the late Professor Theodor Förster. This paper presents some elementary considerations which make the authors' conclusions difficult to accept, and I would venture to say, likely to be indefensible.

The photochemical reaction is the nitrosation, in the 1-position, of 2-naphthol in a buffered (pH 7.0) aqueous solution, a process which is reported to occur only on irradiation and to have a quantum yield of 10^{-4}. The authors believe that the concentration of nitrous acid is a crucial factor and that this is increased by irradiating the naphthol which is a much stronger acid ($\Delta pK_a \sim 6$) in the excited singlet state. The nitrosation is said to involve the reaction of ground-state 2-naphthol with nitrous acid.

Let us consider first the maximum change in the nitrous acid concentration that could possibly be photochemically induced. The aqueous solution is buffered (phosphate) at pH 7.0; the nitrite is initially present at 10^{-3} M. The ionization constant of $HNO_2 = 4.6 \times 10^{-4}$ and the concentration of HNO_2, due to the normal hydrolysis of NO_2^-, is then calculated to be 2.2×10^{-7} M.

The light flux in a Rayonet reactor equipped with 3000-Å lamps is given by the manufacturer as 4×10^{17} quanta $cm^{-3}\ min^{-1}$; this is 7×10^{15} photons $cm^{-3}\ s^{-1}$ or 4.7×10^{-3} J $cm^{-3}\ s^{-1}$. The optical density of the solution, using the published absorption spectrum,[2] should be about 1 cm^{-1}. Let us assume that the flux is actually much larger (~200×), or 1 J $cm^{-3}\ s^{-1}$, and that it is absorbed in a 1-cm path. Now, using the published lifetime for 2-naphthol (ethanol solution) of $\sim 10^{-8}$ s,[2,3] making the usual steady-state assumption, and assuming that every excited naphthol molecule ionizes, we calculate that the steady-state concentration of photochemically produced protons, and hence HNO_2 molecules according to the authors, is 1.5×10^{10} cm^{-3} or 2.5×10^{-11} M. We have previously calculated that $[HNO_2]$ at pH 7.0 is 2.2×10^{-7} M. It is obvious that even under the very large light flux we have assumed the photochemical perturbation of the nitrous acid concentration would be infinitesimal and could not possibly explain the experimental result.

There is another important nonphotochemical point that should be noted. The reaction was carried out in a buffered solution and the authors state that it is possible to change the microscopic acidity of the solution by irradiation. Proton-transfer reactions of oxygen bases in water are among the fastest known chemical processes, and there is no reason to believe that the buffer present at moderate concentration would not function effectively on the nanosecond time scale to maintain the pH at its normal value. In fact, in fluorescence studies of excited-state acidity, buffers are frequently used to fix the solution pH so that the relative amounts of phenol and phenolate ions can be determined as a function of pH, thus making it possible to measure the pK_a^*. The rate of establishment of the excited-acid-base equilibrium becomes an important consideration at low buffer concentrations ($< \sim 10^{-3}$ M). This area has been studied extensively by Weller[4,5] and much of it has been summarized by Parker.[6] The proton-transfer rates in the naphthol-phosphate system would appear to be more than fast enough to allow equilibrium to be established. If there is a slow step, it is probably the ionization of the naphthol which would result in fluorescence (or reaction) from the un-ionized form. Further, we are asked to believe that the nitrite ion (10^{-3} M) is responsible for deprotonation of the excited naphthol when the sum of the concentrations of $H_2PO_4^-$ and HPO_4^{2-} in a standard phosphate buffer of pH 7.0 is 0.05 M, 50 times as high as the nitrite concentration. However, this line of argument is not worth pursuing further in view of the finding that the change in $[HNO_2]$ caused by irradiation could only be 0.01% of its normal concentration.

There are more questions that could be raised but they are not as important as the elementary ones discussed above. The basic point is that the interpretation of any photochemical reaction having a quantum yield of 10^{-4} should be made with at least a modest degree of caution, and that attractive, elegant mechanisms cannot be proposed simply on the basis of esthetic merit. It would indeed be very nice to find some chemical consequences of Förster's discovery but this search is severely hampered by the short lifetimes of excited singlet states.

