A Method for Separation of Homogeneous and Inhomogeneous Components of Spectral Broadening of Rigid Systems

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A method is suggested that allows separation of the contributions from homogeneous and inhomogeneous broadening (IB) to a total spectral contour of rigid systems. Based upon a simple convolution model of inhomogeneous broadening, the method allows calculation of homogeneously broadened spectra and an inhomogeneous distribution function (IDF) from the measured excitation-wavelength-dependent fluorescence spectra of the system. The method is applied successfully to the solid solution of coumarin 334 (C334) in poly(methyl methacrylate) (PMMA) glass at 293 K.

1. Introduction

Fluorescence and absorption spectroscopy is an important tool in the arsenal of researchers which serves in the investigation of structural and dynamic properties of matter. Though recent advances in experimental techniques have made spectroscopic data comparatively easy to obtain, their interpretation is far from being straightforward. Measured absorption and fluorescence spectra are affected by many factors, including external conditions and the environment of the chromophore, and in most cases it is impossible to attribute explicitly the slight changes in spectral contours. The problem is further complicated by the fact that in condensed media the measured spectra ordinarily exhibit inhomogeneous broadening. This means that these spectra are indeed the sum of many spectra of individual chromophores different from each other due to either conformational diversity of the chromophore itself or different local environments. It is well-established that at limiting low temperatures (e.g., 4.2 K) inhomogeneous broadening (IB) provides a predominant contribution to the total width of spectral contours of rigid condensed-matter systems. The conventional techniques of selective line-narrowing[1] and spectral hole-burning[2,3] are used routinely to resolve IB and obtain spectral characteristics of individual molecules. These techniques are based on the presence of extremely intense and narrow zero-phonon lines (ZPL) in individual spectra at very low temperature.[4] At higher temperatures ZPLs disappear, making the task of separation of the inhomogeneous and homogeneous contributions to the spectral broadening very nontrivial.

Currently among researchers there is a growing appreciation of the importance of the IB effects in understanding many photophysical and photochemical phenomena taking place at normal temperatures (e.g., 293 K). Among those phenomena photoexcitation harvesting by a photosynthetic system,[5,6] protein fluorescence,[7] and light generation by rare-earth-doped glasses[8,9] are only a few examples. The role which IB plays as well as its molecular mechanism in most cases is still poorly understood, mainly owing to the lack of methods allowing the determination of relevant quantitative parameters of IB. Though spectral hole-burning at 120 K [10] and even at room temperature[11] has been reported recently, generally at room temperature IB manifests itself only in the slight dependence of a fluorescence spectrum on the excitation wavelength observed in rigid and quasi-rigid media.[12] This "red-edge excitation" effect may serve to estimate some quantitative properties of IB. So far researchers have limited themselves to plotting fluorescence maximum or center of gravity against excitation frequency and trying to derive some relevant quantitative parameters of IB from the dependence.[12,13] Obviously such an approach does not make full use of the information contained in the excitation-wavelength-dependent fluorescence spectra, particularly the information associated with the changes in the shape of the fluorescence contour with the excitation wavelength. It is our goal to determine whether it is possible to resolve IB and obtain homogeneously broadened spectra on the basis of information provided by the red-edge excitation effect. In order to do so a model based on certain approximations will be introduced.

2. Theoretical Model

At first we assume that spectra of individual chromophores differ from each other only in 0−0 transition frequency, and the probability of finding a chromophore with a given 0−0 frequency is described by an inhomogeneous distribution function (IDF), $\gamma(\nu)$. In other words the absorption and fluorescence spectra of individual chromophores can be described by functions

$$\alpha(\nu,\nu_{0-0}) = \alpha(\nu-\nu_{0-0}),\ \varphi(\nu,\nu_{0-0}) = \varphi(\nu-\nu_{0-0}) \quad (1)$$

