THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 104, NUMBER 4, FEBRUARY 3, 2000

LETTERS

The Effect of Correlation of Inhomogeneous Environmental Shifts on Raman Depolarization Ratio Dispersion

Gregory P. Harhay[†] **and Bruce S. Hudson***

Department of Chemistry and Chemical Physics Institute, University of Oregon, Eugene, Oregon 97403, and Department of Chemistry and Keck Center for Molecular Electronics, Syracuse University, Syracuse, New York 13244-4100

Received: November 23, 1999

The magnitude and sense of correlation between the inhomogeneous broadening distributions of two neighboring electronic states is shown to have a significant effect on the dispersion of the depolarization ratio, ρ, for Raman scattered radiation. To examine this effect quantitatively we treat numerically a model in which two electronic excitations with mutually perpendicular transition dipole orientations are represented by shifted one-dimensional harmonic potentials. The inhomogeneous broadening is treated in the static limit as a Gaussian fluctuation in each of the two electronic origins. The correlation of these shifts is treated as a variable with the fully correlated and fully anti-correlated limits spanning the uncorrelated case. It is shown that the degree of correlation (and its sign) strongly influences the value of the depolarization ratio in some cases which should be amenable to experimental study. Three cases are treated which differ in the separation of the electronic origins of the two states from larger than the total transition width, less than the transition width, and zero. If the state degeneracy is due to symmetry, then in this last case the correlation of the inhomogeneous fluctuations becomes equivalent to symmetric and anti-symmetric environmental variations.

Inhomogeneous broadening effects on electronic excitations due to variations in the environment at the molecular level are of interest from the point of view of the effect on the intensities and dispersion of the spectral properties and also on the insight that might be obtained on the statistical fluctuations of the solvent medium and the response of the chromophore to these fluctuations. A variety of experimental methods have been developed for the measurement (or elimination) of inhomogeneous broadening effects,[1] and a number of recent studies have dealt with the theoretical description of such effects. One aspect of inhomogeneous broadening that has arisen recently concerns the relative influence of site variations on two distinct transitions. The issue is the extent to which the fluctuation of the transition energy (relative to its mean value) for one transition is correlated with that for another transition of the same molecule. This consideration arises naturally when, for example, narrow band excitation is used to select a subset of the absorption transitions of a singlet−singlet transition and then phosphorescence due to a triplet−singlet transition is observed. Line-narrowing will be observed only to the extent that these two transition energy fluctuations are correlated (and, in this case, persistent for the triplet lifetime).

A discussion of the effect of correlations of inhomogeneous broadening distributions in liquids and glasses has been presented by Sevian and Skinner[1] in the context of hole burning experiments. In the present work we will show the consequences of correlated inhomogeneous fluctuations on the dispersion of the depolarization ratio for resonance Raman scattering of a

---

* Corresponding author. E-mail: bshudson@syr.edu.
[†] Present address: HARD Industries, 26 John St., Chicopee, MA 01013.

10.1021/jp994179f CCC: $19.00

totally symmetric vibrational mode. We restrict our attention to the static broadening case. Work by Wynne and Hochstrasser[2] deals with very similar considerations in a much more general context. Here we model this effect with reasonably realistic parameters to explore the magnitude of the effect and to determine when it will be most easy to observe.

It is well-known that inhomogeneous broadening can have a significant effect on the absolute Raman cross section[3] and that the overall broadening observed in the absorption spectrum can be separated into its homogeneous and inhomogeneous contributions via a simultaneous analysis of both the absorption and absolute resonance Raman intensities.[4] This is a consequence of the fact that Raman scattering is a coherent phenomenon (at a molecular level) involving contributions from the amplitudes of all states that are within a homogeneous line width of the excitation frequency. It is the square of this sum of contributions that is averaged over the inhomogeneous distribution. The physical basis for this use of absolute Raman intensities to separate homogeneous and inhomogeneous contributions to the total line width can be seen from the fact that if most of the line width is homogeneous then the damping term Γ is large and the total Raman scattering observed on resonance is small. A smaller homogeneous contribution with a correspondingly larger inhomogeneous contribution results in sharper resonances for each subset of the ensemble. This more than compensates the lower number concentration at resonance. This method has been used many times for the separation of homogeneous and inhomogeneous contributions to the total line width. A summary of the results of application of this method has been previously presented in tabular form.[5] The numbers chosen for use in these simulations are typical of the results presented by us and by other workers for a wide variety of polar and nonpolar molecules in both polar and nonpolar solvents.

