The Nature of Solution Spectra. Inhomogeneous Broadening and Phonon Effects in Frozen Solutions

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Abstract: The optical spectra of a number of organic compounds have been examined in low-temperature, glassy solutions. According to the experimental conditions of excitation, a given sample can yield either the usual broad bands complete with Stokes shift or a set of very narrow fluorescence lines ($\sim$1 cm^{-1}). Our comparisons of these two distinct types of spectra from the same sample make it possible to explain such features of the conventional spectra as their broad bandwidths, peak positions, and Stokes shifts.

I. Introduction

Despite differences in structure and physical properties, most organic compounds in solution share one common spectroscopic feature: their optical absorption and emission spectra are broad and poorly resolved. This spectral breadth persists even at low temperatures; the observed line widths at liquid-helium temperatures are typically 100–200 kT. This is in marked contrast to molecules which enter substitutionally into the lattice of a host crystal, where transition line widths at liquid-helium temperatures are less than kT.

The broad bandwidths are illustrated in the comparatively well-resolved spectra of tetracene (Figure 1). Although the vibronic transitions near the 0–0 transition region (at $\sim$4800 Å) are resolved, higher vibrational levels are congested. Figure 1 also illustrates a second characteristic feature of the broad solution spectra: the peaks of the 0–0 transition in absorption and fluorescence do not coincide but are separated by an amount known as the Stokes shift. Although the broad bandwidths and the Stokes shift are not intrinsic properties of organic molecules, it has only recently become possible to probe their cause directly.

With a relatively new technique called optical site selection spectroscopy, it is now possible to obtain sharp, narrow-line ($\sim$1 cm^{-1}) spectra of many organic compounds even in amorphous hosts.[3-9] We have used this technique to obtain narrow-line spectra of a number of organic compounds in frozen solutions.[3,4] In this paper, we will show how studies of these special, narrow-line spectra can explain such features of conventional spectra as their broad bandwidths, peak positions, average state energies, and Stokes shifts.

We first review the techniques of site selection spectroscopy and illustrate our experimental findings. Then, having shown that the usually broad solution spectra can be reduced to narrow lines, we reverse the procedure. Starting with the behavior of guest molecules in a single type of host local environment, we show how the broad, conventional bands are reconstructed. Finally, we compare the measured Stokes shifts of several compounds with the values that would be expected from parameters determined from their narrow-line fluorescence spectra.

II. Implications of Site Selection Spectroscopy Studies

A. The Basis of Site Selection Spectroscopy. If a guest compound is dissolved in solvent and then cooled to form a frozen solution, host inhomogeneities will produce spectral differences in the otherwise identical guest molecules. Thus, guest molecules are said to be in different "sites" if their 0–0 absorption frequencies are different. The bandwidth over which these different 0–0 absorption frequencies are found is the inhomogeneous broadening. This can be contrasted with the intrinsic bandwidth attributable to a molecule in any one site.

Since the guest molecules no longer behave identically, by virtue of their different sites, they are distinguishable. While the presence of different sites is less easily observed in the absorption spectrum, requiring either excitation techniques[10] or hole burning,[11-13] it can often be readily discerned in the fluorescence if a narrow-bandwidth excitation source is used. Instead of exciting guests in all the sites, such a source will excite only a narrow range of resonant sites, producing a sharp fluorescence spectrum with vibronic lines of 1–5 cm^{-1} instead of the usual 200–500-cm^{-1} bandwidths.[3-9] This is the basis of the technique of site selection spectroscopy.

B. Site Selection Results. With this technique we have examined a number of organic compounds in low-temperature vitreous hosts, using a continuously tunable, narrow-bandwidth, cw dye laser excitation source. Summarized here are those results of our site selection studies relevant to an understanding of the broad conventional spectra. First, we find that, with better than 1 cm^{-1} resolution, the distribution of sites within the broad 0–0 band is essentially continuous. Second, the 0–0 emission line obtained from excitation in the 0–0 absorption band is always resonant with the excitation source. And third, the primary effect of different local environments is to change the 0–0 transition frequency of the guest molecules without (greatly) affecting the vibrational spacings.