where ν_{0-0} is the 0−0 transition frequency and $\alpha(\nu)$ and $\varphi(\nu)$ are universal functions of their arguments describing absorption and fluorescence, respectively. Another necessary assumption is that absorption and fluorescence for a given ν_{0-0} obey the Levshin law of mirror images; namely, $\varphi(\nu-\nu_{0-0}) = \alpha(\nu_{0-0}-\nu)$. And finally we assume that the fluorescence quantum yield does not depend on the 0−0 frequency of an individual chromophore. Although often reasonable these assumptions are not necessarily always satisfied, the mirror symmetry requirement being the most restrictive. Accordingly, proper justification should be made before the model can be applied to any particular case. Here we just restrict ourselves to noting that without those assumptions the complexity of the task stated grows enormously, making it practically hopeless. With these assumptions in place the excitation-dependent fluorescence will be given by[13]

$$\Phi(\nu_e,\nu_f) = \int_{-\infty}^{+\infty} \gamma(\xi)\ \alpha(\nu_e-\xi)\ \varphi(\nu_f-\xi)\ d\xi \quad (2)$$

where $\xi = \nu_{0-0}$ is the 0−0 transition frequency. The model is

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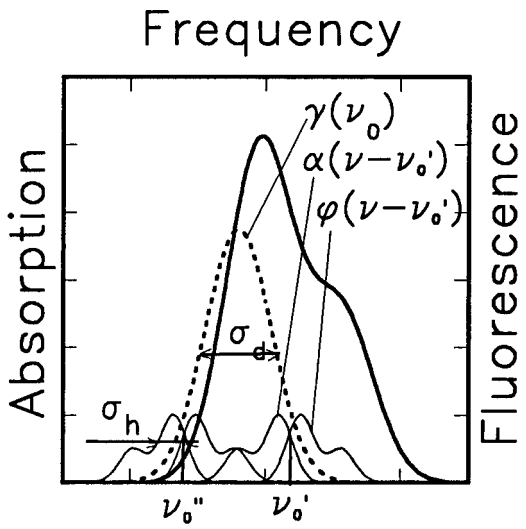


Figure 1. Schematic representation of the convolution model of inhomogeneous broadening showing absorption (α) and fluorescence (ϕ) spectra of individual chromophores with two different 0−0 transition frequencies (ν' and ν'') together with the inhomogeneous distribution function (γ) and the inhomogeneously broadened fluorescence spectrum (thick solid).

illustrated by Figure 1, depicting IDF, homogeneous absorption, and fluorescence spectra for chromophores with two different 0−0 transition frequencies as well as inhomogeneously broadened fluorescence as registered for one particular excitation wavelength. Applying to $\Phi(\nu_e,\nu_f)$ a two-dimensional Fourier transform procedure, we get

$$F(\tau_e,\tau_f) = f[\Phi(\nu_e,\nu_f)] = \mathbf{g}(\tau_e+\tau_f)\,\mathbf{a}(\tau_e)\,\mathbf{f}(\tau_f) \qquad (3)$$

where $\mathbf{g}(\tau) = f[\gamma(\nu)]$, $\mathbf{a}(\tau) = f[\alpha(\nu)]$, and $\mathbf{f}(\tau) = f[\varphi(\nu)]$ are the respective one-dimensional Fourier transforms of $\gamma(\nu)$, $\alpha(\nu)$, and $\varphi(\nu)$. Taking into account that $\varphi(\nu) = \alpha(-\nu)$ and using the identity

$$f[\alpha(-\nu)](\tau) = f[\alpha(\nu)](-\tau) \qquad (4)$$

we have

$$F(\tau_e,\tau_f) = \mathbf{g}(\tau_e + \tau_f)\,\mathbf{a}(\tau_e)\,\mathbf{a}(-\tau_f) \qquad (5)$$

