of second-harmonic generation from centrosymmetric crystals of *R*,*S*-*N*-acetyl valine ($P2_1/c$) using a fundamental wave having elliptic polarization in most parts of the trajectory through the crystal. These results demonstrate the existence of optical activity in the hyperpolarizability term β, similarly to the well-known optical-rotation phenomena in the linear polarizability.

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Efficient second-harmonic generation (SHG) is possible in organic media like polar crystals and poled polymers.[1] In such systems the more or less parallel alignment of molecules with a high hyperpolarizability β results in large values of the second-order nonlinear susceptibility $\chi^{(2)}(-2\omega,\omega,\omega)$. In a centrosymmetric structure, however, the even-order nonlinear susceptibilities ($\chi^{(2)}$, $\chi^{(4)}$, etc.) are, in the electric dipole approximation, zero for symmetry reasons.[2] Other symmetry rules are operative when the electric quadrupole and magnetic dipole moments are considered.[3,4] The observation of very weak SHG from silicon and calcite[5] is assumed to be based on quadrupoles.[2] SHG based on the presence of magnetic transition dipole moments, however, has not yet been observed. Moreover, it has been stated that the effect will probably be so small that it might be detected at resonance only.[3,6] The present Letter gives the first observation of nonresonant SHG attributed to electric-dipole–magnetic-dipole interactions.

In centrosymmetric crystals the inversion center connects, in general, two *identical* atoms or molecules with each other. However, in various organic crystals the center of symmetry connects two *different enantiomers* of chiral molecules.[7] Although enantiomers (*R* and *S*) are known to be identical with respect to most of their chemical and physical properties, they cannot be superimposed and differ with respect to their interaction with (circularly polarized) light.[8-10] This difference, leading to optical activity, is generally ascribed to sizable contributions of magnetic transition dipole moments. For chiral molecules in solution quadrupoles do not participate in this linear effect, but in optically active crystals minor contributions from quadrupoles cannot be excluded.[10] In the special class of centrosymmetric media of chiral molecules, the action of the inversion center reverses the sign of the electric transition dipole moments, but not the sign of the magnetic transition dipole moments. Therefore, it should be possible to obtain SHG, provided that the fundamental wave has elliptic polarization. Of course, in general a crystal cannot support a circularly polarized field. The birefringence of a crystal will give rise to a variation of phase with propagation depth, changing an incoming circular polarization into an oscillatory function between circular and linear. This implies that almost everywhere in the crystal the field is elliptically polarized; i.e., one circular polarization will dominate the other.

We have studied the centrosymmetric crystal of the racemic mixture of *N*-acetyl valine. *R*,*S*-*N*-acetyl valine crystallizes from ethanol in the space group $P2_1/c$ and large single crystals are easily grown.[7,11] The unit cell consists of two *R* enantiomers and two *S* enantiomers. The array of *R* enantiomers with 2_1 symmetry yields a polar $+b$ axis, while the array of *S* enantiomers yields similarly a polar $-b$ axis.[7]

A linearly polarized wave incident perpendicularly to the crystal *b*-*c* plane and having its polarization parallel to the *b* or *c* axis remains virtually unchanged upon passing through the crystal. For all other polarization directions in the *b*-*c* plane, the outgoing light shows elliptic polarization, brought about by the birefringence of the crystal. This implies that here we have indeed such an oscillatory behavior of the polarization between circular and linear as indicated above.

The nonlinear optical measurements were performed using a Nd-doped yttrium aluminum garnet laser (2×10^8 W/cm^2, 30 ps) at 1064 nm. SHG at 532 nm was detected through bandpass filters. The SH intensity was compared with that of a *y*-cut crystal quartz plate tuned to a Maker fringe maximum. Irradiation of an *R*,*S*-*N*-acetyl valine crystal with a plane wave directed perpendicularly to the *b*-*c* plane shows only minor SHG if the fundamental wave has its polarization parallel to the *b* or *c* axis of the crystal. At intermediate values of ψ, the angle between the crystal *c* axis and the direction of the polarization of the incoming wave, the amount of SHG increases significantly, reaching a maximum at about $\psi=\pi/4$ (Fig. 1). The observed intensity of the SHG is quadratic in the fundamental intensity and polarized parallel to the *b* axis.