These findings are illustrated by the spectra of Figure 2 which shows the narrow-line fluorescence of tetracene excited at three different arbitrary wavelengths in its first excited vibronic band. The sharp lines in each case represent the vibronic transitions of tetracene guests in the particular local environment or "site" selected. By subtracting these transition frequencies from that of the 0–0 transition, the ground-state vibrational levels of the tetracene are obtained. Excitation of tetracene in its 0–0 band yields the same vibrational spacings if the obscured 0–0 fluorescence line is assumed to coincide with the excitation frequency.[3]

Figure 2 shows that the narrow-line fluorescence spectrum follows the shifts in the excitation frequency as the dye laser is tuned across the absorption band. This verifies the presence of discrete site frequencies throughout the broad bands. Moreover, the narrow-line spectra arising from these different sites are quite similar, apart from the overall shift in frequency.[14] In particular, the vibrational spacings are the same to within 2–5 cm.$^{-1}$ Here, as in the case of the Shpol'skii multiplets[15,16] and some mixed crystals,[17] the different local environments appear to shift only the electronic contribution to the

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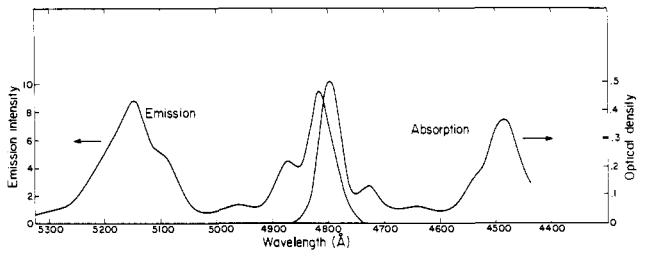

Figure 1. The absorption and emission spectra of tetracene in a 2-methyltetrahydrofuran glass at 4.2 K. The absorption and emission mirror one another and show a small Stokes shift (~90 cm^{-1}).

guests' vibronic transition energy with little change in the vibrational frequencies. We have observed similar tuning behavior in such compounds as pentacene and the anionic dye resorufin.

The continuous distribution of the sites within the broad absorption bands, the resonance of the 0-0 absorption and emission at each site, and the similarity of the fluorescence spectra of different sites lead us to the following important conclusion. The broad and poorly resolved spectra of organic compounds in frozen solution can be viewed as the sharp, narrow-line spectra of a guest in a single site with the addition of large inhomogeneous broadening.

Thus, the study of the broad frozen-solution spectrum is reduced to the comparatively well-understood study of guest molecules in a single host site.[18,19] The latter has been pursued in atomic mixed crystals or glasses,[20,21] crystalline color centers,[22] molecular mixed crystals,[23,24] and Shpol'skii systems.[15,16]

III. Synthesis of the Broad-Band Spectra

A. Spectral Behavior at a Single Site. Characteristic of all mixed-crystal or color-center system spectra in which discrete sites can be observed is the fact that each guest or color-center transition may contribute either as a sharp line or a broader sideband. The sidebands represent transitions of the guest or color center which are accompanied by the creation of phonons in the host crystal. These phonon sidebands accompany the sharp lines at higher energies in absorption and lower energies in fluorescence. The sharp lines, representing transitions of the guest or color center alone, are called zero-phonon lines. The sharp lines and broad bands of the site selection spectra are derived from such zero-phonon lines and phonon sidebands.[25]

The coupling between the phonons of the host crystal and the guest molecule or color center occurs because changes in the electronic state of the guest or color center produce slight changes in the equilibrium position of the surrounding host molecules. To this positional change there corresponds a displacement energy. The greater the displacement energy or coupling,[26] the weaker will be the zero-phonon line as compared to the phonon sideband. The fraction of the transition intensity in the zero-phonon line is called the Debye-Waller factor.[6,8,16]

As we consider how features of the broad conventional spectra occur, the important parameters at a single site will be the bandwidths and relative probabilities of the zero-phonon line and phonon sideband and the frequency separation between them.

