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Contribution No. 3368 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Triboluminescence of Uranyl Nitrate

JEFFREY I. ZINK

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The triboluminescence (TL) of uranyl nitrate hexahydrate is a phosphorescence centered on the uranyl ion. The vibronic structure in both the TL and the photoluminescence spectra have the same relative intensities and energy spacings as is expected when the lifetime of the TL is long compared to mechanical relaxation processes in the crystal. The title compound is the first nonaromatic molecule whose TL originates from a molecular excited state and not from a gas discharge. The physical origins of the TL within a crystal and the implausibility of an intramolecular TL excitation mechanism are discussed.

Triboluminescence (TL) is the emission of light caused by the application of mechanical stress of crystals. The phenomenon was known in the 16th century[1] and was named by Wiedemann in 1895.[2] The prefix originates from the Greek "tribein," to rub. Historically, the best known triboluminescent crystal was sugar.[1]

The original explanation of TL was based on triboelectrification or piezoelectrification, *i.e.*, the buildup of a static charge as a result of the mechanical action applied to the solid, followed by electrical arcing to produce a gas discharge. Nonspectroscopic proof of the gas-discharge origin of TL was provided by the observation that *cis*-octene produced blue-white TL flashes in air but orange-red flashes in an atmosphere of neon.[3] The gas-discharge origin of the TL of NaF was proven spectroscopically.[4] The motion of mercury over solids has been shown to produce both luminescence and a large electric potential difference.[5,6] Two additional excitation mechanisms, intermolecular interactions and intramolecular deformations, have been recently proposed (*vide infra*).

Our interest in TL stems from our discovery that the emission can occur from sources other than ambient gas discharge. In particular, we have spectroscopically found examples of fluorescence (coumarin),[7] phosphorescence (hexaphenylcarbodiphosphorane[8] and phthalic anhydride[9]), and both simultaneously (acenaphthene[9]) from the respective molecules in the crystal. The latter two compounds are unusual because the tribophosphorescence occurs at room temperature while the photophosphorescence occurs only at much lower temperatures. Together with the semiquantitatively identified tribophosphorescence of tetrakis(dibenzoylmethido)europium(III) salts,[10] the above list encompasses all of the previously known triboluminescent compounds whose emission origins are excited states of molecules in crystals.

TL originating from excited states of molecules in the crystal is important for two reasons. First, for practical applications, it will be desirable to be able to "tune" the wavelength and intensity of the emission by modifying the molecular constituents of the crystal. Second, new excitation mechanisms may be operating which will probe the mechanical and optical properties of the triboluminescent crystals. We have found[7] that the short-lived ($\sim 10^{-9}$ sec) fluorescence of coumarin contains new dynamic features, absent in the photoluminescence spectrum, which are characteristic of the crystal under stress.

A feature common to all of the above triboluminescent molecules whose TL has been identified as a molecular fluorescence or phosphorescence is the presence of one or more phenyl groups. In this paper the TL of uranyl nitrate hexahydrate, the first example of tribophosphorescence originating from a nonaromatic molecule in a crystal, is reported. The photoluminescence spectra and TL excitation mechanism are also discussed.

Experimental Section

All spectra were recorded using a Jarrell-Ash 0.25-m grating monochromator with an EMI 9558 photomultiplier in a Products for Research variable-temperature refrigerator housing and were not corrected for the response characteristics of the instrument. The photoluminescence spectra were excited by a 100-W high-pressure mercury lamp focused through a Bausch and Lomb grating monochromator. The spectra were unaffected by the wavelength of the exciting light. The samples for both the photoluminescence and the TL spectra were contained in Pyrex vials.

The TL spectra were obtained by grinding 4-g samples contained in 0.75-in. diameter Pyrex vials with a stainless steel rod. TL was also excited by grinding the sample with nonconducting implements such as quartz, wood, and Teflon as well as with metals other than stainless steel. Intense TL could also be excited by the thermal shock of dipping the sample into liquid nitrogen. All of the above mechanical methods produced TL of qualitatively the same intensity and all methods produced the same TL spectrum as visually observed through a spectroscope.

