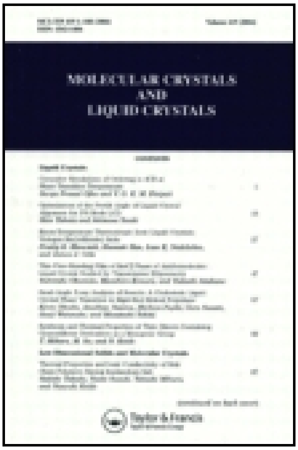

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Internal Electric Fields and Inhomogeneous Broadening: Protoporphyrin-IX in Myoglobin

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INTERNAL ELECTRIC FIELDS AND INHOMOGENEOUS BROADENING: PROTOPORPHYRIN-IX IN MYOGLOBIN

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Abstract Estimates of the relative contributions of dispersive and electrostatic interactions to the solvent shift of the Q_x excitation energy of protoporphyrin-IX in myoglobin are derived from measurements of the dependence of Stark splitting on frequency.

INTRODUCTION

The resolution increase attained through photochemical hole burning makes it possible to clearly see the effect that an external electric field has on the transition energy of a probe molecule in solid solution. Transition energy shifts induced by both external and internal electric fields can be treated by adding a perturbation term ($-\underline{E} \cdot \underline{\mu}$ in the case of molecular resolution, site energies in the case of atomic resolution) to the Hamiltonian that reproduces the measured excitation energies .This leads to simple quantum mechanical models that can be applied to measurements of the effects that external electric fields have on the profile of a photochemical hole to determine the internal electric field at the guest site at molecular[1] and even atomic[2] resolution.

The interactions that shift the transition energy of a guest molecule from its gas phase value to the value observed in solution can be divided into dispersive and electrostatic contributions which are distributed by variations in local structure to give the observed inhomogeneous band profile. Since the electrostatic contribution may be expressed in terms of the internal electric field, the ability to directly determine this field means that, at least in principle, the relative importance of dispersive and electrostatic contributions can be assessed. In this paper we report a preliminary examination of these issues for the case of protoporphyin-IX in myoglobin.

DATA

The molecular resolution level determination of the internal electric field at protoporphyrin-IX in myoglobin is reported in another contribution to this volume. The values obtained for the internal field as a function of burning frequency in the Q_x band are tabulated in the first three columns of Table 1 and plotted in Figure 1.

TABLE 1. Dependence of internal field on position in the inhomogeneous Q_x profile with the corresponding electrostatic shifts and relative probabilities.

Burn Frequency (cm^{-1})	E_x (MV/cm)	E_y (MV/cm)	Electrostatic Shift* (cm^{-1})	Relative Probability†
16051	29.1	35.0	32.8	0.32
16091	26.7	37.5	33.8	0.70
16112	28.8	39.7	38.3	0.88
16131	29.8	38.3	37.5	0.98
16151	31.8	38.9	40.0	0.99
16171	32.7	43.1	46.6	0.88
16191	33.7	46.4	52.4	0.71

* From Equation 1.
† From the Gaussian that fits the 1.2K Q_x excitation profile.

HAMILTONIAN

Again, the reference for describing the effect of an external electric field on photochemical hole profile is the porphin molecule which forms the conjugated core of protoporphyrin-IX. In the point dipole approximation the effect of an electric field on the Q_x excitation energy of the D_{2h} symmetry porphin core is described by the Hamiltonian

$$H=\begin{pmatrix} 0 & -E_x\mu_{Qx} & -E_y\mu_{Qy} & -E_x\mu_{Bx} & -E_y\mu_{By} \\ -E_x\mu_{Qx} & W(Q_x) & 0 & 0 & 0 \\ -E_y\mu_{Qy} & 0 & W(Q_y) & 0 & 0 \\ -E_x\mu_{Bx} & 0 & 0 & W(B_x) & 0 \\ -E_y\mu_{By} & 0 & 0 & 0 & W(B_y) \end{pmatrix} \qquad (1)$$