The condition $\tau_e = -\tau_f$ defines a straight line in the (τ_e, τ_f) plane. The cross-section of the two-dimensional Fourier transform $F(\tau_e,\tau_f)$ along this line is a function of only one variable $F(\tau_e,-\tau_e)$ and in the case of the discrete Fourier transform corresponds to the second diagonal of the appropriate image matrix. According to (5) this function can be expressed as

$$F(\tau_e,-\tau_e) = \mathbf{g}(0)\{\mathbf{a}(\tau_e)\}^2 \qquad (6)$$

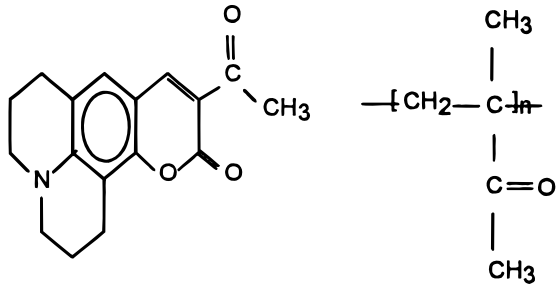
IDF ($\gamma(\nu)$) represents the probability distribution for an individual chromophore to have its 0−0 frequency between ν cm^{-1} and (ν + 1) cm^{-1} and is normalized to give

$$\int_{-\infty}^{+\infty}\gamma(\nu)\,d\nu = 1 \qquad (7)$$

Therefore

$$\mathbf{g}(0) = \int_{-\infty}^{+\infty}\gamma(\nu)\,e^{i\nu\cdot 0}\,d\nu = 1 \qquad (8)$$

$$F(\tau_e,-\tau_e) = \mathbf{a}^2(\tau_e) \qquad (9)$$



Coumarin 334 (C334) Polymethylmetacrylate (PMMA)

Figure 2. Chemical structures of coumarin 334 and poly(methyl methacrylate).

yielding the expression for $\alpha(\nu)$

$$\alpha(\nu) = f^{-1}[\{F(\tau_e,-\tau_e)\}^{1/2}] \qquad (10)$$

where $f^{-1}[\ ]$ denotes the inverse Fourier transform.

Thus, we managed to extract a homogeneously broadened absorption spectrum $\alpha(\nu)$ from the information contained in the two-dimensional excitation-dependent fluorescent spectrum. The *inhomogeneous distribution function* can be determined afterward from known homogeneously and inhomogeneously broadened absorption spectra which are related to each other by the convolution relation with IDF:

$$A(\nu) = \int_{-\infty}^{\infty}\gamma(\nu')\,\alpha(\nu-\nu')\,d\nu' \qquad (11)$$

So $\tilde{A}(\tau) = \mathbf{g}(\tau)\,\mathbf{a}(\tau)$, where $\tilde{\mathbf{A}}(\tau) = f[A(\nu)]$ and

$$\gamma(\nu) = f^{-1}[\mathbf{g}(\tau)] = f^{-1}[\tilde{\mathbf{A}}(\tau)/\mathbf{a}(\tau)] = f^{-1}[\tilde{\mathbf{A}}(\tau)/\{F(\tau,-\tau)\}^{1/2}] \qquad (12)$$

3. Experiment and Calculations

Practical implementation of the proposed procedure will involve determination of the two-dimensional excitation-fluorescence spectrum, evaluation of the second-diagonal elements of its two-dimensional Fourier transform, and extraction of the square root of these elements with a subsequent inverse Fourier transform to yield the homogeneously broadened absorption contour sought.

The system we chose for this purpose is coumarin 334 (C334) solid solution in poly(methyl methacrylate) (PMMA) at room temperature. Figure 2 shows the structures of the dye and the polymer. The reason we chose C334 is that its fluorescence and absorption spectra exhibit significant mirror symmetry with the second electronic absorption band lying far to the higher frequencies from the lowest energy band, thus allowing a meaningful cutoff, necessary for successful application of the *discrete Fourier transform algorithm*. Besides, the absorption and fluorescence of C334 are very sensitive to the polarity of the medium, suggesting the presence of a large inhomogeneous broadening caused by significant statistical irregularities in the environment characteristic of polymer systems below the glass-transition temperature. It is also important that the C334 structure does not allow any *large amplitude motions* (LAM) which could introduce a dynamic component to a total "red-edge" effect.[14] Finally, a system can be called rigid and the suggested method may be applied only when the condition $\tau_{SD} \gg \tau_F$ is satisfied, where τ_{SD} is a characteristic time of spectral diffusion and τ_F is a fluorescence lifetime. In other words, a 0−0 transition frequency of an individual chromophore should