The TL is emitted in the form of green flashes whose intensity is directly related to the mechanical energy exerted on the crystals. As the crystals were ground to an increasingly fine powder, the intensity diminished. In order to obtain the TL spectrum, the intensity at a given wavelength was normalized using the experimental arrangement shown in the block diagram in Figure 1. A TL flash was monitored at a given wavelength with the monochromator described above. The total intensity of the flash was simultaneously monitored using a 1P28 photomultiplier. The two signals were recorded and the ratio of "wavelength" intensity to total intensity was computed and plotted. The primary source of error in the spectrum is the slightly different geometric positions of the two photomultipliers relative to the TL flash. The signal to noise ratio is 53.

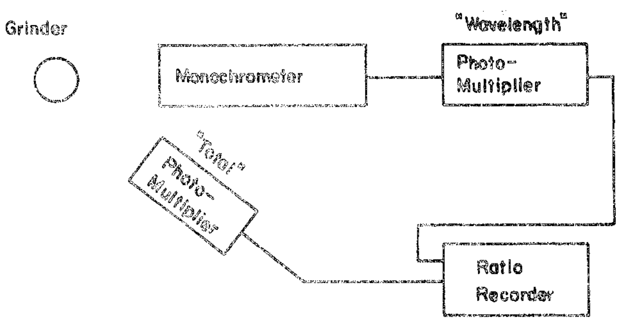

Figure 1. Block diagram of the triboluminescence spectrometer.

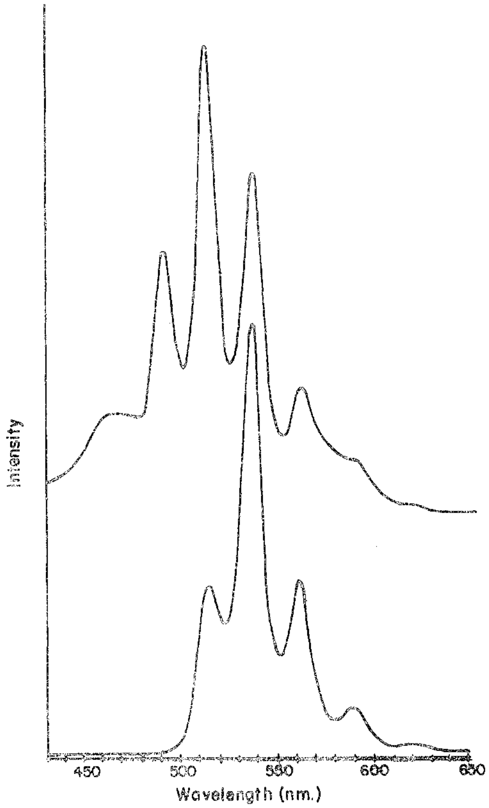

Figure 2. Room-temperature photophosphorescence of $UO_2(NO_3)_2 \cdot 6H_2O$: a (top), powder; b (bottom), large crystals.

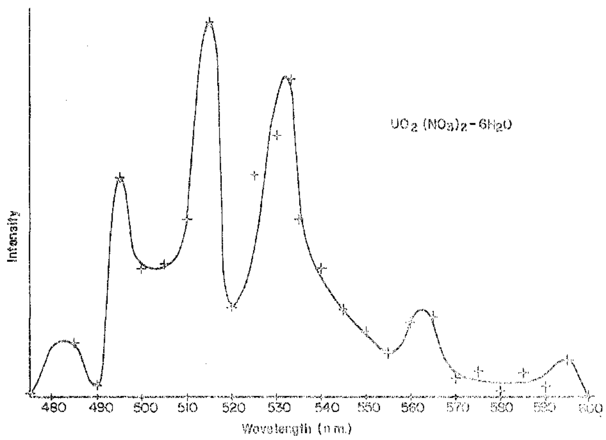

Figure 3. Triboluminescence spectrum of $UO_2(NO_3)_2 \cdot 6H_2O$.