B. The Addition of Inhomogeneous Broadening. Clearly, the amount of the broadening will greatly affect the appearance of the spectrum. The relevant parameter for comparison is the separation between the zero-phonon line and the peak of the phonon sideband. If the inhomogeneous broadening is small compared to this separation, as in the case of mixed crystals, then zero-phonon lines and phonon sidebands (albeit broadened ones) will be distinguishable in the spectra. Although small, such inhomogeneous broadening may be large in comparison to the intrinsic or homogeneous line widths. Site selection techniques can then further reduce the observed zero-phonon line widths.[20,21,27,28]

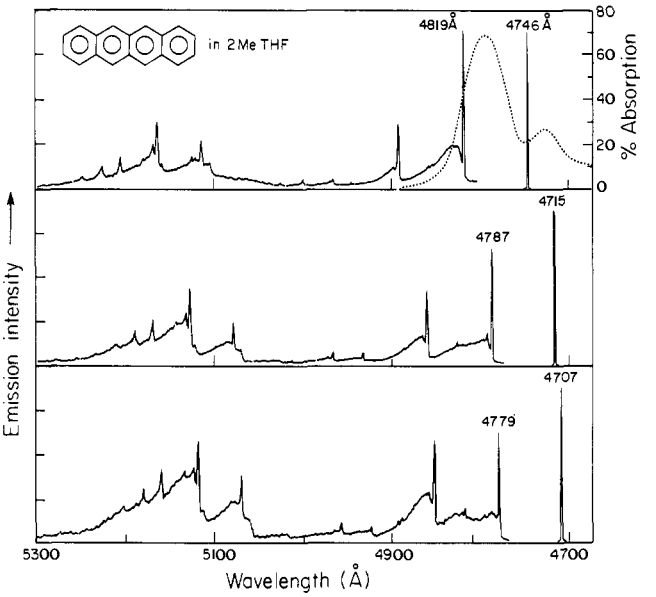

Figure 2. The site selection spectra of a dilute (~10^{-4} M) tetracene in a 2-methyltetrahydrofuran glass at 4.2 K. The spectra are excited at three different wavelengths in the first vibronic band. The attenuated exciting laser line is shown in each case as an isolated line between 4700 and 4750 Å. The laser line width was less than 0.5 cm^{-1}.

If, instead, the inhomogeneous broadening is large compared to the separation between the zero-phonon line and the peak of the phonon sideband, then these two contributions overlap and can no longer be distinguished.[29] This is the case for the solution spectra which we now consider. The discussion will be limited for simplicity to the broad 0-0 band in absorption and fluorescence but results can readily be extended to include the other vibronic levels.

As discussed above, the absorption line shape function $f(\nu - \nu')$ for a guest molecule at a single site whose 0-0 transition frequency is ν' will consist of two parts: a narrow zero-phonon line $z(\nu - \nu')$ and a broad phonon sideband $p[\nu - (\nu' + \Delta)]$, where Δ is the shift of the phonon sideband to higher frequencies. Then, the absorption line shape of a guest molecule at this site is given by[4,8]

$$f(\nu - \nu') = \alpha z(\nu - \nu') + (1 - \alpha)p[\nu - (\nu' + \Delta)] \quad (1)$$

Both z and p are normalized to unit area; their relative contributions to the absorption are given by the Debye-Waller factor α. An illustrative model for the site absorption of eq 1, with physically reasonable parameters, is shown in Figure 3.

If the probability density of the sites is given by $n(\nu')$, then the line shape function $A(\nu)$ for the total 0-0 absorption is simply the weighted sum (convolution) of the contributions from each site:

$$A(\nu) = \alpha \int_{-\infty}^{\infty} n(\nu')f(\nu - \nu')d\nu' \quad (2)$$

or

$$A(\nu) = \alpha \int_{-\infty}^{\infty} n(\nu')z(\nu - \nu')d\nu' + (1 - \alpha) \int_{-\infty}^{\infty} n(\nu')p[\nu - (\nu' + \Delta)]d\nu' \quad (3)$$