The effects of environmental fluctuations that lead to inhomogeneous broadening are usually modeled in terms of a distribution (usually Gaussian but sometimes, for simplicity, Lorentzian) of values for the electronic origin of a vibronic transition. The vibrational intervals and equilibrium geometry of the molecule are assumed to be independent of specific site. This appears to be consistent with experimental results where spectral resolution is observed. When two or more electronic transitions are considered the issue of the correlation of the shifts may require consideration.

There are several limiting cases of the correlation of the inhomogeneous shifts of two electronic excitations. In the completely uncorrelated case the fluctuations are independent. In this case a molecule that finds itself in an environment such that one of its excitations is at a relatively elevated energy, will have any of the possible values (within the inhomogeneous distribution) for its other excitation. In the fully correlated case, fluctuations which raise (or lower) the excitation of one transition relative to its mean value cause the same directional shift for the other transition. If the two inhomogeneous distributions have the same width, then this fully correlated situation corresponds to a constant separation of the two excitation energies for all molecules in the sample. In the case of negative correlation, an environment that results in upward shifts for one transition reduce the excitation energy of another.

One can imagine situations that might correspond to each of these cases. Correlated behavior is expected for cases where the inhomogeneity is dominated by variations in dispersion interactions due to fluctuations in the density. This may occur for two strongly allowed transitions of a nonpolar molecule in a nonpolar solvent. For excitations that result in changes in the dipole moment of a molecule, the dominant inhomogeneous effect in polar solvents may be determined by fluctuations in the dipole moments of the field felt by the chromophore. In a simulation calculation for 3-methylindole in aqueous solution it was found that the fluctuations of the L_a and L_b transitions were highly correlated.[6] In this case the dipole moments in both states (and thus the change in the dipole moment upon excitation from a common state) are in the same direction and thus at least the dipole term responds in the same direction to fluctuations in the surrounding field. For the case of nπ^* and $\pi\pi^*$ excitations (where the transition dipole orientations will tend to be perpendicular), hydrogen bonding will usually result in an increase in the excitation energy of the nπ^* excitation and may result in a downward shift in the energy of the $\pi\pi^*$ excitation. This will result in negative correlation of the inhomogeneous distributions that result from fluctuations in the extent of hydrogen bonding.

When two or more electronic states each have displacements along a particular mode of motion of the molecule, they may both contribute to the resonance Raman effect. If those two electronic excitations have noncollinear transition dipole orientations, then the fact that both transitions contribute to the scattering in a way which varies with excitation will result in a dispersion of the depolarization ratio for the Raman scattering radiation, ρ. Some applications of this behavior have been described.[7] If only one transition contributes to the Raman scattering the value of ρ is 1/3; if two transitions contribute equally to the scattering (as for a degenerate transition), $\rho =$ 1/8. For two nondegenerate states the value of ρ will vary as the relative contributions of the two states varies with excitation frequency.

It is a straightforward matter to set up and evaluate simple models (or parametrized fits to data) corresponding to the case of two electronic excitations each making a contribution to a particular Raman scattering transition and to evaluate the resulting Raman excitation profiles and depolarization ratios. Inhomogeneous broadening may be included in this analysis by subsequently performing an average of the observed quantities corresponding to a sub-ensemble (with a particular pair of excitation energies) over a proposed inhomogeneous distribution. The new feature (so far as Raman scattering is concerned) is the need to specify the extent to which the two inhomogeneous distributions are correlated. We anticipate that the effect of changes in the degree of correlation of inhomogeneous distributions will be larger for the depolarization ratio than for the absolute intensity.