where $W(Q_x)$, $W(Q_y)$, $W(B_x)$ and $W(B_y)$ are the zero field energies of the Q_x, Q_y, B_x and B_y states, respectively, μ_{Qx}, μ_{Qy}, μ_{Bx} and μ_{By} are the corresponding transition dipoles, and the basis is restricted to the π-electron states of the 4-orbital model[3] (Q and B or Soret states). $W(Q_x)$ was chosen so that diagonalization of Eq. 1 for zero external field (internal field only) gave the center frequency of the photochemical hole; the other zero field energies were $W(Q_y)$, $W(B_x)$ and $W(B_y)$ equal to 18840 cm^{-1}, 23180 cm^{-1} and 23350 cm^{-1}, respectively (as would be expected from the smallness of the electric field perturbation relative to the excitation energies, the excitation energy shifts calculated for a given electric field are quite insensitive to the values of the zero field energies). The transition dipoles come from theory[4] (μ_{Qx}, μ_{Qy}, μ_{Bx} and μ_{By} equal to 0.102, 0.152, 1.104 and 1.151 Debye, respectively). Our choice of 2.1 for the local field factor is discussed elsewhere.[5]

ELECTROSTATIC CONTRIBUTION TO INHOMOGENEOUS BROADENING

The fact that the Q_x fluorescence excitation band for protoporphyrin-IX in myoglobin is inhomogeneously broadened means that local structure in the neighborhood of the chromophore is distributed. This can be described in terms of a fundamental probability distribution function $P(\underline{R})$ that gives the probability of a given local structure specified by the relevant coordinates $\underline{R}$. (For the time scale and temperature of these experiments $P(\underline{R})$ can be assumed to be time independent.) Associated with any given local structure is a well defined dispersive and electrostatic shift, so the fundamental distribution function $P(\underline{R})$ could be used to construct $P(\bar{\nu})$, the function that gives the probability of a given transition frequency or, alternatively, $P_{disp}(\bar{\nu})$ and $P_{elec}(\bar{\nu})$, functions that respectively give the probability of a given dispersive or electrostatic shift. Of course, $P(\bar{\nu})$ is just the normalized inhomogeneous profile. To go the other way, that is to construct $P(\bar{v})$ from $P_{disp}(\bar{v})$ and $P_{elec}(\bar{v})$ requires information on the correlations between dispersive and electrostatic shifts. The observed systematic dependence of internal electric field on position in the inhomogeneous profile tells us that in this particular case the dispersive and electrostatic shifts are significantly correlated, as might be expected from the fact that both interactions depend on inverse powers of intermolecular distances and the fact that the total range of $\underline{R}$ only spans small distortions of a single local structure. If the $P_{disp}(\bar{v})$ and $P_{elec}(\bar{v})$ distributions can be described as correlated Gaussians, then knowledge of the inhomogeneous profile $P(\bar{v})$ and the dependence of internal electric field on $\bar{v}$ is enough information to almost completely specify $P_{disp}(\bar{v})$ and $P_{elec}(\bar{v})$.

How distributed but correlated dispersive and electrostatic interactions convert the narrow homogeneous band of the isolated molecule into the observed inhomogeneous profile is sketched in Figure 1.