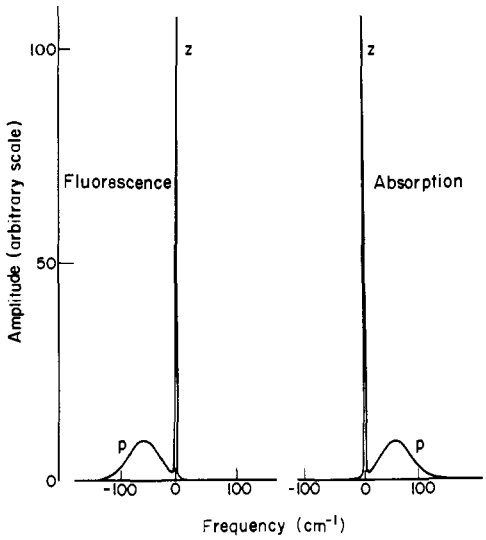

Figure 3. A model for the absorption and fluorescence of a guest molecule in a single host site for the special case in which z and p of eq 1 are Gaussian curves. The half-widths of z and p at the $1/e$ point are 1 and 35 cm^{-1}, respectively. The separation, Δ, between the zero-phonon line and the peak of the phonon sideband is 50 cm^{-1}. The area ratio of p to z is 3. This set of parameters is also used in Figures 4 and 5.

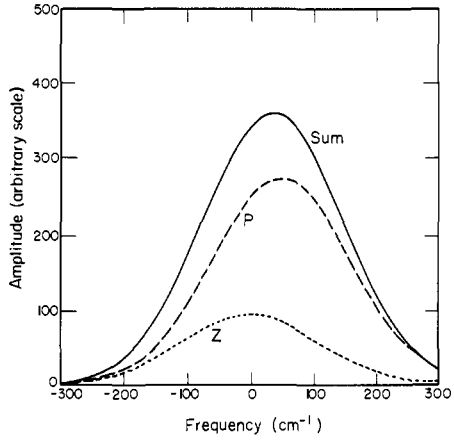

Figure 4. Components of the broad-band absorption of eq 3 for the Gaussian parameters of Figure 3. $n(\nu')$ is also Gaussian with a $1/e$ half-width of 150 cm^{-1} and is centered at zero frequency. Z is the contribution of the zero-phonon lines, P is the contribution of the phonon sidebands, and the solid curve is their sum.

Here we have shifted the origin of the frequency scale so that $n(\nu')$ peaks at $\nu' = 0$ in order to simplify the notation.

Equation 3 shows that there are two contributions to the broad-band absorption even though it represents a single broadened transition. The first integral gives the contribution of all the sharp zero-phonon lines at the different sites. The second is the contribution of all the broad phonon sidebands. These two terms and their sum are illustrated in Figure 4, assuming a Gaussian distribution of sites and the same site parameters as in Figure 3.

Equation 3 and Figure 4 point out some important aspects of the broad-band spectra. First of all, the presence of two different contributions to the broad 0-0 absorption band suggests that no particular line shape should be expected for the broad-band transitions; for instance, the bands should not necessarily be Gaussian. Similarly, the spectral bandwidths and peak positions are not intrinsic properties of the guest spectrum but represent "averages" over the different sites. Moreover, this "averaging" may be different for different vibronic transitions, as suggested by the differences in the phonon-like bands among the various transitions in Figure 2. These

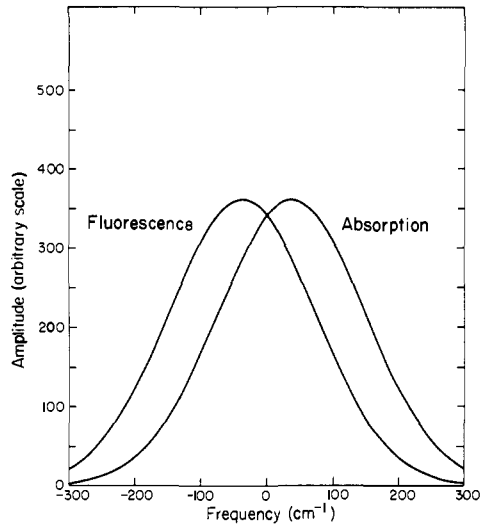

Figure 5. The broad-band absorption from eq 3 and the broad-band emission from eq 4 illustrating the Stokes shift. The absorption curve is the same as the solid line in Figure 4. The parameters of Figures 3 and 4 were used.