Spectroscopic Studies

Photoluminescence. The photoluminescence spectrum of solid $UO_2(NO_3)_2 \cdot 6H_2O$ at room temperature is shown in Figure 2. This luminescence is characteristic of the hydrated UO_2^{2+} ion and has been assigned as a $^3\Pi_u \rightarrow {}^1\Sigma_g^+$ phosphorescence[11] (*vide infra*). The lifetime is between 10 and 70 msec.[11] The prominent vibronic peaks in the spectrum, spaced at an average interval of 840 cm^{-1}, arise from coupling with the symmetric O–U–O stretch (σ_g^+).[12] The phosphorescence spectrum is independent of the wavelength of absorbing light and the quantum yield is near unity.[11]

Several aspects of our spectra merit further comment. First, the spacings and relative intensities of the vibronic structure remain almost identical in the phosphorescence spectra of the sample in the solid state and in aqueous solutions although the spectrum of the solid is slightly blue-shifted (*ca.* 30 cm^{-1}). The phosphorescence of the uranyl ion has been shown to be relatively insensitive to the nature of the anion and to the number of waters of hydration.[12] (The maximum shift is several hundred reciprocal centimeters.) The above observations support the assignment of the phosphorescence as a transition localized on the uranyl ion. Second, the relative intensities of the first several vibronic bands are very sensitive to the size of the crystals. Self-absorption of the highest energy vibronic bands of the phosphorescence by the absorption band of unexcited molecules in large crystals accounts for the diminished intensity. Finally, as was first discussed by McGlynn,[11] the excited state as well as the ground state of UO_2^{2+} is linear. If a previous proposal[13] that the emitting state is bent were correct, long progressions of the bending mode would be expected contrary to experiment.

Triboluminescence. The TL spectrum of uranyl nitrate hexahydrate is shown in Figure 3. The TL is almost identical with the photophosphorescence of uranyl nitrate powder and exhibits almost identical vibronic intervals and relative intensities. Because of the correspondence of the photophosphorescence and TL spectra, the TL is identified as the uranyl $^3\Pi_u \rightarrow {}^1\Sigma_g$ phosphorescence.

The similarity of the two spectra is consistent with our previous discovery[8] that the tribophosphorescence spectra of molecules which photophosphoresce at the same temperature do not exhibit any new or unusual features. Because of the relatively long lifetimes of phosphorescence (microseconds), the emission occurs after the crystal and/or molecules have relaxed from the effects of the mechanical stress. In contrast, the spectra of tribofluorescent crystals, whose emission occurs on a much shorter time scale (nanoseconds or shorter), do contain new features characteristic of the system under stress.[7] For the third class of crystals, those which triboluminesce but do not photoluminesce at the same temperature, the two luminescence energies correspond closely but the band shapes do not because of the different temperature conditions at which the spectra must be measured.[9]

A qualitative assessment of the physical origin of the TL in the uranyl nitrate crystal can be made from the observed intensity distribution of the vibronic bands in the TL spectrum. If the TL originated primarily from the center of large crystals, the TL spectrum would have the vibronic pattern of Figure 2b, while if the TL originated from the surfaces of large crystals or from small crystals, the spectrum would look like Figure 2a. From a qualitative comparison of Figure 3 with Figure 2 it would appear that the TL originates primarily either from small crystals or from near the surface of large crystals.

