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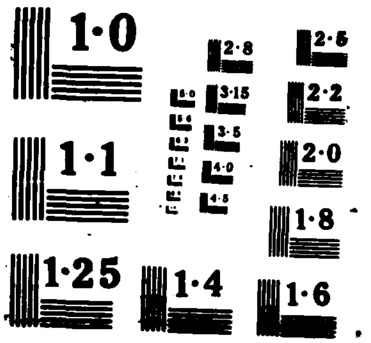
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Applications of thermal modulation in luminescence spectroscopy

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Abstract

The utility of thermally modulated emission (TME) spectroscopy as a technique for elucidating the properties of the excited states of molecules and complexes with near-degenerate excited electronic states is reviewed. A description of the TME method, its realm of application, and the type of information obtained are given. Particular emphasis is placed on the use of infrared heating as a tool for observing spectra in diverse media.

Introduction

Properties of the low-lying electronic excited states of metal complexes in condensed phases are most conveniently studied by monitoring the luminescence generated by UV excitation.[1] For most substances the parameters generally obtained are the energies of the emitting states above the ground state and the lifetimes of the excited states. Additional information can be obtained about the radiative and radiationless constants of the states if optical quantum yield measurements are carried out, although this determination can be tedious.[2]

If the emitting level in a luminescence experiment is nondegenerate, the interpretation of the luminescence results is usually unambiguous, since only one state is involved. Often, however, the 'state' is not a state at all but a group (usually three) of excited states in close proximity. If information is desired on the individual components of the 'state', then other experimental methods must be employed. For organic molecules the lowest excited triplet is a well-known example of a set of states that are closely packed, within a few cm^{-1}. The elucidation of the properties of the individual components can be effected by the use of Optically Detected Magnetic Resonance (ODMR) in which optical pumping is supplemented with microwave irradiation that pumps systems between the closely-lying components.[3] Since the splittings of the low-lying triplets of numerous molecules, including many metal complexes, lie in the region spanned by commercial microwave generators, the ODMR method has been used by numerous laboratories to measure properties of the individual triplet components.

For many metal complexes, particularly those of the second and third transition series, the lowest-lying excited states are only near-degenerate. Often the splittings range from a few wavenumbers to several hundred cm^{-1}, and ODMR cannot be used to stimulate transitions among them. The level splittings are in the frequency range of vibrations in solids and complex molecules, and tunable IR radiation would be required to effect transitions between the levels. Even if available, tunable IR radiation would be absorbed by the numerous vibrational modes present in the samples, and electronic transitions would be difficult to identify.

Recently we have been developing the technique of Thermal Modulation Emission (TME) spectroscopy to study the excited states of transition metal complexes. These complexes display photoluminescence from several excited states that are thermally accessible from the lowest one either by resistive heating or by direct IR heating. TME measurements supply complementary information on the excited state splittings in these molecules, information that is particularly difficult to obtain by other techniques because of the intrinsically diffuse nature of the emission spectra. The band widths are often orders of magnitude wider than the level splittings.

Description of the thermal modulation emission method

When a sample of a metal complex is held at low temperature and excited with UV radiation, broad band visible emission is frequently observed. Often the emission is a composite of bands originating from several excited states of the system and spans the entire near-UV and visible regions of the spectrum. Under steady excitation the emission band may display evidence of several transitions underlying it, but the contour is often uninformative. If, however, the sample is periodically heated while under constant UV irradiation, then three possible ideal behaviors of the emitted light are manifest. These are shown in Figure 1. In the figure we see that the intensity of a transition may increase, decrease, or remain constant as the sample is heated. Thus, a periodic signal possessing the frequency of the heat pulse will be superimposed on the steady-state

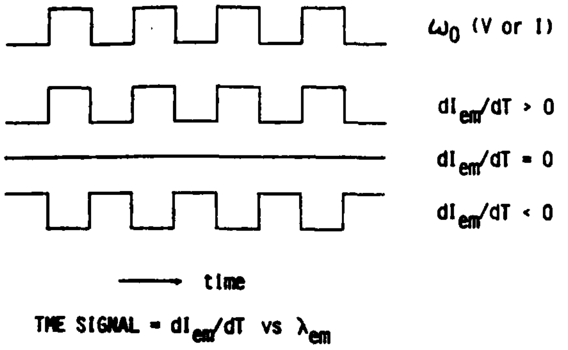

Figure 1. Schematic representation of ideal TME signals. ω_0 = frequency of heat pulse, joule or infrared radiation heating; $(\partial I_{em}/\partial T)$ = derivative of emission intensity with temperature.

emission. It is not necessary that the emitting levels be in thermal equilibrium; nor is it necessary that all the levels be thermally accessible. What is necessary, however, is that the heat transfer to and from the sample be fast enough to produce reproducible temperature excursions at a frequency detectable by a lock-in amplifier. This condition is most easily achieved by mounting the sample on a resistive heater inside a low-temperature dewar that uses an exchange gas to conduct heat efficiently from the sample.