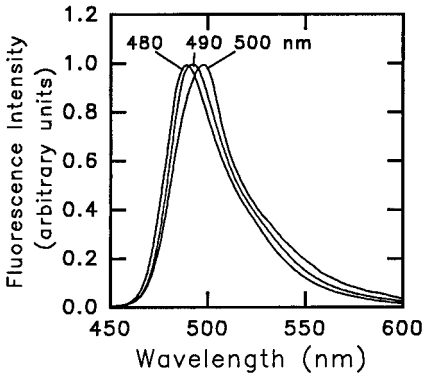


Figure 3. "Red-edge" effect observed on coumarin 334 in the PMMA matrix at 293 K. Dye fluorescence at different excitation wavelengths.

not change during the lifetime of its excited state. The room temperature is well below the glass-transition temperature for PMMA, so that matrix relaxation processes occur on a much slower time scale than the fluorescence decay of C334 ($\tau_F \approx 7$ ns). In this sense the system can be considered rigid, and its IB is of a static character.

Laser grade coumarin 334 (99%) was acquired from Acros and used without further purification. The C334 and PMMA (Scientific Polymer Products, Ontario, NJ) were dissolved in spectral grade methylene chloride (Fisher Chemical, Fair Lawn, NJ). The solution was poured into rectangular Teflon casts and left to dry under conditions of limited convection until all methylene chloride evaporated, yielding transparent uniform films 50 ÷ 100 μm thick. A special precaution was taken to remove the residual solvent from the sample. In the presence of solvent molecules in the environment of a chromophore, characteristic relaxation time becomes shorter than fluorescence lifetime and the rigidity condition is no longer satisfied. In fact, freshly prepared samples do not exhibit any red-edge excitation effect, thus suggesting that the IB has a dynamic character much like in liquid solutions. To remove the remaining solvent, the samples were kept under vacuum for 2 days. It was found that these samples were spectrally identical with those kept for 10 or more days in the open under normal atmospheric conditions and exhibited the red-edge effect characteristic of inhomogeneously broadened systems (Figure 3). The optical density of the samples used in the measurements was 0.05 ÷ 0.1 with dye concentrations of $5.0 \times 10^{-5} \div 1.0 \times 10^{-4}$ M. It should be noted that the concentration of chromophore is low enough to prevent spectral diffusion due to radiationless excited state energy transfer between the dye molecules. An increase in the concentration of C334 causes a red shift of the fluorescence spectra as well as a weakening of the red-edge excitation effect as the rate of energy transfer within the inhomogeneously broadened ensemble becomes comparable with the fluorescence decay rate. The fluorescence spectra were measured with FluoroMax spectrofluoremeter (Spex Industries, Edison, NJ). The absorption spectra were measured with a Shimadzu UV-2100 spectrophotometer (Shimadzu Corp., Kyoto, Japan). To generate a sufficient array of data, the fluorescence of the samples was measured for 21 different excitation wavelengths: 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 455, 460, 465, 470, 475, 480, 485, 490, 495, and 500 nm. All of the spectra were taken under precisely the same conditions, with their intensities being corrected for spectral dependency on the intensity of the excitation source. Each curve was fitted with four Gaussians, and the Gaussian corresponding to the excitation line was subsequently removed. The excitation bandwidth was 0.7 nm, which is 2 orders of magnitude smaller than spectral width of the C334 absorption band, allowing us to consider the

