Nonphotochemical, Polarization-Dependent, Laser-Induced Nucleation in Supersaturated Aqueous Urea Solutions

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We report a new photophysical phenomenon in which 1.06 μm pulses from a *Q*-switched Nd:YAG laser induce crystallization in supersaturated solutions of urea in water. Because the solutions are transparent at the incident wavelength, a photochemical mechanism is unlikely. The needle-shaped crystals that initially form tend to be aligned parallel to the electric field vector of the light, suggesting a Kerr-like field-induced alignment of urea molecules that aids in organizing prenucleating clusters. The effect has application to pump-probe nucleation studies and to clean nucleation in sealed systems. [S0031-9007(96)01456-1]

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The study of the light-induced condensation of supersaturated vapors dates back to the work of Tyndall in 1869 [1]. More recent interest has centered on the formation of atmospheric aerosols [2], laser-induced chemical vapor deposition [3], and laser-induced clustering in atomic and molecular systems [4]. The mechanism typically involves the photochemical generation of a nonvolatile product that acts as a nucleus for the growth of the condensed phase [5].

Nucleation in liquid solutions is a more complex problem involving two components, and, to our knowledge, there have been no reports of light-induced nucleation from supersaturated solutions. Nevertheless, this problem is of great theoretical and commercial importance, such as in industrial crystallization processes [6].

Recently, while attempting to observe second harmonic generation in supersaturated solutions of urea in water, we have noticed that pulses from a *Q*-switched Nd:YAG laser can induce nucleation in such solutions. Because the incident light source is near infrared, a photochemical mechanism is unlikely. The orientation of the crystallites that are formed depends on the plane of polarization of the incident radiation, suggesting an electric-field-induced effect.

Aqueous urea solutions, with concentrations, c, in the range of 11.5-13.5M, were prepared by combining solid urea and water in a 1.3-cm diameter pyrex test tube, which was then heat sealed with a torch. Great care was taken to exclude dust from samples. Supersaturated solutions were generated and regenerated by heating the tubes to 45 °C and holding them at that temperature for several days. Once the urea was completely dissolved, the solutions were slowly cooled to room temperature. Solutions prepared in this way lasted for several weeks before spontaneously nucleating. At 25 °C, the solubility of urea, c_{sat}, is 10.47M [7], so the solutions studied had supersaturations, c/c_{sat}, ranging from 1.10 to 1.29.

After aging for one to two weeks, solutions were illuminated with the 1.06-μm wavelength, plane-polarized output of a Quanta-ray DCR-1 *Q*-switched Nd:YAG laser. The polarization of the beam was controlled with a zero-order quartz half-wave retardation plate. The polarization was switched between vertical and horizontal by rotating the wave plate. A portion of the doughnut-shaped beam with approximately constant intensity was selected by passing the beam through an aperture with an area of ~ 2 mm^2. With the oscillator alone, the measured energy per pulse was 0.02 J, while with the amplifier added, it was 0.1 J. The measured pulse width was 20 ns, and the pulse repetition rate was 10 pps. The unamplified and amplified pulses thus had intensities of 50 and 250 MW/cm^2, respectively.

Test tubes containing aged solutions were placed in the path of the laser beam. The oscillator alone was not sufficient to induce nucleation. With the amplifier added, nucleation typically occurred within 10–20 s. The onset of nucleation was observed visually by the formation of a needle-shaped crystallite. Shortly thereafter (within tens of seconds), the complete sample solidified, forming a complex polycrystalline mass.

When the laser was vertically polarized, the initial crystallite was observed to be oriented approximately vertically (to within $\sim 5°$). When the laser was horizontally polarized, the initial crystallite was oriented approximately horizontally. These correlations were consistently observed for 12.0, 12.5, and 13.0M solutions. The 11.5M solutions failed to nucleate on exposure to the laser beam. The 13.5M solutions were difficult to get into solution, and generally did not last long enough to study, owing to spontaneous nucleation.