Although the thermal modulation (TM) technique had been employed in the measurement of reflectance spectra[4] and absorption spectra,[5] application of TM spectroscopy to luminescence measurements on molecular crystals was first introduced by Francis and coworkers, who demonstrated the equivalence of TME and ODMR on an organic crystal system.[6] Later Hipps and Francis applied TME to inorganic compounds with near-degenerate excited states and showed the usefulness of TME for distinguishing between proposed excited state models.[7] With the introduction of several simplifying mathematical approximations these authors also derived expressions for the expected magnitude of the TME signal in the limit of small temperature excursions of the sample [for details see ref. 7]. For a lock-in amplifier properly phased and tuned to ω_0, the TME output signal is

$$\Delta I \simeq \frac{4(\bar{T}-T_b)}{\pi[1+(\omega_0\tau)^2]^{1/2}}\left(\frac{\partial I}{\partial T}\right)_{\bar{T}}$$

In this expression ω_0 is the frequency of the square wave heat pulse in the resistive heater attached to the sample; T_b, the temperature of the bath; $\bar{T}$, the average temperature of the sample, and $(\partial I/\partial T)_{\bar{T}}$ is the temperature derivative of the band intensity. τ is the thermal relaxation time of the sample. We see that the TME signal, $\Delta I(\lambda)$, is directly proportional to $(\partial I/\partial T)_{\bar{T}}$ under these somewhat restrictive conditions. Ideal behavior of the emitted light is represented in Figure 1. In the real case the signal is not a step function; it is periodic, however, with a phase lag that is a complicated function of the heat conductivity of the sample.[7]

In the present work we are concerned with the development and refinement of TME spectroscopy as a technique for the investigation of the excited states of inorganic complexes. Particular emphasis is placed on the correspondence of the results obtained from different methods of heating the sample and the extension of the technique to the study of the same molecule in various solvent (glass) environments.

Description of experimental measurements

Both steady-state and TME spectra were recorded by illuminating the sample with filtered UV light from a mercury lamp and directing the emitted light through a monochromator supplied with UV blocking filters before the entrance slit. The signal from the photomultiplier detector was amplified and stored. The sample, usually a single crystal or a mass of crystals, was bonded with mineral oil to a thin-film nichrome heater and mounted in a variable temperature helium dewar. Cooling was achieved by suspending the sample just above the liquid helium reservoir.

For the TME measurements periodic temperature excursions within the sample were produced by driving the thin-film nichrome heater (R ∿ 20 ohms) with a square wave voltage oscillator of variable frequency, duty cycle, and pulse voltage. The oscillator was generally operated between 4 and 6 Hz to ensure optimal temperature excursions within the sample. Signal forms were insensitive to both the frequency and the duty cycle chosen. The AC component induced on the emission spectrum was detected by a properly phased lock-in amplifier whose output was amplified and recorded. Determination of the absolute sign of a given TME signal was accomplished by passing a single large-amplitude heat pulse through the sample and monitoring the sense of the phototube response with an electrometer.

Infrared heating of the samples was achieved by substituting a 10-W tungsten lamp and a mechanical chopper or a 4-W CO_2 continuous wave laser for the resistive heater. The broad-band output of the tungsten lamp was passed through a Corning 7-56 glass filter and focussed on the sample through the same window that transmitted the UV excitation beam. Since quartz windows are opaque at 10.6 μ, a modified optical arrangement was employed to direct the CO_2 laser beam to the sample. In this case the sample was mounted at the bottom of a stainless steel tube that was equipped with a NaCl window at the top. The IR beam from the laser was routed by mirrors through the window down to the sample.

For the determinations employing IR pumping (the laser and the tungsten lamp) the sample excitation was essentially front surface. Excitation of glasses was achieved by cooling the block initially to 77 K, depositing a drop of solution into a depression on the block and quickly transferring the apparatus to the helium dewar. The power of the IR heating was estimated to be 150 mW by comparison of the recorded TME signals with those obtained by resistive heating.