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Molecular Mechanics of the Ferroelectric to Paraelectric Phase Transition in $LiTaO_3$ via Optical Second Harmonic Generation

Sir:

We report the first use of optical second harmonic generation (SHG) as a technique for determining the molecular structure and mechanics of the phase transition in an octahedrally coordinated system, ferroelectric lithium tantalate.

We relate the bulk SHG coefficient d_{333} to the microscopic Ta–O bond hyperpolarizability β_{lmn} via[1]

$$d_{ijk} = \frac{1}{V} A_{il} A_{jm} A_{kn} \beta_{lmn} \tag{1}$$

where the 3 × 3 matrix A represents the transformation from our microscopic (bond) coordinate system into our macroscopic (crystal) coordinate system and V represents the volume of the unit cell. We assume here that the temperature dependence of A is much greater than that of β, i.e. ($\partial A/\partial T \gg \partial\beta/\partial T$), hence any changes in d vs. temperature can be attributed to changes in A.

In a regular octahedron (Figure 1) the acute angle θ_1 between the top set of Ta–O bonds and the C_3 axis is 54.73° and the obtuse angle θ_2 between the other three Ta–O bonds and the C_3 axis is 125.27°, i.e. ($\theta_2 = 180° - \theta_1$). In our trigonally distorted octahedron ($LiTaO_3$, $R3c$, six molecules per cell[2]), we shall use ϕ to measure the deviation of θ_1 and θ_2 from ideality, viz.,

$$\phi \equiv \theta_1 - 54.73° = \theta_2 - 125.27° \tag{2}$$

This relation mimics the rigorous space group operations ($R3c$) over the expected range of deformation angles, i.e., $0 \leq \phi \leq 6°$. Expanding eq 1 in terms of θ we find

$$d_{333} = \frac{\beta^{\parallel}}{V} (18 \cos^3 \theta_1 + 18 \cos^3 \theta_2) \tag{3}$$

where the 36 Ta–O bonds per unit cell are divided into two types, 18 with positive direction cosines ($\cos^3 \theta_1$) and 18 with negative direction cosines ($\cos^3 \theta_2$). The $\beta^{\parallel}$ term repre-

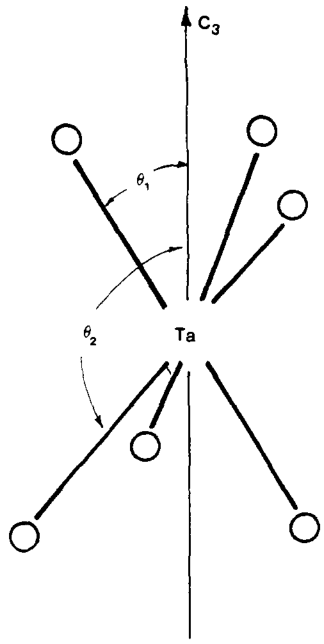

Figure 1. Octahedral distribution of oxygen about Ta in $LiTaO_3$, showing the angles between the crystallographic threefold axis and the top and bottom sets of Ta–O bonds. The deformation angle ϕ ($\phi \equiv \theta_1 - 54.73° = \theta_2 - 125.27°$) defines the degree to which the octahedron is trigonally distorted.

