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Long-lived luminescence from commonly used Apiezon compounds

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Abstract

Long-lived (~ 12 s) luminescence from Apiezon compounds (greases and wax) has been measured following ultraviolet or visible excitation in the temperature regime 8–300 K. A typical spectrum consists of a single Gaussian band centered near 2.2 eV. The intensity of this band is maximum at the lowest temperature investigated (8 K), decreases nonlinearly with increasing temperature, and becomes undetectable near 250 K. Spectral peak position and full-width at half-maximum remain approximately constant throughout this temperature interval for fixed measurement times. Time decay measurements at 8 K show an increase in peak position with increasing time lapse since optical excitation. The time dependence of peak intensities as a function of temperature can be described by $I(t) = [A\exp(-\alpha t)]/[1 + B\{1 - \exp(\alpha t)\}]$, consistent with P-type delayed fluorescence arising from triplet-state deexcitation in organic molecules. Although the composition of Apiezon compounds is proprietary they are known to contain a high proportion of hydrocarbons. The single Gaussian emission band and long fluorescence lifetime is consistent with previous observations on hydrocarbons. Because Apiezon compounds are easily excited, yielding fairly intense luminescence, caution must be exercised when using them in optical experiments.

1. Introduction

Apiezon [1] products (oils, greases and waxes) are widely used in research laboratories for myriad applications, especially those involving vacuum work. Development of these compounds resulted from a need to have an excellent leakproof lubricant with extremely low vapor pressure at temperatures of interest. Because of the enhanced adhesiveness of Apiezon greases at low temperature ($T < 300$ K), they are frequently used to mount samples, sensors, or other devices in vacuum apparatuses. In recent luminescence measurements on solids, where we used Apiezon grease to mount a temperature sensor, we found a relatively intense luminescence signal emanating from Apiezon grease when subjected to ultraviolet (UV) or visible excitation. Measurements on greases L, M and N, and wax W demonstrated that each could be easily excited by UV or visible radiation. Luminescence is not observed above 250 K, but below this temperature luminescence is readily detected; the intensity increases nonlinearly with decreasing temperature, reaching a maximum at the lowest temperature investigated (8 K). Emission consists of a single Gaussian band with maximum near 2.2 eV. Presence of this luminescence can obviously interfere with optical measurements and consequently must either be eliminated or properly accounted for when interpreting data. To gain fundamental knowledge of the excitation and emission properties of these compounds, we have investigated the

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luminescence of commonly-used Apiezon greases and wax in the temperature interval 8–300 K and wavelength region 300–800 nm.

2. Experimental technique

Specimens of either Apiezon grease or wax were mounted onto an aluminum sample holder of a continuous-flow He cryostat and irradiated for 15 s with broadband UV or visible radiation in the temperature regime 8–300 K. Simultaneous closure of a shutter controlling the UV source and opening of the entrance slit of an optical multichannel analyzer (OMA) allowed measurements of the luminescence within about 1 s after exposure. Light emanating from the sample, located in an evacuated cryostat (2×10^{-6} Torr), was delivered to the OMA via an optical fiber. Sequential spectra were recorded in the interval 300–800 nm for each fixed temperature. The data were corrected for the nonlinear response of the spectrophotometer, plotted as a function of energy, and fitted with a Gaussian line shape. Time and temperature dependences of optical parameters (peak position, bandwidth, and intensity) were also extracted from the fitted data.

In addition to UV and visible radiation exposure the samples were also subjected to X-radiation. Surprisingly, no measurable luminescence was detected as a result of this illumination. Moreover, thermally stimulated luminescence (TSL) experiments were done on the compounds following either UV, visible or X-ray excitation but no signal was detected. Optical absorption of some of the greases was measured at room temperature with a Cary 5E optical absorption spectrophotometer.

3. Experimental results

Shown in Fig. 1 are typical luminescence emission spectra of Apiezon greases (N, M and L) and wax (W) taken at 8 K following a 15 s UV exposure. The spectra are very similar in shape but vary in intensity, with grease N being the most intense. Similar spectra were observed following excitation by a household flashlight but, surprisingly, no luminescence was detected after excitation by