Results

Emission spectra of $Zn(4\text{-}Me\text{-}PhS)_2(phen)$* crystals at 6.5 K are reproduced in Figure 2. In Figure 2a the steady-state luminescence is shown. Presented in 2b and 2c are TME spectra taken with resistive and IR laser heating, respectively. The data clearly reveal that the first spectrum is composed of at least two bands, a structured emission spanning the region of 18,000 to 22,000 cm^{-1} and an overlapping band almost devoid of structure that extends into the red region. The high energy band decreases in intensity as the temperature rises and the low energy one displays the opposite behavior. After flash excitation the former decays with a long life (0.34 s), whereas the latter dies out in milliseconds.[8] These ancillary transient measurements demonstrate that at least two excited states not in thermal equilibrium at the temperature of the steady-state experiment give rise to the observed emission. The TME results show conclusively that the high energy state loses intensity and the lower energy one gains intensity as a result of the heat pulse. Detailed studies on a similar molecule[9] lead to the inference that $Zn(4\text{-}Me\text{-}PhS)_2(phen)$ has two excited states of widely disparate natures that are separated by a thermally accessible barrier. Each state decays independently at the temperature of the experiment until the relative populations are changed by the heat pulse. Systems are driven from the high energy (long-lived) state to the lower energy one thermally, thus producing a decrease of the intensity of the former and an increase of the intensity of the latter. A comparison of the curves in Figure 2a and 2b also shows that the TME results do not depend upon the method of heating. Indeed, a tungsten lamp can be substituted (see below) for the resistive heating source.

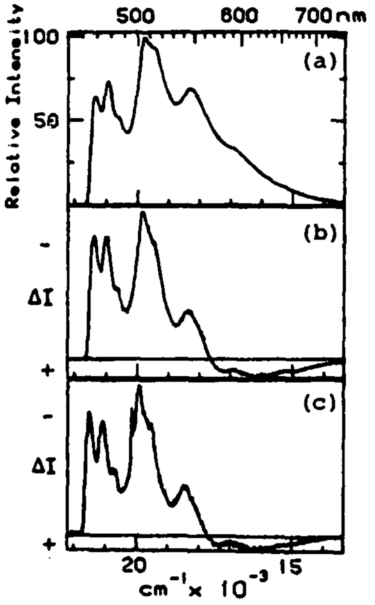

Figure 2. Emission spectra of $Zn(4\text{-}Me\text{-}PhS)_2(phen)$ crystals at 6.5 K. (a) steady state; (b) thermally modulated by resistive heating at 5 Hz; (c) TME via CO_2 laser at 4 Hz.

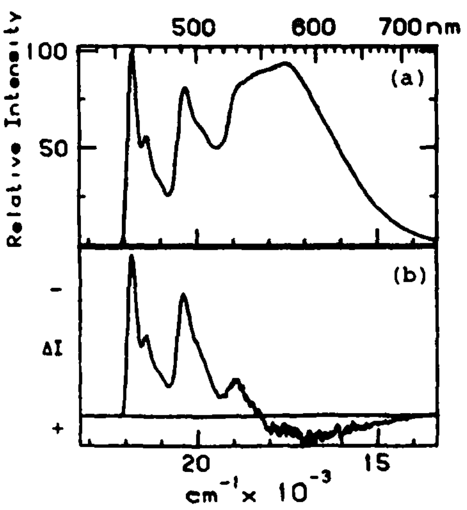

Figure 3. TME spectrum of $Zn(PhS)_2(2,9\text{-}Me_2\text{-}phen)$ crystals at 6.5 K. (a) steady state emission; (b) heated with tungsten lamp at 4 Hz.

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* For names, abbreviations, and preparations of these zinc complexes, see ref. 8.

In Figure 3 we have plotted the TME signal from the $\mathrm{Zn(PhS)_2(phen)}$* complex in the crystalline state at 6.5 K. In this experiment the heating element for the TME measurement was a tungsten lamp whose radiation was directed into the dewar through a quartz window. The TME signal clearly reveals the composite nature of the steady-state spectrum. At least two electronic transitions occur under the band contour, a structured one lying at higher energies and a diffuse one at lower frequencies. This molecule also displays a barrier between the two emitting excited states that prevents thermal communication at 6.5 K. Thermal redistribution of the ensemble population is induced by the periodic heat pulses leading to the recorded TME spectra.