Simulation Calculations

To explore the magnitude of the effect of correlation of the inhomogeneous distributions on depolarization ratios we adopt a simple model for the resonance Raman scattering when two electronic excitations (with mutually perpendicular transition dipole orientations) contribute to the scattering. We assume allowed electronic transitions (and thus A-term Raman scattering), equal intensities for the two electronic transition matrix elements, and equally displaced one-dimensional harmonic oscillators with vibrational frequencies that are chosen to be typical. We fix the (equal) values of the homogeneous and the Gaussian inhomogeneous width parameters and then calculate the depolarization ratio as a function of excitation wavelength for various values of the separation of the two excited states and for various degrees of correlation of the two inhomogeneous distributions. The formalism of Sevian and Skinner[1] is used for the inhomogeneous distribution functions. If we chose the two transition dipole orientations to be x and y, then the two nonzero components of the scattering tensor in the molecule fixed coordinate system are α_{xx} and α_{yy} each of which exhibit dispersion as prescribed by the Kramers–Heisenberg–Dirac formalism. For this special case,

$$\rho = \frac{(|\alpha_{xx}|^2 + |\alpha_{yy}|^2 - J)}{3(|\alpha_{xx}|^2 + |\alpha_{yy}|^2 + 2J/3)}, \quad J \equiv (\alpha_{xx}{}^*\alpha_{yy} + \alpha_{xx}\alpha_{yy}{}^*)/2$$

The numerator and the denominator of this expression for ρ are, except for a proportionality factor, independently observable quantities ($I_{\|}$ and $I_{\perp}$) and each must be averaged over the ensemble distribution. The averaging process for the quantities $|\alpha_{ii}|^2$ requires only a knowledge of the distribution for the one state in question but the cross term J requires a knowledge of the joint probability distribution since both states are involved.

Following Sevian and Skinner,[1] we describe the normalized joint distribution that the two states A and B have the *excitation* energies E and E' and inhomogeneous distributions with variances D_{AA} and D_{BB} by

$$P_{\mathrm{AB}}(E,E') = [2\pi\sigma]^{-1} \exp\{-[D_{\mathrm{AA}}(E' - E_{\mathrm{B}})^2 - 2D_{\mathrm{AB}}(E' - E_{\mathrm{B}})(E - E_{\mathrm{A}}) + D_{\mathrm{BB}}(E - E_{\mathrm{A}})^2]/2\sigma^2\}$$

where $\sigma \equiv \sqrt{D_{\mathrm{AA}}D_{\mathrm{BB}} - D_{\mathrm{AB}}{}^2}$. (The conditional probability distribution given by eq 2.21 of Sevian and Skinner[1] is used in the actual calculation.) The value of D_{AB} is limited by $D_{\mathrm{AB}}{}^2 \leq D_{\mathrm{AA}}\,D_{\mathrm{BB}}$. If $D_{\mathrm{AB}} = +\sqrt{D_{\mathrm{AA}}D_{\mathrm{BB}}}$ the transition energy fluctuations are fully correlated; if $D_{\mathrm{AB}} = -\sqrt{D_{\mathrm{AA}}D_{\mathrm{BB}}}$ the transition energies are fully anti-correlated. In either case the joint probability distribution becomes a delta function. $D_{\mathrm{AB}} = 0$ corresponds to the uncorrelated case, and the distribution separates into two independent factors. We define the correlation coefficient as $C_{\mathrm{AB}} = D_{\mathrm{AB}}/\sqrt{D_{\mathrm{AA}}D_{\mathrm{BB}}}$ so $-1 \leq C_{\mathrm{AB}} \leq +1$. In the present work we consider only the limiting cases of full correlation, $C_{\mathrm{AB}} = +1$, and full anti-correlation, $C_{\mathrm{AB}} = -1$. The intermediate cases, including the uncorrelated case $C_{\mathrm{AB}} = 0$, result in intermediate values for ρ between the values obtained with these extreme limits.