sents the hyperpolarizability parallel to the bond axis. Since the $\beta^{\perp}$ term appeared to make a negligible contribution to d_{333} it has been neglected. Recasting eq 3 in terms of ϕ and recalling that $0 \leq \phi \leq 6°$ one readily finds that

$$d_{333} = \left(-\frac{29.4\beta^{\parallel}}{V}\right)\sin\phi \tag{4}$$

Using the room temperature structural results[2] ($V = 3.171 \times 10^{-22}$ cm^3 and $\phi = 5.3°$) and the room temperature SHG coefficient[3] ($d_{333} = -62 \times 10^{-9}$ esu) we find $\beta^{\parallel} = 7.2 \times 10^{-30}$ esu giving us

$$d_{333} = (-668 \times 10^{-9}\ \text{esu})\sin\phi \tag{5}$$

Since d_{333} vs. temperature has been measured,[4] we can therefore calculate ϕ vs. temperature. The calculated deformation angle ϕ is plotted as a function of temperature in Figure 2. The observed deformation angle's (Δ's in Figure 2) were determined[2] by conventional (x-ray and neutron) techniques. The agreement between the observed (Δ) angle and that calculated via SHG results is quite good.

We now use our ϕ vs. temperature curve to explain another solid-state property, the temperature dependence of the spontaneous polarization P. Using the same formalism as eq 1, i.e.,

$$P_i = \frac{1}{V}A_{ij}\mu_j \tag{6}$$

where P is the observed macroscopic crystalline spontaneous polarization, μ is the microscopic Ta–O bond dipole moment, and A and V are defined as in eq 1. Expanding eq 8 in terms of θ we find

$$P = \frac{\mu}{V}\left[18\cos\theta_1 + 18\cos\theta_2\right] \tag{7}$$

where, as in eq 3, the 36 Ta–O bonds per unit cell are divided into two types, 18 with positive direction cosines ($\cos\theta_1$) and 18 with negative direction cosines ($\cos\theta_2$). Again using eq 2 and the fact that $0 \leq \phi \leq 6°$ we find

$$P = -\frac{29.4\mu}{V}\sin\phi \tag{8}$$

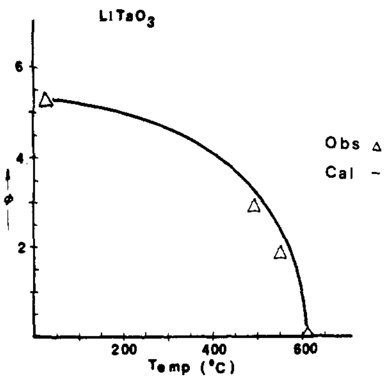

Figure 2. Calculated (—) and observed (Δ) trigonal distortion angle ϕ vs. temperature in $LiTaO_3$.

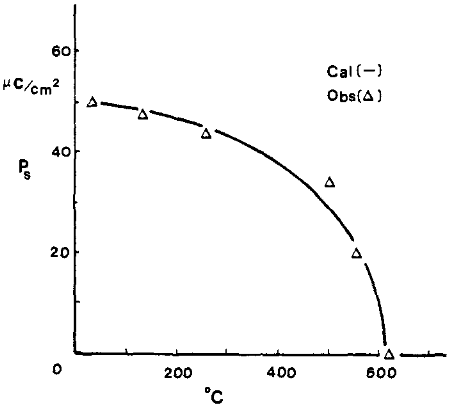

Figure 3. Calculated (—) and observed (Δ) spontaneous polarization (P) of $LiTaO_3$ as a function of temperature.

Combining the room temperature structure results[2] with the measured[4] value of P ($-50\ \mu$C/cm^2 at 25 °C) we find $\mu = 17.5$ D which gives us

$$P = (-541\ \mu\text{C/cm}^2)\sin\phi \tag{9}$$

Since the SHG results gave us the temperature dependence of ϕ, we can thus predict the temperature dependence of P. This is shown in Figure 3. The observed[4] results (Δ's) are in quite close agreement.

This SHG approach represents the first case of an octahedral deformation which is characterized by nonlinear optical results and only the second case[5] where any structural information (intra- and intermolecular bond angles) has been so realized. Previously,[6-8] the temperature-dependent SHG results were either analyzed via order parameters or correlated with other crystalline properties (spontaneous polarization, heat capacity, etc.). We feel that since the experiment (SHG) is so straightforward[1] (laser light into the crystal–optical second harmonic detected leaving the crystal) and the theory so simple, the technique should prove highly useful as a tool for investigating the microscopic details of solid-state phase transitions.

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