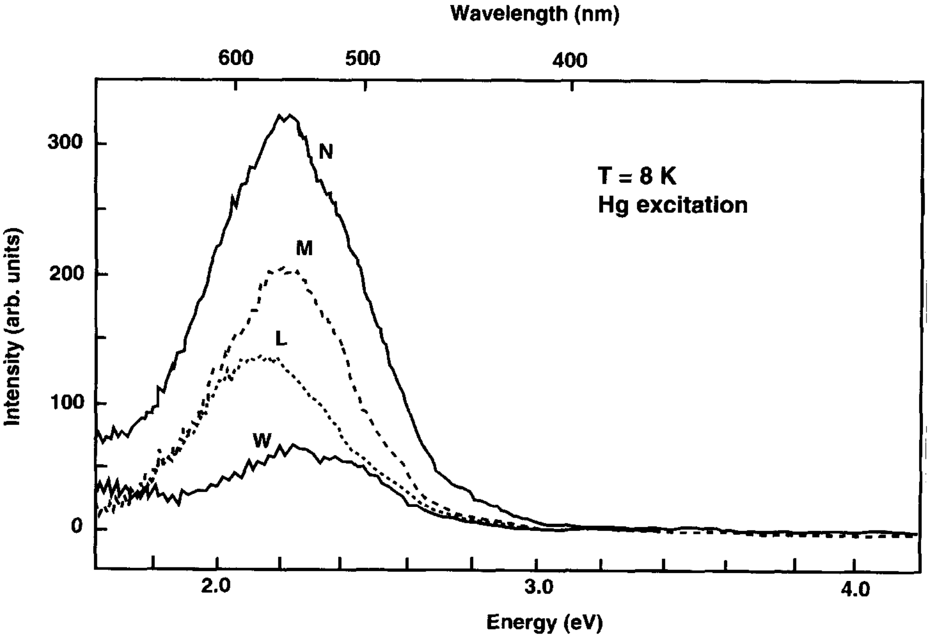

Fig. 1. Luminescence emission spectra from Apiezon greases (N, M and L) and Wax (W) following broadband Hg light excitation at 8 K. The data were taken 1 s after excitation and have been corrected for the nonlinear spectrophotometer response.

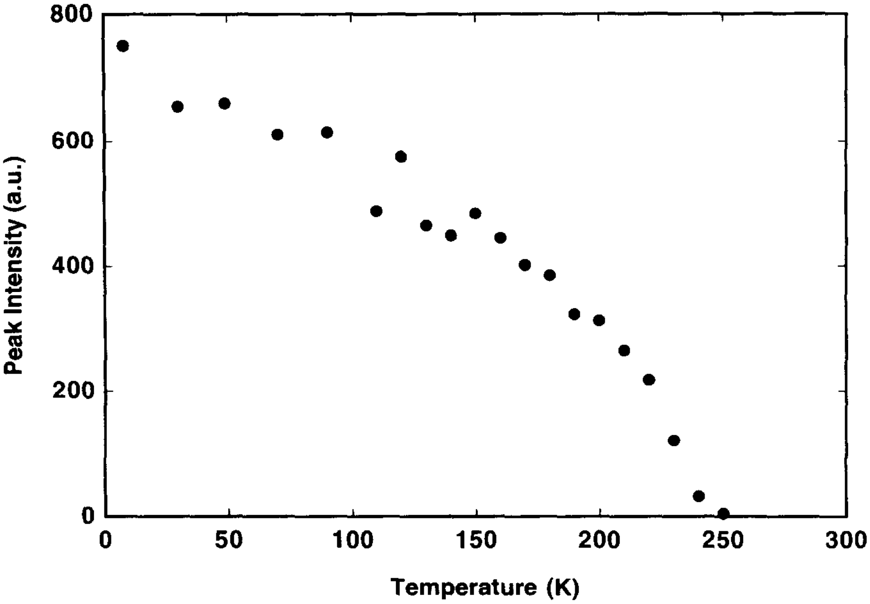

Fig. 2. Temperature dependence of Apiezon luminescence peak intensity. Error bars are smaller than plot symbols. Data were taken 1 s after excitation.

X-radiation. All spectra were fitted with a single Gaussian line shape from which the optical parameters were extracted. Representative data showing the temperature dependence of the luminescence intensity are given in Fig. 2. The intensity decreases nonlinearly with increasing temperature up to 250 K ($T_{co} \equiv 250$ K); above this temperature we were unable to detect luminescence from any of the greases or wax. However, upon cooling the material to 8 K, we found that the original luminescence intensity was recovered; in fact, there was no measurable hysteresis of intensity as a function of the temperature cycle. It should be emphasized that the data shown in Fig. 2 refer to spectra taken 1 s after sample excitation. These results indicate that spurious luminescence due to the use of Apiezon greases or wax should not be a problem in experiments conducted at or near room temperature. In contrast, low-temperature optical experiments will be plagued by this luminescence, and caution must be used to ensure that it does not interfere with measurements.

