

## Intense Mechanoluminescence and Gas Phase Reactions from the Sonication of an Organic Slurry

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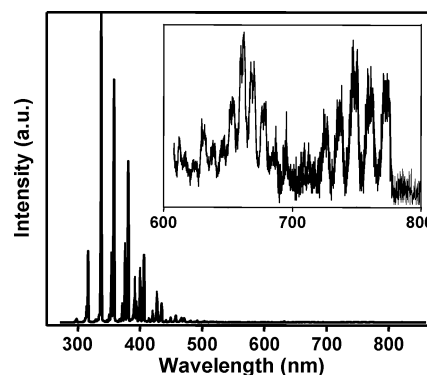
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Mechanoluminescence (ML, also known as triboluminescence or fractoluminescence) is the emission of light due to the application of mechanical stress to a crystal.<sup>1</sup> This light is the result of a dielectric breakdown of the intervening gas and the crystal caused by internal electrification at the fracture plane of a piezoelectric crystal. When ML is induced by such mechanical means as grinding, scratching, or cleaving, a spectrum is observed consisting of line emission of the gas present and sometimes the crystal itself.<sup>1,2</sup> In fact, the first report of ML goes back to 1605, when Francis Bacon noted that lumps of sugar emitted light when scraped.<sup>3</sup> When a liquid is irradiated with high-intensity ultrasound, micron-sized bubbles can be driven into violent collapse, sending shockwaves outward into the liquid.<sup>4</sup> If small solid particles are suspended in the liquid, the shockwaves can accelerate them to high velocities (several hundred m/s vs cm/s for manual grinding) causing intense interparticle collisions.

We report here the initiation of ML using acoustic cavitation and observe extensive atomic and molecular emission not previously seen during a mechanoluminescent event. In addition, we have the first evidence of chemical reactions occurring during a ML event. We recently reported ML from sonication of slurries of piezoelectric organic crystals in long chain alkanes,<sup>5</sup> and the N<sub>2</sub> ML emission from sonication of sucrose was an order of magnitude more intense than that from grinding. We report here that sonication of a slurry of resorcinol in dodecane sparged with N<sub>2</sub>, the N<sub>2</sub> (C<sup>3</sup>Π<sub>u</sub> – B<sup>3</sup>Π<sub>g</sub>) and the N<sub>2</sub><sup>+</sup> (B<sup>2</sup>Σ<sup>+</sup><sub>u</sub> – X<sup>2</sup>Σ<sup>+</sup><sub>g</sub>) emission spectrum (Figure 1), is more than 1000-fold more intense than that from manual grinding. We have also observed new emission lines not previously seen during ML (including CO, CO<sup>+</sup> and CO<sub>2</sub><sup>+</sup>, H, C<sub>2</sub>, and CH) showing the existence of chemical reactions during the ML event.

When a slurry of resorcinol is sonicated in the presence of He, several new atomic and molecular emission series are observed, in addition to the crystal luminescence and strong He discharge. These include He<sup>+</sup> (~77 eV above the 1s state of He), multiple transitions from the Swan band of C<sub>2</sub> (d<sup>3</sup>Π<sub>g</sub> – a<sup>3</sup>Π<sub>u</sub>), the CH (A<sup>2</sup>Δ – X<sup>2</sup>Π) transition, and the H α line (Figure 2A). When the same slurry is sparged with O<sub>2</sub>, the same crystal luminescence, C<sub>2</sub> and CH discharges are still present, and in addition, emissions from O, CO (b<sup>3</sup>Σ – a<sup>3</sup>Π), (C<sup>1</sup>Σ – A<sup>1</sup>Π) and (B<sup>1</sup>Σ – A<sup>1</sup>Π), CO<sup>+</sup> (B<sup>2</sup>Π – X<sup>2</sup>Σ), and CO<sub>2</sub><sup>+</sup> (A<sup>2</sup>Π – X<sup>2</sup>Π) are newly observed (Figure 2B). The emission of C<sub>2</sub>, CH, CO, CO<sup>+</sup>, and CO<sub>2</sub><sup>+</sup> has never been reported before from any ML event. It should be noted that the Swan band of C<sub>2</sub> as well as the CH transition at 431 nm are commonly observed in simple sonoluminescence (SL) of hydrocarbons,<sup>6</sup> but the lines from such SL are substantially broader and very much weaker than the observed ML (cf. Supporting Information, Figure S1).