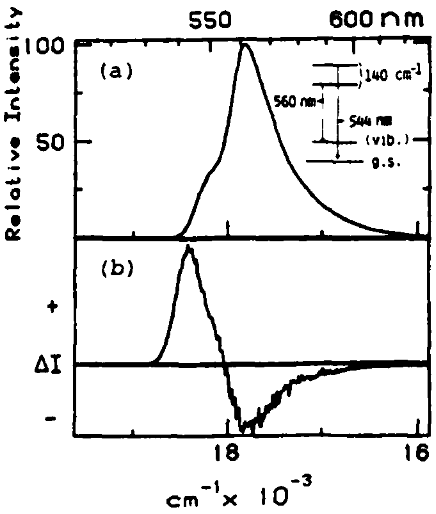

Figure 4. Emission spectra of $\mathrm{[Ir(2{=}phos)_2]ClO_4}$ in 16:4:1 v/v ethanol/methanol/methylene chloride glass. (a) steady state at 6.5 K, insert displays published energy level system; (b) thermally modulated emission at 8.5 K via $\mathrm{CO_2}$ laser heating at 2 Hz.

Figure 4 shows both the steady-state and the TME spectra of the open-shell complex $\mathrm{[Ir(III)(2{=}phos)_2]ClO_4}$**. The normal spectrum is clearly composite since the TME curve shows both a positive and a negative intensity excursion as a function of the heat pulse. Unlike the two previous cases, however, the entire spectrum decays with a single life at all temperatures showing that the relative populations of the two emitting levels are controlled by the Boltzmann law.[10] No evidence for a barrier between the two emitting states is present but the TME signal is strong. Evidently the heat pulse redistributes the excited population continuously as the temperature changes. Another interesting feature of this experiment is the physical state of the sample. The complex was dissolved in a glass, rather than maintained in the crystalline state, thus allowing a TME signal to be obtained on a molecularly dispersed system.

Discussion

The results presented above show the power of TME spectroscopy as a tool for the study of inorganic complexes possessing near-degenerate excited states. Moreover, the results demonstrate that thermal equilibrium among the levels is not a prerequisite for obtaining TME signals. If a barrier separates the emitting levels, however, the magnitude of the heat pulse must be high enough to pump systems over it.

Resistive heating can be employed to generate TME signals, but several problems arise. Wires to the heater must be led into the dewar and attached to the heater, a tedious procedure. Also, attaching the sample to the heater by mineral oil is not always entirely satisfactory. Frequently the crystal pops off the heater when a large heat pulse is delivered to it at low temperatures. Finally, the resistive heating technique is limited by the rate of heat conduction to the sample from the heater, and we have devised no reliable method of measuring the amount of heat actually absorbed by the crystal during the heating cycle.

Employing an infrared radiative source to deliver heat to the crystal has several definite advantages over the use of resistive heating. Because the radiation is absorbed directly by the crystal, more uniform heating occurs. The limiting factor becomes the rate of dissipation of heat to the bath rather than the rate of heat conduction to the sample. This virtually dictates that an exchange gas must be present to cool the sample. Nonetheless, we have obtained TME signals from samples mounted in a displex cryostat where no exchange gas was present. The slower cooling vitiated the TME signal and a lower frequency (~1 Hz) was required to produce any result. There was interfering scattered light from the tungsten lamp, which could have been, however, eliminated by interposing a silicon window to pass IR radiation of wavelengths longer than 1.1 microns (this filter was not available to us for taking the data presented here). Another advantage of IR heating is the ease of shaping the excitation pulse and modifying the duty cycle by means of simple choppers. A third, but extremely important, advantage of IR heating is the ease of working with samples dispersed in glasses, thus affording an opportunity for studying the effect of solvent matrix on the excited state properties. Finally, one can measure the absolute energy deposition rate in the samples by optical methods when an IR heating source is employed.

** The name, synthesis, and a detailed spectroscopic investigation of $\mathrm{[Ir(III)(2{=}phos)_2]ClO_4}$ are given in ref. 10.

Thermally modulated emission spectroscopy is a valuable tool for studying the properties of near-degenerate excited states of luminescent materials. Coupled with decay time, quantum yield, and conventional emission measurements, TME is providing new information on transition metal complexes of interest to spectroscopists and photochemists.

Acknowledgments

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