The behavior of the Gaussian peak position and width (full-width at half-maximum) as a function of temperature was investigated. Unlike the smooth decrease of intensity with increasing temperature (Fig. 2), both peak position and width remain essentially constant (peak position – 2.21 eV; width – 0.57 eV) up to very near T_{co} where they decrease precipitously. This abrupt decrease is probably associated with our inability to measure accurately the spectral parameters of the very weak emission.

Time decay of the luminescence peak intensity for a typical Apiezon specimen is shown in Fig. 3. The speed of the OMA allows a complete spectrum from 300 to 800 nm to be obtained in 33 ms, and we have plotted data taken at sequential 1 s intervals following excitation. Values of peak intensity were taken from the corrected, Gaussian-fitted data and plotted for several temperatures with typical results shown in Fig. 3. The solid lines are fits to a model calculation describing P-type delayed fluorescence [2] of excited triplet states. Details of this calculation will be given in the next section.

For completeness we show in Fig. 4 the optical transmission of a typical specimen. The salient feature with respect to the present work is the complete absorption observed below about 400 nm, which we associate with peak emission near 550 nm.

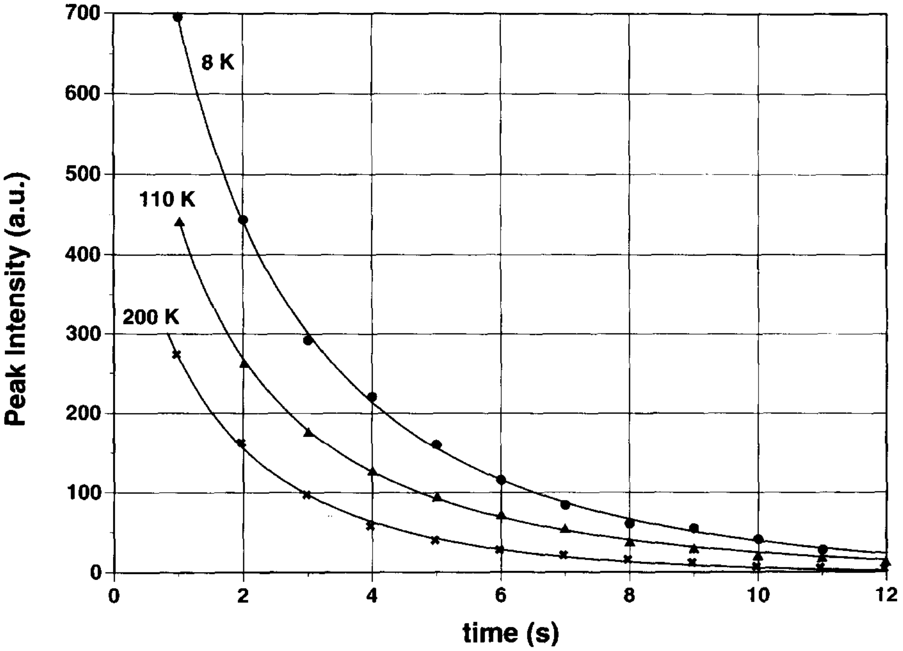

Fig. 3. Time dependence of Apiezon spectral intensity taken at three temperatures. Error bars are smaller than plot symbols. Solid lines are fits to the data obtained from Eq. (3) of the text.

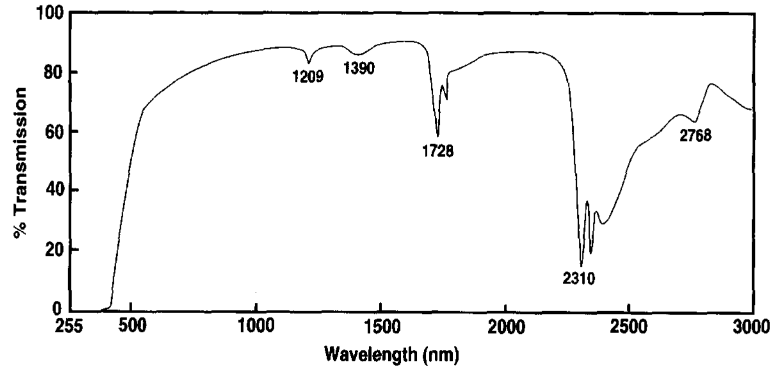

Fig. 4. Optical transmission of a typical Apiezon compound. Complete absorption occurs below about 400 nm.