differences, which are of order Δ as defined previously, reflect variations in the coupling of different guest vibrational modes with the phonon spectrum of the host. Accordingly, one might expect a percentage error ($\sim\Delta/\omega_{vib}$) in the vibrational frequencies obtained from broad-band spectra of as much as 10-20%. Finally, it bears repeating that for inhomogeneous broadening there is no single 0-0 transition, but a whole distribution of 0-0 transition energies having some average value. Because of the contribution of phonon sidebands, this average 0-0 energy will not coincide with the broad-band absorption peak, but will always lie at lower energies.

A similar analysis holds for the broad 0-0 fluorescence band assuming that all sites are excited. Because of the approximate mirror symmetry[30] often observed between the broad absorption and fluorescence curves, the fluorescence of a guest in a site at ν' is chosen to have the same functional form as the absorption of eq 1. However, ν and ν' are interchanged, reflecting the fact that in fluorescence the phonon sidebands occur on the low-energy side of their zero-phonon lines. With this choice, the 0-0 transition at any site ν' is resonant for absorption and emission as suggested by Figure 3 and in agreement with experimental observations. The emission line shape is then given by

$$E(\nu) = \alpha \int_{-\infty}^{\infty} n(\nu')z(\nu' - \nu)d\nu' + (1 - \alpha) \int_{-\infty}^{\infty} n(\nu')p[\nu' - (\nu + \Delta)]d\nu' \quad (4)$$

Again, there are two contributions to the broad 0-0 fluorescence, just as for the absorption in eq 3. The observations made for the broad-band absorption are also valid for the broad fluorescence, except that, while the broad 0-0 absorption peak lies at higher energies than the average 0-0 energy, the fluorescence peak will lie at lower energy. Consequently, a Stokes shift results as shown in Figure 5. In this special case of mirror symmetric absorption and fluorescence at each site, the average 0-0 energy is at the intersection of the normalized broad absorption and fluorescence bands. Thus, the phonon sidebands are responsible for substantial Stokes shifts observed in frozen solution, even though the absorption and fluorescence zero-phonon lines at any individual site are resonant!

Equations 3 and 4 and Figures 3 and 4 show that the Stokes shift depends not on the broadening but on the parameters α and Δ at the individual sites. If all the absorption and emission

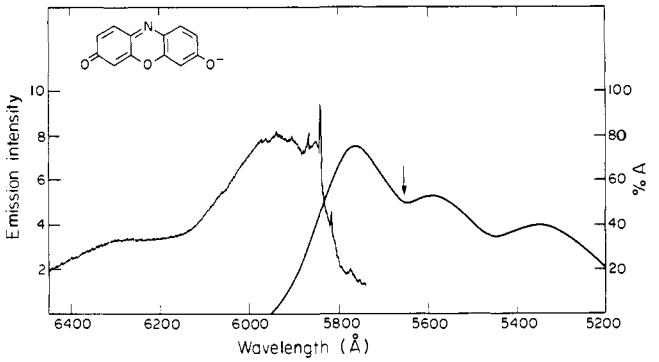

Figure 6. The absorption and site-selection spectra of resorufin in an ethanol-methanol glass at 4.2 K excited by a narrow line ($\lesssim 0.5$ cm^{-1}) dye laser. The arrow indicates the wavelength of excitation.

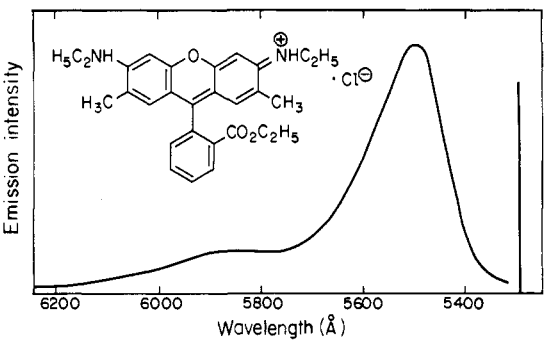

Figure 7. The site selection spectrum of rhodamine 6G in an ethanol-methanol glass at 4.2 K excited with a laser line at ~5300 Å. This spectrum is identical with the normal emission of rhodamine 6G.