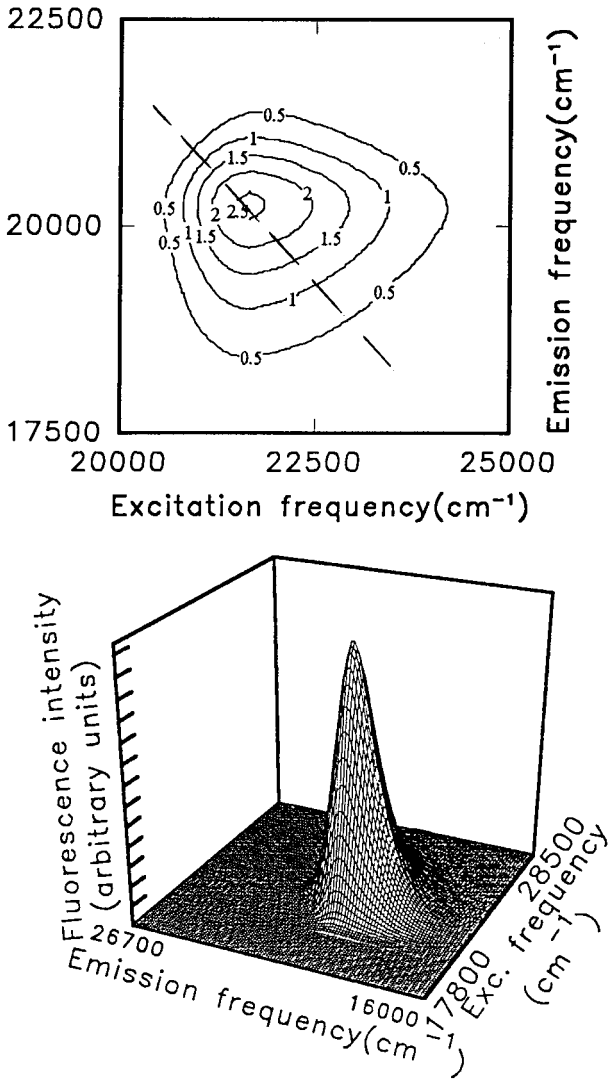


Figure 4. Two-dimensional fluorescence-excitation spectrum of coumarin 334 in the PMMA matrix at 293 K. The dashed line on the contour plot represents an expected axis of symmetry.

excitation as monochromatic. The high- and low-wavelength wings of each spectrum were extrapolated with a Gaussian curve as it was found that the procedure of padding it around with zeroes (commonly employed in image processing before applying a Fourier transform) introduces an artificial periodic distortion (ringing) due to discontinuity in the initial data array. The spectra from four different samples were averaged with equal weights and further converted from nanometers to reciprocal centimeters and interpolated in such a way as to give a square array of data 101 × 101 points with sampling points equally spaced in both excitation and emission frequency (Figure 4). This data array was used for further calculations. All of the calculations were done using a conventional *discrete Fourier transform* (DFT) *algorithm* (for example, see ref 15) implemented in the form of C++ code on a 486 PC computer.

4. Results and Discussion

The results of the calculations are represented in Figure 5, which pictures the inhomogeneously broadened absorption spectrum of the sample (curve 1) together with the calculated homogeneously broadened spectrum of the individual chromophore (curve 2) and calculated inhomogeneous distribution function (curve 3, solid). We can see that the individual chromophore absorption differs in width and shape from the

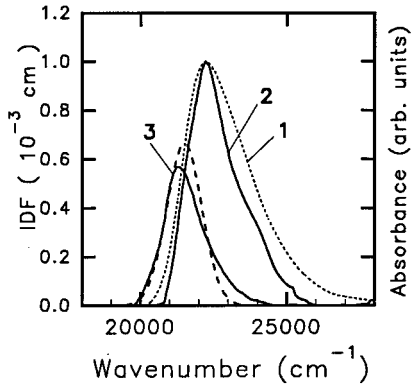


Figure 5. Inhomogeneously broadened absorption (1) and calculated homogeneous absorption (2) spectra together with calculated inhomogeneous distribution function (3, solid) and the normal distribution (3, dashed) found by fitting its convolution with 2 to 1 for coumarin 334 in the PMMA matrix at 293 K.