4. Discussion

Spectral emission from Apiezon compounds can be analyzed in terms of organic molecular luminescence from hydrocarbon-containing samples [3]. Given the long lifetime of the luminescence emission (~ 12 s; see Fig. 3), it is evident that deexcitation occurs via the excited triplet–to–ground–state manifold of the molecular species. We suggest the observed luminescence is P-type delayed fluorescence similar to that previously observed in crystals, rigid solutions and fluid solutions of aromatic molecules [3]. Specifically, it is due to interactions between pairs of triplet-excited molecules (T_1)

which have a total energy greater than an excited singlet state (S_1):

$$T_1 + T_1 \rightarrow S_1 + S_0, \tag{1}$$

where S_0 is the singlet ground state. These triplet–triplet interactions are most likely to occur for high concentrations of excited triplet states via triplet exciton migration.

We now model the time dependence of luminescence intensity in Apiezon compounds by assuming the existence of an initial concentration of triplet states due to excitation, and calculating the change due to triplet–triplet interaction (k_{TT}) and triplet phosphorescence (k_T). We follow the general formalism previously outlined by Birks and Grzywacz [4]. The rate equation describing the decay is

$$\mathrm{d}[T_1]/\mathrm{d}t = -k_T[T_1] - k_{TT}[T_1]^2, \tag{2}$$

where we have neglected the intersystem crossing from the excited singlet to the excited triplet state. The solution to Eq. (2) is

$$[T_1] = [T_1]\exp(-k_T t) \times \{1 + [T_1](k_{TT}/k_T)(1 - \exp(-k_T t))\}^{-1}. \tag{3}$$

The measured luminescence peak intensity as a function of time was fitted to Eq. (3) and the results are shown as solid lines in Fig. 3. Values of the rate constant (k_T) extracted from the fits at 8, 110 and 200 K are 0.246, 0.231 and 0.344 s^{-1}, respectively; corresponding k_{TT} values are 0.474, 0.733 and 0.564 s^{-1}. The excellent agreement between experiment and theory suggest that the luminescence is indeed due to P-type delayed fluorescence.

Quenching of the luminescence with increased temperature (see Fig. 2) may be due to triplet interactions with various molecules resulting in enhanced radiationless transitions. Various mechanisms describing these interactions have been previously discussed [3] and we offer no specific model here because we do not have information on the exact composition of the material. We certainly expect our specimens to consist of more than one species of aromatic molecule; however, we observe only one well-defined Gaussian emission band, indicative of a single type of molecule.

The overall temperature and time dependence of the spectral parameters extracted from the experimental data are reasonably consistent with similar data on hydrocarbon-containing compounds [3]. It is somewhat surprising, however, that no change in the width of the spectra as a function of temperature or time was observed. For crystalline material we would expect the width to follow the usual relation [5] $W(T) \propto [\coth(a/T)]^{1/2}$ where W is the full-width at half-maximum and a is the energy of phonons emitted at temperature T. Such an analysis has been done for fluorescence in pyrene crystals [6]. Although our Apiezon specimens are amorphous and therefore not expected to obey such a well-defined relation, we did expect to observe a measurable increase in width due to enhanced lattice vibrations at higher temperature. Perhaps the small changes in width for amorphous specimens are outside the experimental limits of our technique.

5. Conclusion

We have measured the long-lived (~ 12 s) luminescence from specimens of commonly used Apiezon greases and wax and attribute the emission to P-type delayed fluorescence arising from deexcitation of the excited triplet state. Theoretical calculations describing the triplet phosphorescence and triplet–triplet interaction as a function of time are in excellent agreement with the experimental data. From the fitted results we have extracted rate constants for the two processes. Spectral parameters of the single-Gaussian line shape (centered near 2.2 eV) as a function of temperature and time after excitation have also been measured. The data are typical of P-type delayed fluorescence previously observed in aromatic hydrocarbons. It is known that Apiezon does indeed contain a high proportion of hydrocarbons with extensively branched and unsaturated structures; the exact composition is, however, proprietary information. Nevertheless we suggest that aromatic hydrocarbons are responsible for the luminescence.

It was not the purpose of this work to elucidate the structure of Apiezon compounds but to inform researchers of the intense luminescence induced by excitation with UV/visible light in the temperature interval 8–250 K. Because of the excellent vacuum and adhesive properties of Apiezon, it is commonly used in cryogenic experiments for a variety of purposes, including optical work. We caution researchers to not overlook this contribution when performing optical experiments in which Apiezon compounds may be excited.

Acknowledgements

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