intensity occur in the broad phonon sidebands ($\alpha \approx 0$) for a guest molecule in frozen solution, then the Stokes shift will have its maximum value of 2Δ, as is the case for certain color centers.[31] This represents a shift of Δ for the absorption and fluorescence peaks away from the average 0-0 energy. On the other hand, strong zero-phonon lines with no phonon sideband contributions will yield only resonant absorption and emission with no Stokes shift. The actual value of the Stokes shift between 0 and 2Δ depends on the Debye-Waller factor α.

IV. Results. Broad-Band Spectra

The difficulty with quantitative experimental verification of these predictions for the Stokes shift is that each of the phonon-like sidebands observed in the site selection spectra, although it contains the contribution of the phonon sidebands, contains two other contributions as well.[4,8] These latter contributions occur because, as Figure 4 indicates, only part of the energy at a given frequency is absorbed by resonant zero-phonon lines at that one site. This effect can be minimized by exciting in the low-frequency edge of the broad absorption.[8] The phonon-like bands then most closely resemble the actual phonon sidebands, and estimates of the parameters α and Δ can be made. In the case of tetracene, the spectrum of Figure 2a was used. By taking the ratio of the 0-0 zero-phonon line to the total 0-0 emission, we estimte the probability α of zero-phonon emission to be between 0.3 and 0.4. The measured value of Δ is 45 ± 10 cm^{-1}. Based on these data, the maximum Stokes shift of 2Δ for tetracene in this solvent at 4.2 K is 90 ± 15 cm^{-1}. Our experimental value for the Stokes shift taken from Figure 1 is 87 ± 10 cm^{-1}, in good agreement considering that the phonon sideband is assumed to have a Gaussian shape.

Whether or not the fluorescence is excited in the optimum region, qualitative agreement with the model is obtained. For example, chrysene in 2-methyltetrahydrofuran at 4.2 K, excited with the 3511-Å line of an argon-ion laser, has a very sharp fluorescence spectrum with little phonon-like structure.[4] Accordingly, its Stokes shift should be much smaller than that of tetracene. Our measured value obtained from conventional 4.2 K spectra is only 15 ± 5 cm^{-1}. A further example is the ionic dye resorufin in an ethanol-methanol (1:1) solution. Its site selection spectrum shown in Figure 6 has a few zero-phonon lines but contains a great deal of broad phonon-like emission shifted well away from the zero-phonon lines. As expected, its apparent Stokes shift is large, about 360 cm^{-1}. The more extreme example of rhodamine 6G is shown in Figure 7. This dye exhibited no zero-phonon emission with laser excitation. In this instance, the measured Stokes shift is 540 cm^{-1}.[32]

Site selection and conventional spectra taken on azulene in several solvents indicate that both the site selection spectra and the Stokes shifts are solvent dependent. In a solvent series of increasing polarity, the Stokes shift grows with the phonon-like intensity from 70 cm^{-1} in methylcyclohexane to 80 cm^{-1} in 2-methyltetrahydrofuran to 100 cm^{-1} in ethanol-methanol (1:1). The more polar host interacts more strongly with the polar guest, thus decreasing the probability of a zero-phonon transition. These results are indeed in qualitative agreement with the predictions of the model.

We have considered only frozen solutions at liquid-helium temperatures, but we believe that with increasing temperature, our model goes over to the room temperature liquid model in a continuous fashion. Evidence of a distribution of sites has been observed up to about 240 K.[33] But, as the temperature increases in the frozen solution, the probability for zero-phonon emission decreases[5,8,16] to become vanishingly small leaving only phonon sidebands in the spectra. Anti-Stokes phonons may also become important in determining the size of the Stokes shift.[34] As the solution thaws, the degrees of freedom represented by the phonon modes defer to the rotational and translational motions of the solvent molecules. Viewed instantaneously, the broad range of local environments still exists; however, these no longer remain fixed during the guest fluorescence lifetime.