The multitude of new features arising in the ML spectra could have arisen from either the liquid or the solid. The results of sonication of slurries of resorcinol in dodecane (C<sub>12</sub>H<sub>26</sub>) versus

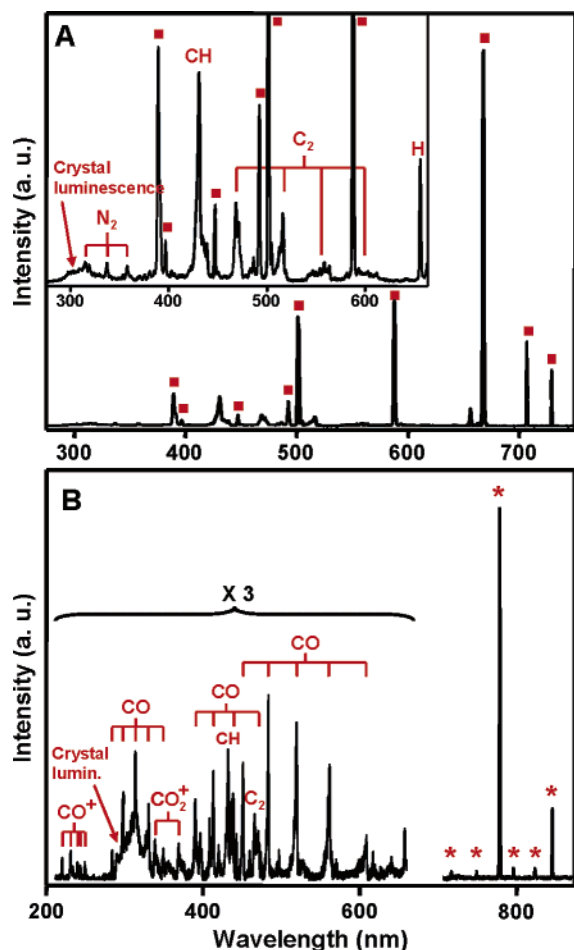


**Figure 1.** ML from sonication of resorcinol crystals in hexadecane (10% w/w), sparged with N<sub>2</sub> at 300 K irradiated with ultrasound at 20 kHz, 6 W/cm<sup>2</sup>. The spectrum contains N<sub>2</sub> (C<sup>3</sup>Π<sub>u</sub> – B<sup>3</sup>Π<sub>g</sub>) and N<sub>2</sub><sup>+</sup> (B<sup>2</sup>Σ<sup>+</sup><sub>u</sub> – X<sup>2</sup>Σ<sup>+</sup><sub>g</sub>) progressions (from 300 to 500 nm). The inset (~1000-fold intensity enlargement) shows very weak emission from N<sub>2</sub> (B<sup>3</sup>Π<sub>g</sub> – A<sup>3</sup>Σ<sup>+</sup><sub>u</sub>), which has not been reported for any prior mechanoluminescent system (presumably due to its inherently low emissivity).

perdeutero-dodecane (C<sub>12</sub>D<sub>26</sub>) are shown in Figure 3. In the dodecane slurry, only CH emission is observed, whereas in the perdeutero-dodecane slurry, only CD emission is present. This indicates that the carbon-containing small molecules in the ML spectra are from the liquid and *not* the crystal.

The low vapor pressure of the dodecane and hexadecane, however, presents us with a paradox because it seems unlikely that the new emitting species can arise *directly* from the vapor of the liquid itself. Sonication of long chain alkanes, however, is known to produce small hydrocarbons (i.e., CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>) and H<sub>2</sub>;<sup>7</sup> moreover, when a reactive gas is present (such as N<sub>2</sub> or O<sub>2</sub>), other sonolysis products are formed, such as CN and CO<sub>2</sub>.<sup>6,7</sup> We hypothesize that the observed CH, C<sub>2</sub>, and H originate from the dielectric discharge of sonolysis products and *not directly* from the low volatility liquid hydrocarbons themselves. To test this, a slurry of resorcinol and dodecane was sparged with He and then sonicated in a sealed cell *without* further sparging; the intensity of the CH and H emission increased upon multiple sonications, which is consistent with our hypothesis that the volatile sonolysis products of the liquid play a major role in the discharge emission.