Very similar results are obtained by changing the ellipticity of a fundamental wave, initially plane polarized

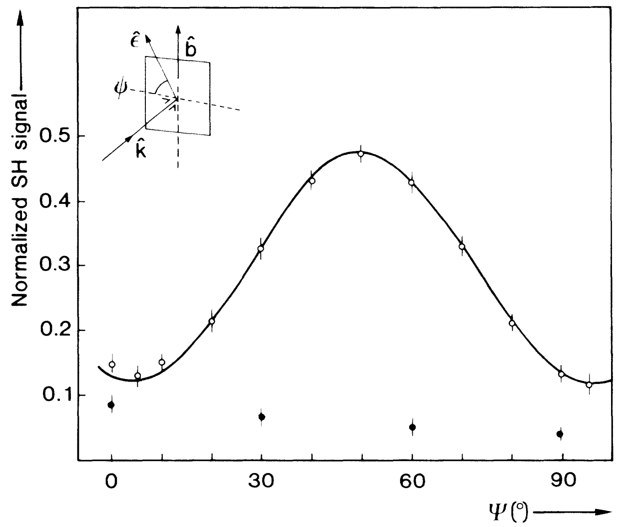

FIG. 1. The intensity of SHG vs ψ, the angle between the crystal c axis and the linear polarization of the fundamental wave, incident perpendicularly to the b-c plane. The SHG measured with the analyzer parallel to the crystal b axis is given with the open symbols, while the closed symbols represent the SHG measurements with the analyzer parallel to the c axis. The solid line represents the calculated function $\sin^2(2\psi)$, with a small offset in ψ that is within the experimental uncertainty.

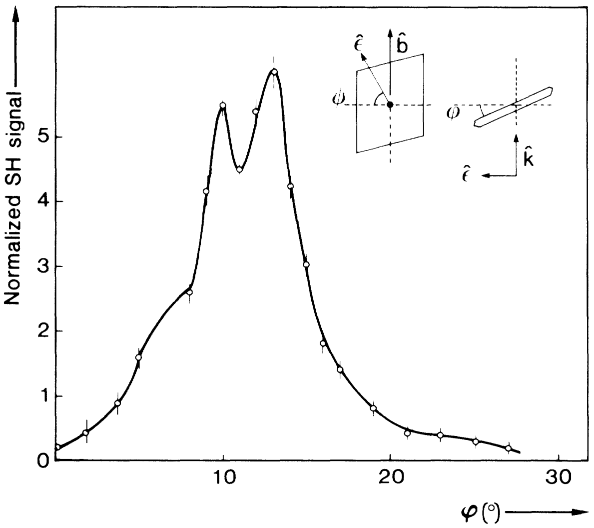

FIG. 2. The intensity of SHG vs the angle ϕ of the rotation around the b axis of the crystal, with $\psi = 45°$.

parallel to the c axis, by rotating a quarter-wave plate. The plot of the intensity of the SHG versus the rotation angle of the quarter-wave plate, ϕ, can hardly be distinguished from that versus ψ in Fig. 1.

In these experiments no phase-matching conditions are constructed, and only a single coherence length will, in general, contribute to the observed SHG. However, by rotating the crystal around the b axis partial phase matching is observed at special angles of incidence (Fig. 2). The intensities of SHG, again polarized along the b axis, increase strongly and reach a value of about 1% of that of the quartz plate. The possibility of partial phase matching proves that the observed SHG is indeed a bulk effect and not due to surface asymmetry. In comparison, SHG in crystals of centrosymmetrical molecules like hexamethylbenzene and p dichlorobenzene was below the detection limit of our setup, which lies at 2×10^{-6} of that of the quartz reference.