Rejection of an Intramolecular Excitation Mechanism for UO_2^{2+}. Three general triboexcitation mechanisms are currently under active consideration: electrical excitation, intermolecular interactions, and intramolecular deformation (IMD). The first is in essence a pressure-induced electroluminescence.[4] It was proposed as a mechanism for the TL of doped zinc sulfide on the basis of the similarity of the electroluminescence and TL spectra.[4,14] It was also proposed for the TL of scintillator compounds excited by mercury flowing over their surfaces.[6] The second mechanism, intermolecular interactions, would excite the crystal by forcing the system to follow an intermolecular state potential surface (*e.g.*, a charge-transfer state) as the pressure is applied. Spectroscopic evidence for a possible pressure-induced charge-transfer state[9] and for pressure-induced excimers[7,9] has been reported. The limit of a pressure-induced charge transfer would be charge separation in the crystal which could provide a link with the electrical mechanism. The intermolecular mechanism is most probable in aromatic systems which readily form charge-transfer complexes[15] and excimers.[16] A third possible triboexcitation mechanism is the intramolecular deformation of the chromophore. According to this mechanism, the effect of pressure on a crystal results in the deformation of molecules in the crystal such that (i) the total energy of a molecule is raised above that of the lowest excited state of the undeformed molecule and (ii) an efficient mechanism of energy transfer to the state of the deformed molecule which correlates with the emitting state of the undeformed molecule is produced by the deformation. The two general requirements of the mechanism will be clarified by the discussion to follow. We originally proposed the IMD mechanism as an explanation for the TL of hexaphenylcarbodiphosphorane which contains a P–C–P chromophore.[8] However, we recognized that it cannot be general for all triboluminescent crystals.[7]

Because of the localized nature of the electronic transition on the $O{-}U{-}O^{2+}$ chromophore and the detailed electronic and vibrational parameters which can be derived from the photophosphorescence and TL spectra, the $O{-}U{-}O^{2+}$ ion provides an ideal system for which the IMD mechanism can be analyzed in detail. In this section, two semiquantitative theoretical treatments are presented which cast doubt on the plausibility of the IMD mechanism for the uranyl ion.

The two distinct intramolecular distortions induced by pressure on the linear O–U–O chromophore are O–U–O bond bending and O–U bond compression. The bond bending destroys the axial symmetry while the bond compressions (both symmetric and antisymmetric) retain the axial symmetry. The vibrational normal modes of the ground-state molecule corresponding to the above pressure-induced deformations are (1) the bend (ν_b 140 cm^{-1}) and (2) the symmetric stretch (ν_s 880 cm^{-1}) and the asymmetric stretch (ν_a 950 cm^{-1}),[12,17] respectively.

The effects of bending and of symmetrically compressing the $UO_2{}^{2+}$ chromophore on the one-electron molecular orbitals are respectively shown on the right and left sides of the correlation diagram (Figure 4). The correlation of molecular geometry with orbital energies was pioneered by Walsh[18] and has been profitably used to understand the geometries of many triatomic entities such as a recent application to M–N–O.[19] Exactly the opposite use will be made of the correlation diagram here. Instead of determining the geometry from the relative orbital energies, we will examine the energetics on the basis of the pressure-induced geometrical distortions.

The construction of the diagram makes use of the known linear geometry in both the ground and lowest excited states, the measured decrease of the force constants in the lowest excited state,[11] and the molecular orbital calculations of McGlynn of the ground-state molecule.[11] Only the two sets of highest occupied molecular orbitals (HOMO's, $1\pi_u$ and $1\pi_g$) and the two sets of lowest unoccupied molecular orbitals (LUMO's, δ_u and ϕ_u) of the $D_{\infty h}$ molecule taken from McGlynn's calculations will be considered. The two HOMO's are both weakly π bonding while the two LUMO's are both comprised of nonbonding f orbitals. The photoluminescence and the TL arise from a $(1\pi_g)^3(\delta_u)^1 \rightarrow (1\pi_g)^4$ transition.

The effects of a symmetrical compression are shown on the left of the diagram. All four levels will rise in energy. The nonbonding orbitals rise primarily because of increased crystal field effects. The energy of the $1\pi_g$ set should increase more rapidly than the others because of increased out-of-phase overlap of the oxygen p orbitals. The final form of the diagram is qualitatively correct and consistent with (i) the relative orderings expected in the united atom limit (*i.e.*, complete compression) and (ii) the decreased U–O force constant in the lowest excited state.