The origin of the CO, CO<sup>+</sup>, and CO<sub>2</sub><sup>+</sup> and their emission must arise during the dielectric breakdown from chemical reactions, either of CO<sub>2</sub> produced during sonolysis or of O<sub>2</sub> with small hydrocarbon sonolysis products (e.g., CH<sub>4</sub> or C<sub>2</sub>H<sub>2</sub>). When a slurry of resorcinol in hexadecane sparged with CO<sub>2</sub> was sonicated, the CO<sub>2</sub><sup>+</sup> (A<sup>2</sup>Π – X<sup>2</sup>Π) and (A<sup>2</sup>Σ<sup>+</sup> – X<sup>2</sup>Π) emission bands were observed, with no visible emission from CO, CO<sup>+</sup>, or O, which are the main components of the ML from O<sub>2</sub> sparged slurries containing resorcinol (Figure 2b). The production of CO and CO<sup>+</sup> is therefore due to discharge reactions of small hydrocarbons with O<sub>2</sub> and not

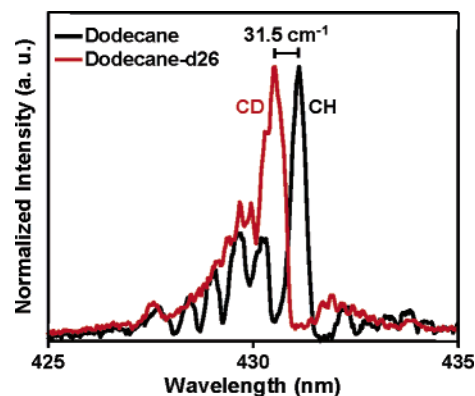


**Figure 2.** (A) ML from sonication of a slurry of resorcinol powder (150–250  $\mu\text{m}$ ) in hexadecane (10% w/w) sparged with He, showing very strong emission from He excited states (■). The inset (10-fold intensity enlargement) shows extensive  $\text{C}_2$  ( $d^3\Pi_g - a^3\Pi_u$ ), CH ( $A^2\Delta - X^2\Pi$ ), and H  $\alpha$  line emission. Under these conditions, no SL was observed. (B) ML from sonication of resorcinol in hexadecane sparged with  $\text{O}_2$ , showing both O atom emission (\*) and extensive molecular emission. The intensity of the region from 200 to 650 nm is multiplied by 3 to show the features, including  $\text{CO}^+$  ( $B^2\Pi - X^2\Sigma$ ), CO ( $b^3\Sigma - a^3\Pi$ ) (280–350 nm), ( $C^1\Sigma - A^1\Pi$ ) (368–466 nm) and ( $B^1\Sigma - A^1\Pi$ ) (450–610 nm),  $\text{CO}_2^+$  ( $A^2\Pi - X^2\Pi$ ),  $\text{C}_2$  ( $A^3\Pi_g - X^3\Pi_u$ ), and CH ( $A^2\Delta - X^2\Pi$ ). Under these conditions, direct SL is broad, featureless, and of low intensity (<4% of the O line at 774 nm (see Supporting Information, Figure S1); this weak SL has been subtracted from the spectra shown).

from  $\text{CO}_2$ . Consistent with our results, electric discharge through  $\text{CH}_4$  or  $\text{C}_2\text{H}_2$  and  $\text{O}_2$  (used for the production of diamond films) gives emission from CH,  $\text{C}_2$ , H, CO,  $\text{CO}^+$ , and O.<sup>8</sup>

Another possible source of the intense discharge could have been frictional electrification caused by rubbing two dissimilar materials together (i.e., static charging). To determine whether crystal fracture or frictional electrification are responsible for our observed ML, the sonication cell was equipped with replaceable windows. The windows were varied from insulator (Plexiglas) to semiconductor (quartz and glass) to conductor (ITO coated glass); in otherwise identical experiments, no change in the intensity of ML was observed. This makes frictional electrification an untenable explanation because no electrification could have occurred with the conductive ITO window.<sup>9</sup>

Exposing slurries of solid resorcinol to acoustic cavitation yields very intense ML, up to 1000-fold brighter than that from grinding. Interestingly, it is the gas emission that is dramatically increased, whereas the crystal luminescence increase is nearly negligible



**Figure 3.** ML spectra from sonication of resorcinol slurry (10% w/w) in dodecane or deuterated dodecane ( $\text{C}_{12}\text{D}_{26}$ ), sparged with He. Unlabeled dodecane gives CH emission; deuterated dodecane gives CD emission.

(Figure S2); this means that the increased ML intensity cannot be due exclusively to the simple increase in the number of interparticle collisions or fractures per second, but must also reflect the increase in velocity of the collisions and the efficacy of the fractures during sonication compared to simple grinding. With this increased ML intensity, we have also observed new emission lines not previously seen during ML and have obtained evidence of gas phase chemical reaction between  $\text{O}_2$  and small hydrocarbons during the ML event. With this new mechanism to induce mechanoluminescence, we expect that the ML event can now be analyzed more rigorously, using plasma diagnostics, to determine temperature, pressure, and electron energy and density during the discharge events.

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**Supporting Information Available:** Experimental details and additional ML spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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