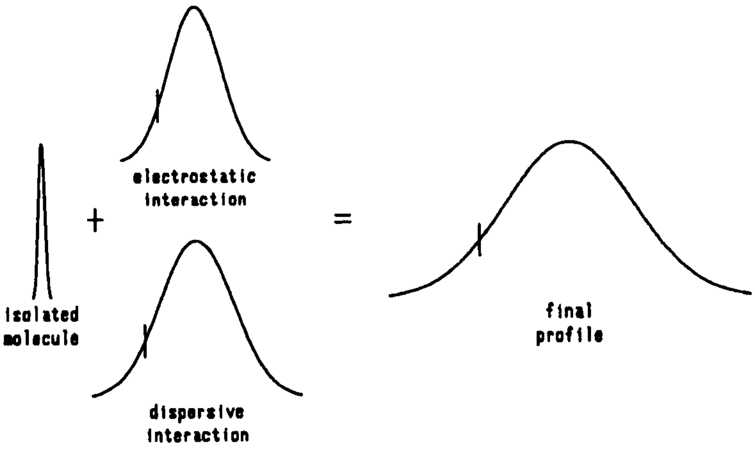
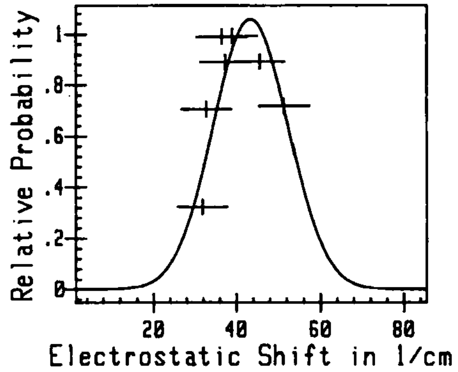


FIGURE 1 Mapping of dispersive and electrostatic interactions for the case of complete correlation. Corresponding points are indicated by vertical bars.

The key idea is that, if there is complete correlation, then, in units of standard deviations, the probability of obtaining a frequency is the same for $P(\bar{v})$, $P_{disp}(\bar{v})$ and $P_{elec}(\bar{v})$. Thus, we can use the fact that at 1.2K the Q_x 0-0 band is well fit by a Gaussian centered at 16140 cm^{-1} with FWHM 140 cm^{-1} to assign probabilities to the internal fields in Table 1 and Equation 1 to convert these internal fields into electrostatic shifts. This gives us

$P_{elec}(\bar{\nu})$ as summarized in the last two columns of Table 1. The best fit of a Gaussian (center at 40 cm^{-1}, FWHM 20 cm^{-1}) to these data is shown in Figure 2.

FIGURE 2 Gaussian distribution of electrostatic shifts. Shifts calculated from Eq. 1 for a given burn frequency are plotted against the relative probability of that frequency in the inhomogeneously broadened profile as crosses. The smooth curve is a 20 cm^{-1} Gaussian centered at 40 cm^{-1}.



For perfect correlation the 140 cm^{-1} width of $P(\bar{\nu})$ must be the sum of the widths of $P_{disp}(\bar{\nu})$ and $P_{elec}(\bar{\nu})$ so the FWHM of $P_{disp}(\bar{\nu})$ is estimated to be 120 cm^{-1}. Thus, in this case the dispersive and electrostatic contributions to the inhomogeneous broadening are estimated to be 86% and 14%, respectively. We also know that the electrostatic contribution to the shift of transition frequency is 40 cm^{-1} and that the sum of gas phase transition frequency and dispersive shift is 16100 cm^{-1}. Thus, the Q_x transition frequency measured for vapor phase porphine (15940 cm^{-1})^6 would fix the dispersive shift at 160 cm^{-1}. The usual expectation of a negative dispersive shift in transition energy is based on a two level model that is only appropriate for strong transitions. In this case this model is most appropriate for the B state transition energies, which would certainly be expected to experience a negative dispersive shift, reflecting the fact that their energy is lowered more than is the energy of the ground state. Precisely because of the strength of the B state/ground state interaction, the stabilization of the ground state could exceed that of the weakly allowed Q states resulting in a shift of the Q_x transition to higher energy. However, the fact that the gas phase energy represents the center of a high temperature band contour means that the actual value of the dispersive shift is quite uncertain.

CONCLUSION

The fact that the internal electric field at protoporphyrin-IX in myoglobin exhibits a smooth and systematic dependence on frequency means that the dispersive and electrostatic contributions to the solvent shift of the Q_x transition must be correlated. In the case of complete correlation the Hamiltonian that describes the electric field shifts can be used to determine the electrostatic contribution to the inhomogeneous broadening

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