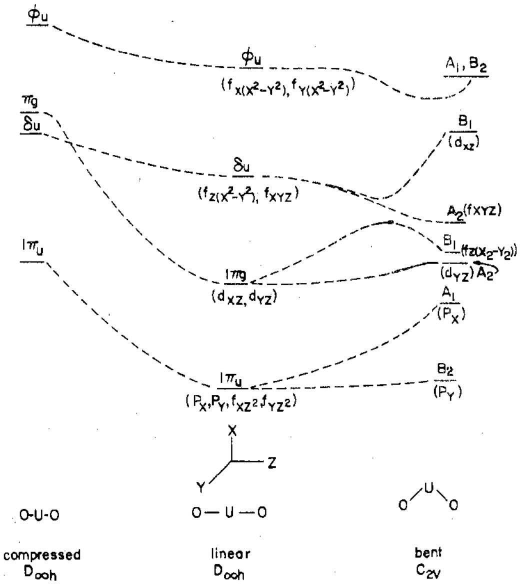

Figure 4. Correlation diagram for the two highest filled molecular orbitals ($1\pi_u$ and $1\pi_g$) and for the two lowest empty molecular orbitals (δ_u and ϕ_u) of $UO_2{}^{2+}$ as a function of compression (left) and bending (right).

The effects of bending $UO_2{}^{2+}$ are shown on the right side of the diagram. All of the π-bonding orbitals will be destabilized with $1\pi_g$ rising faster than $1\pi_u$ because of increased out-of-phase overlap of the oxygen p orbitals. The correlations for the π orbitals as the symmetry is changed from $D_{\infty h}$ to C_{2v} are $\pi_u \rightarrow A_1 + B_2$ and $\pi_g \rightarrow A_2 + B_1$. As the bend increases, the gain of O–O out-of-phase overlap is largest in the direction of the bend (the x direction). These results are consistent with orderings expected in the "united oxygen" limit (*i.e.*, the bending limit where the oxygens are superimposed on the x axis). The formally nonbonding δ_u and ϕ_u f orbitals in $D_{\infty h}$ can interact with linear combinations of oxygen orbitals of A_2 and B_1 and of A_1 and B_2 symmetries, respectively, in C_{2v}. Only the bonding interactions of δ_u and ϕ_u are illustrated in the diagram. The components of ϕ_u need not in general remain degenerate. They are drawn as such because their relative energies cannot be readily estimated. At large bends, the B_1 (and more weakly the A_2) orbitals from π_g will mix with B_1 and A_2 from ϕ_u as shown on the far right. It should be emphasized here that the following discussion will rely only on the increase of π_g and the decrease of δ_u with increasing bend and not on the details of the energetics of the other orbitals. Thus, the discussion will be based on the changes known with the most certainty.

The IMD mechanism can be explicitly analyzed using the diagram. As a pressure-induced distortion increases, the electronic population of $1\pi_g$ will follow the rising curve until it crosses or strongly mixes with another curve. At the crossing point or point of minimum vertical separation, a transition to the new state can occur with a probability given by the Zener–Landau expression.[20,21] Upon release of the pressure, the molecule will revert back to its ground-state geometry and the electronic population will again follow the appropriate curves. If, as a result of the distortion the δ_u orbital becomes occupied, triboluminescence can occur.

The bending distortion is not a plausible mechanism for populating δ_u. When the molecule is bent, the point of minimum vertical separation occurs at an energy lower than that of the δ_u orbital in the undistorted molecule. Thus, populating δ_u in the bent geometry would require that additional energy be supplied in order for δ_u to be populated in the linear geometry. This additional energy either could be abstracted from the crystal or could originate from vibrational energy of the UO_2^{2+} ion itself if the total energy of the states at the crossover point were greater than that of the $^3\pi_u$ state in the linear molecule. In either case, a consequence of this analysis is that the TL intensity should decrease as the temperature is decreased, contrary to our experimental observations. Thus, the bending IMD is not a likely mechanism.