It was outlined above that the centrosymmetry of our crystal, verified by x-ray diffraction, rules out that the SHG is due to the normal electric-dipole-effect term in the interaction energy, leading to $\chi^{(2)}(-2\omega,\omega,\omega):\mathbf{E}(2\omega)\cdot\mathbf{E}(\omega)\cdot\mathbf{E}(\omega)$. In view of the presence of chiral molecules in the crystal, we therefore propose that the SHG must be described with a term ${}^{eeh}\chi^{(2)}:\mathbf{E}(2\omega)\cdot\mathbf{E}(\omega)\cdot\mathbf{H}(\omega)$, a nonlinear magnetic term first order in the magnetic field strength.[2-4] This term gives SHG because the circularly polarized component in the fundamental beam interacts differently with the array of R and S enantiomers. The symmetry of our experiments allows a restriction to ${}^{eeh}\chi^{(2)}_{bbb}$ and ${}^{eeh}\chi^{(2)}_{bcc}$.[12] The latter is probably the most important, as the crystal structure is such that the main components of all transition moments (magnetic and electric) are perpendicular to the crystal b axis. In the proposed mechanism of SHG the intensity of the second-harmonic radiation should be quadratic in the total light intensity, as observed. Furthermore, the observed dependence on the rotation angle ψ (see Fig. 1) agrees with the calculated function $\sin^2(2\psi)$, based on the quadratic dependence on (E_cH_c) [or (E_bH_b)]. The remaining constant background (Fig. 1) may be attributed to surface effects. In all cases the second-harmonic wave is mainly plane polarized parallel to the b axis of the crystal (see Fig. 1). This was to be expected as the 2_1 axis that connects the arrays of R (or S) enantiomers forbids any contribution of polarization along the other axes.[13]

The experiment with the quarter-wave plate can be explained directly by noting that it only differs from the experiment of Fig. 1 in the phase at which the fundamental beam enters the crystal. The observation that the intensity of SHG is hardly different in both experiments indicates that the thickness of the crystal is much larger than the difference in optical wavelength for fundamental waves polarized in the b and c directions. Namely, in that case the wave in the crystal varies many times between elliptic and linear polarization, the phase at the surface is irrelevant, and only the intensity of the circularly polarized wave determines the SHG. At present we cannot give a detailed explanation of the partial-phase-matching data because of insufficient knowledge of linear optical data.[14]

It should be remarked that an alternative interpretation of all SHG data in terms of quadrupole effects cannot be ruled out on the basis of symmetry. However, the presence of relatively large magnetic transition moments in the chiral molecules at hand is experimentally well founded. In similar molecules they have been attributed to the n-π^* transition of the CO group ($\simeq 1$ bohr magneton[15]) mixed with the amid π-π^* transition, resulting in a rotational strength of up to 1 Debye-Bohr magneton.[16] No evidence is known in favor of particularly large quadrupole moments. The order of magnitude of the SHG intensity under quasi-phase-match conditions clearly shows that we are not dealing with a weak phenomenon. Therefore, we think that the interpretation given above in terms of magnetic dipoles is by far the most likely one.

The experimental evidence presented above shows for the first time that a nonzero SHG is present in centrosymmetric crystals if chiral molecules and circularly polarized light are used. Moreover, it presents the first demonstration of *optical activity in the nonlinear susceptibility,* similarly to the well-known optical-rotation phenomena in the linear susceptibility. These findings contrast the stated[3] expectation that the magnetic nonlinearity will be so small that it may be detected only because of resonance enhancement, as our results are obtained well off resonance.

It is expected that this phenomenon, or related phenomena due to the interaction term $^{hee}\chi^{(2)}:\mathbf{H}(-2\boldsymbol{\omega})\cdot\mathbf{E}(\boldsymbol{\omega})\cdot\mathbf{E}(\boldsymbol{\omega})$, will be present in a large number of organic crystals of racemic mixtures. The nonzero $\chi^{(2)}$'s found in powders of centrosymmetric crystals of several R,S-amino acids have been explained by possible impurities and crystal defects.[17,18] However, especially the case of R,S-serine (space group $P2_1/a$), showing a rather strong SHG intensity of 0.02 (at 694 nm, relative to potassium dihydrogen phosphate),[17] is most probably explained by the effect of the inherently strong magnetic dipole transition moments, just as the SHG of R,S-N-acetyl valine presented in this Letter. Furthermore, our results show that the well-established method to probe centrosymmetry in crystals by SHG is not strictly valid.

The SHG of centrosymmetric crystals based on chirality and circularly polarized light is not restricted to crystals of pure racemic mixtures. Other candidates are molecules with conformational frozen-in chirality, which are found in some crystals of molecules that are achiral in solution.[19] Even for completely centrosymmetric molecules known as mesocompounds[20] we would expect to find SHG by the mechanism outlined in this Letter. Investigations to study the scope and limitations of this new phenomenon and to increase the SHG by molecular engineering are in progress.

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[12] Note that the last index refers to the direction of the *magnetic* field.

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