We have reviewed the import of inhomogeneous broadening for the broad conventional spectra of organic molecules in solution. It appears that considering these spectra in terms of the behavior at the individual sites is both consistent and useful.

From this work, we can conclude the following about the broad, conventional spectra of molecules in vitreous hosts at liquid-helium temperatures:

1. The spectra are generally composed of both the narrow zero-phonon lines and the phonon sidebands. However, these individual features are normally obscured by the superposed effects of 200-500 cm^{-1} of inhomogeneous broadening.

2. The observed line shapes, since they may contain two types of contributions, are not necessarily Gaussian.

3. Vibronic frequencies determined from the broad solution spectra may be in error by 10-20%, even though the bands in question are well resolved.

4. The phonon sidebands are responsible for the observed Stokes shifts. The size of the Stokes shift appears to correlate with the relative contribution of the phonon sidebands in the corresponding site selection spectrum.

5. The average 0-0 transition energy is the same for both absorption and emission. It lies at neither the absorption peak nor the emission peak, but always between the two.

Some of these conclusions are valid for fluid solutions to the extent that the frozen systems represent an instantaneous picture of the fluid system.

V. Experimental Section

Materials for spectroscopic investigations were dissolved in distilled Spectrograde solvents which form glasses at low temperatures. For

absorption measurements, the concentration was adjusted so that ~50% of the light was absorbed. Lower concentrations were used for emission studies to avoid any problems of reabsorption.

Pyrex NMR tubes (5 mm) were used to hold the samples for the emission experiments. Rectangular (2 × 10 mm) Pyrex cells were used for the absorption measurements. All samples were immersed directly into liquid helium in a Pyrex double Dewar, with windows in the liquid-nitrogen jacket to avoid passing the light through boiling nitrogen.

All absorption and emission spectra were obtained on a 1-m Jarrel-Ash spectrometer. Site selection spectra of azulene and chrysene were obtained using the 3511-Å line of the argon-ion laser. Absorption spectra were obtained with a quartz-halogen lamp. The excitation source for the broad-band emission spectra was a high-pressure mercury lamp in combination with broad-band filters. Site selection spectra were obtained with a tunable continuous-wave jet-flow dye laser pumped with an 8-W argon-ion laser. Rhodamine 110, pumped with all visible lines, could be tuned from ~530 to 595 nm. Coumarin 1, pumped with the UV lines, was tunable from 455 to 485 nm. Intracavity etalons were used to reduce the output bandwidth to less than 1 cm^{-1}.

The curves displayed in Figures 3-5 were generated and plotted on an IBM-1130 computer.

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Conformational Equilibria in Vitamin D. Synthesis and ^1H and ^{13}C Dynamic Nuclear Magnetic Resonance Study of 4,4-Dimethylvitamin D_3, 4,4-Dimethyl-1α-hydroxyvitamin D_3, and 4,4-Dimethyl-1α-hydroxyepivitamin D_3

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Abstract: The title compounds were synthesized and their dynamic properties investigated by variable temperature ^1H NMR. Each of these compounds gave separate signals, at low temperature, for ring A conformers. The temperature-dependent spectra allowed the determination of the activation parameters characteristic of ring A chair-chair interconversion. The free energies of activation ($\Delta G^{\ddagger}$) for the chair inversion in 4,4-dimethylvitamin D_3 (**4a**), 4,4-dimethyl-1α-hydroxyvitamin D_3 (**5**), and 4,4-dimethyl-1α-hydroxyepivitamin D_3 (**6**) were found to be 10.1, 11.0, and 12.0 kcal/mol, respectively. The ^{13}C NMR spectrum of **4a** was recorded at room temperature and at low temperature (ca. −90 °C). The chemical shift separation of the two observed C_3 signals, at low temperature, was used for conformational analysis.

Introduction

Vitamin D is a steroid, whose actual shape considerably differs from other steroids. The difference lies in its cleaved ring B and its C_6-C_7 single bond having an s-trans instead of an s-cis conformation. It appears that this extended structure of vitamin D has the lowest ground state free energy; however, this bond is free to rotate, enabling vitamin D to achieve the

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