In contrast, the compression could populate the δ_u orbital. However, the energy of the crossing point is well above the energy of the δ_u orbital in the undistorted molecule. In order to assess the reasonableness of this mechanism, a quantitative estimate of the amount of compression needed to reach the crossing point is required. Using the harmonic oscillator approximation and the U–O force constant of 0.715 mdyn/Å,[22] a compression of 1.1 Å is required to raise the energy of the system to that observed in emission (2.5 eV). Because of the increase in anharmonicity in higher vibrational levels, the above compression is an overestimate. On the other hand, more than 2.5 eV is required to reach the crossing point requiring a larger compression. A compression on the order of 1 Å is probably a reasonable estimate. However, 1 Å represents a 50% shortening of the 2-Å U–O bond. It is difficult to imagine how such compression can occur before relaxation processes such as shear and fracture of the crystal release the pressure. However, although the compression IMD mechanism appears unlikely, it cannot be totally ruled out.

Although the UO_2^{2+} ion is ideal for analysis of the IMD mechanism, it does not lend itself as readily for analysis of the other triboexcitation mechanisms. Tribofluorescent compounds will probably be more suitable because the short-lifetime emission can capture dynamic features of the system under stress before complete mechanical relaxation can occur. The interpretation of the new spectral features will allow the plausibility of the other mechanisms to be assessed. These aspects of triboluminescence are currently under investigation in our laboratories.

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Registry No. $UO_2(NO_3)_2 \cdot 6H_2O$, 13520-83-7.

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Contribution from the Department of Chemistry,
State University of New York at Stony Brook, Stony Brook, New York 11794

Thermal Decomposition of Oxyhyponitrite (Sodium Trioxodinitrate(II)) in Aqueous Solution[1]

FRANCIS T. BONNER* and BARUCH RAVID

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The decomposition of $Na_2N_2O_3$ in aqueous solution has been studied over a wide range of pH values by kinetic measurements based upon uv absorption, by uv spectroscopy, and by tracer experiments using the labeled form $Na_2(O^{15}NNO_2)$. The decomposition is first order in $HN_2O_3^-$ and occurs at a rate that is independent of pH in the range <4 to >8 [$k_1 = (4.6 \pm 0.4) \times 10^{-4}$ sec^{-1} at 25°]. The reaction products are exclusively $N_2O + NO_2^-$, and the nitrogen atoms in the N_2O come exclusively from the N atom bound to a single O atom, at pH values 3 and above. The rate of decomposition of $N_2O_3^{2-}$ is low and decreases with increasing pH. The rate of decomposition of $H_2N_2O_3$ to give $N_2O + NO_2^-$ is greater than that of $HN_2O_3^-$. The only NO produced at pH 3 is formed by disproportionation of HNO_2, but at pH 2 a mixture of NO and N_2O is produced without any NO_2^- being detected. The nitrogen atoms in this N_2O product derive from both atoms in the $Na_2N_2O_3$. The reaction product is exclusively NO in strong acid. The value of λ_{max} falls from 250 nm at high pH to 237 ± 0.5 nm for solutions in which $HN_2O_3^-$ predominates; ϵ for $HN_2O_3^-$ has the value 5460 ± 240 M^{-1} cm^{-1} at 237 nm. A second peak is found at 196 nm for $HN_2O_3^-$, with some suggestion of a decline in λ_{max} at pH 3 and below. Angeli's hypothesis of HNO (or NOH) as intermediate in the decomposition and direct precursor of N_2O has been confirmed. It is postulated that N=N bond breakage to produce HNO and NO_2^- is the primary controlling process in acidic as well as in basic solutions. Under this postulate, directly produced NO in acid solution is not formed by a dehydration reaction but by a redox process in which a species related to HNO, possibly H_2NO^+, attacks NO_2^- or HNO_2.

Introduction

The decomposition of Angeli's salt ($Na_2N_2O_3$) to form N_2O and NO_2^- in neutral or alkaline medium is the process that led to the first speculation concerning existence of nitroxyl (HNO) as an intermediate species.[2] This substance, formally sodium trioxodinitrate(II), which we shall call oxyhyponitrite as suggested by Addison, *et al.*,[3] but which has been variously named nitrohydroxylamite and hyponitrate elsewhere in the literature, has been the subject of a number of investigations whose principal objects have been elucidation of structure.[3–8]