The urea solutions studied are highly transparent at the laser wavelength of 1.06 μm. Urea has no electronic absorption bands above 200 nm, and no vibrational bands below 1.4 μm [8]. Multiphoton absorption in urea at 1.06 μm is also insignificant. Thus photochemical effects are improbable. Furthermore, the formation of a permanent photochemical product would make solution regeneration difficult owing to spontaneous nucleation; we had no trouble regenerating solutions. The reported absorption coefficient, α, of solid urea is 0.02 cm^{-1} at 1.06 μm

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[9]. Any sample heating owing to this residual weak absorption would tend to make the supersaturated solution *more* stable. In addition, the average power of our 10 pps laser is sufficiently low to make heating negligible.

The polarization dependence of the crystallite orientation is consistent with a mechanism in which the electric field of the light plays a major role. It appears that urea molecules are being aligned by the applied optical field, just as they are in the optical Kerr effect [10], also known as light-induced birefringence. For the optical Kerr effect in liquids (and solutions), the incident electric field induces a dipole moment in the molecule. The same field interacts with the induced dipole, applying a torque to the molecule and causing it to tend to align so that its most polarizable axis is parallel to the field. The resulting medium becomes birefringent, with an optic axis parallel to the direction of the applied field.

In a supersaturated aqueous urea solution, urea clusters are constantly forming and breaking up. In crystallization by nucleation and growth, a urea cluster must form that exceeds the critical size (and, presumably, a critical level of organization) necessary to become stable and continue to grow [11]. The applied electric field aids in organizing the existing prenucleating clusters, increasing the chances that one will nucleate and grow. In other words, the electric-field-induced alignment reduces the entropic contribution to the free energy of activation for the induction of nucleation.

Although urea has a permanent dipole along the twofold C_2 rotation axis [see Fig. 1(a)], only its anisotropic polarizability is responsible for electric-field-induced alignment at optical frequencies [10]. The most polarizable axis of urea coincides with the C_2 axis [12]. The crystal structure and growth habit of urea are shown in Figs. 1(b) and 1(c), respectively. The molecular C_2 axis is parallel to the crystallographic {001} direction, which is also parallel to the needle axis of urea crystals grown from aqueous solution [8,13]. Thus, according to our proposed mechanism, urea molecules in a cluster will tend to align with their C_2 axes parallel to an applied electric field, **E**, growing into a crystallite with the needle axis parallel to **E**. This is consistent with our experimental observations, although it does not rule out possible alternative explanations.

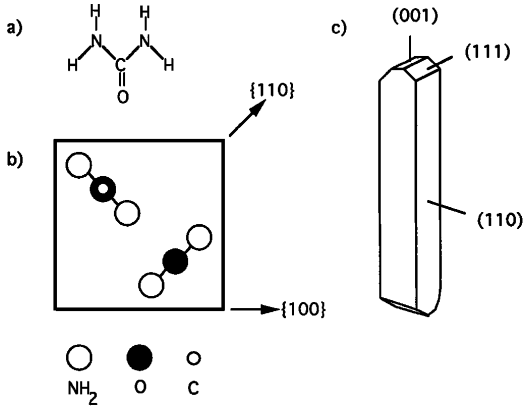

FIG. 1. (a) Structure of urea molecule. The C_2 axis coincides with the $C{=}O$ bond. (b) Unit cell of urea crystal, consisting of two antiparallel urea molecules, projected onto the (001) plane [8]. (c) Needle-shaped urea crystal, formed from aqueous solution, with crystallographic faces indicated [14].

We have observed a new photophysical phenomenon, related to the optical Kerr effect, in which the electric field of a plane-polarized laser beam induces crystallization in a supersaturated solution. We are continuing to study the effect of other polarization states on the urea-water system, as well as expanding the study to other systems. The phenomenon has potential applications in pump-probe experiments in which one could follow the early stages of nucleation and growth in supersaturated solutions. It also provides a method for the "clean" induction of nucleation without the need for introducing impurities into a sealed system.

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