total absorption of the sample, being both more narrow and more structured. The vibrational structure masked under the broad asymmetric inhomogeneously broadened contour appears to be somewhat more pronounced in the homogeneous spectrum. The comparison of widths of the homogeneous spectrum and the IDF gives halfwidths (FWHM) of $\Delta\nu^{HS} = 1700$ cm^{-1} and $\Delta\nu^{IDF} = 1200$ cm^{-1}, respectively. It would be fair to say that for the system studied effects of homogeneous and inhomogeneous broadening give comparable contribution to the total shape of the absorption band. Other studies of solutions of organic dyes in PMMA reported values of $\Delta\nu^{IDF}$ ranging from 200 ÷ 300 cm^{-1} [13,16] to 1500 cm^{-1},[13] indicating that the width of the inhomogeneous distribution is strongly dependent on the nature of the particular chromophore incorporated into the PMMA matrix. The inhomogeneous distribution function found within our model is an asymmetric Gaussian-like distribution. We would strongly expect that 0−0 transition frequencies of individual dye molecules obey a normal probability distribution characteristic of a function of many independent random variables. The fact that IDF determined by our procedure exhibits appreciable asymmetry causes some doubts about the preciseness of the assumptions of the model. The most suspicious of them is the mirror-symmetry requirement imposed on homogeneous fluorescence and absorption spectra. The excitation-dependent fluorescence (EDF) itself exhibits certain asymmetry clearly seen from the contour plot (Figure 4, upper). On the other hand the convolution employed to calculate EDF (eq 2) would always produce a symmetric $\Phi(\nu_e,\nu_f)$ provided that mirror-symmetry condition holds and IDF is also symmetric. On the basis of this observation, we have to conclude that the asymmetry of calculated IDF must be an artifact which appears to compensate for impreciseness of the mirror-symmetry approximation. It is possible to achieve a good fit of the inhomogeneously broadened absorption spectrum by a convolution of the calculated homogeneous absorption spectrum with a normal distribution function also represented in Figure 5 (curve 3, dashed). The degree to which a calculated homogeneous spectrum is affected by the deviations from the mirror-symmetry condition is hard to assess without having an independent procedure free of this restriction. We believe that in the cases when these deviations are small, as indicated by only moderately asymmetric calculated IDF, calculated by our method, homogeneous absorption spectrum would give a fair representation of the real homogeneous absorption.

5. Conclusion

A new method for resolution of inhomogeneously broadened spectra of rigid systems based on a simple convolution model of the broadening is suggested and implemented practically on coumarin 334 doped PMMA at 293 K. The method allows the calculation of the homogeneously broadened spectrum and the inhomogeneous distribution function from the excitation-dependent fluorescence spectra of the system. Though applicable only to rigid systems, where inhomogeneous broadening is static and therefore an excitation wavelength dependence of fluorescence is observed, the method provides valuable information critical for the understanding of many photophysical and photochemical phenomena taking place in various systems of practical interest. The applicability of the method would be significantly extended if the condition of mirror symmetry imposed on absorption and fluorescence spectra of a single molecule could be lifted. Further research is required in this direction. Though the results obtained for the C334−PMMA system at 293 K might appear disappointing, as they fail to reveal a dramatic difference between the inhomogeneously and homogeneously broadened spectra, they are totally consistent with our present understanding of the phenomena involved in formation of spectral contours of condensed-matter systems. To take fuller advantage of the possibilities the method provides, it should be applied to systems with a higher spectral inhomogeniety ($\Delta\nu^{IDF}/\Delta\nu^{HS} = 10...100$), which implies lowering the temperature to minimize the homogeneous broadening caused by electron−phonon interaction.

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