Results

Figure 1 shows three cases illustrating the effect of the correlation of inhomogeneous broadening on the dispersion of ρ. In each case the dimensionless displacement parameter for each excitation is $\Delta = 2$ and the two transitions have equal oscillator strength. The homogeneous line width, Γ, is 400 cm^{-1}, the dispersion of the inhomogeneous line widths of each distribution is taken to be the same and equal to 500 cm^{-1}, $\sqrt{D_{\mathrm{AA}}} = \sqrt{D_{\mathrm{BB}}} = 500$ cm^{-1}. The ground-state frequency is 1050 cm^{-1}, and the excited-state frequency is 950 cm^{-1}. The origins of the electronic transitions are equally shifted above and below 50 000 cm^{-1} in each case. The smooth and dashed curves show the absorption spectra for the two transitions with perpendicular transition dipole orientations. The vibronic components are given the full width of $\Gamma + \Delta = 900$ cm^{-1}.[3] The vibronically resolved trace is for a total line width of 100 cm^{-1} to show the vibronic intensity distribution for $\Delta = 2$.

In the top panel the separation of the two excitations, $\Delta E = 5750$ cm^{-1}, is slightly larger than the full width of the individual vibronic envelope of each transition which is about 4000 cm^{-1}. In the middle panel the separation ΔE is much less than the vibronic bandwidth. In the last case $\Delta E = 0$, corresponding to a degenerate pair. The variation of ρ with excitation wavenumber makes sense in terms of limiting values. At very low frequency both excitations contribute equally and ρ approaches the value of 1/8. This is more obvious for smaller ΔE. As the frequency is increased from a lower value and the first resonance is approached, that lower transition becomes relatively more important. A value of $\rho = 1/3$ is expected when only one state dominates, and that value is seen as a shoulder in the case shown in the upper panel. In all three panels the variation of ρ shown with triangles corresponds to $C_{\mathrm{AB}} = -0.99$, full anti-correlation of the inhomogeneous distributions. The plot denoted with circles is for $C_{\mathrm{AB}} = +0.99$, full correlation of the solvent fluctuations. In this case the state origins remain separated by ΔE for all environments. The uncorrelated case $C_{\mathrm{AB}} = 0$, results in intermediate curves as do all other cases.

The positively correlated case results in the lowest value of ρ. The effect with $\Delta E = 500$ cm^{-1} is rather large and should

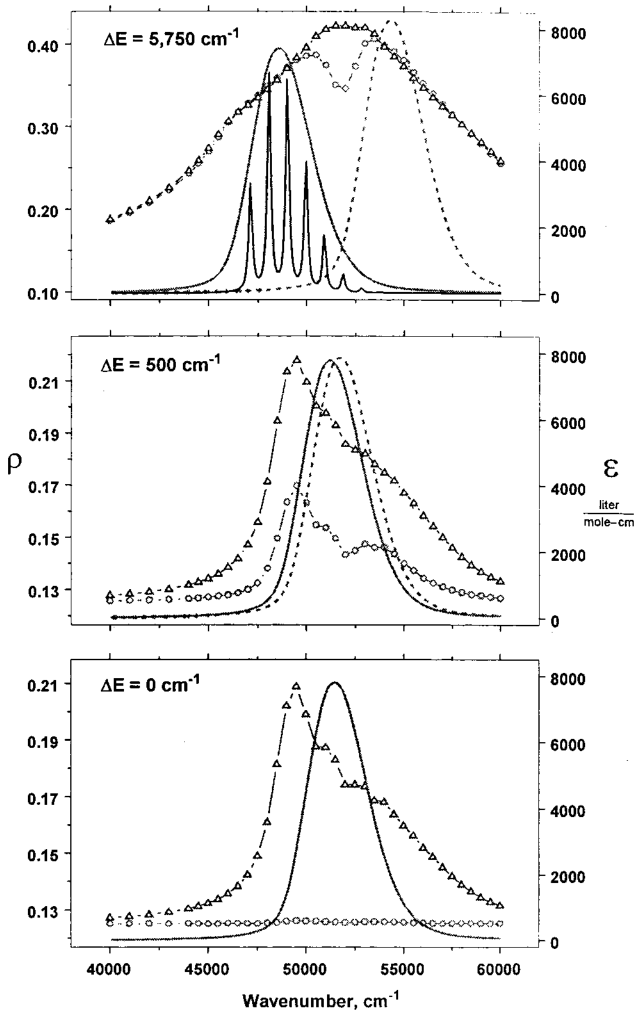

Figure 1. Plots of the variation in the depolarization ratio, ρ, as a function of excitation wavenumber for models with three different origin separations. In all three panels the two equal intensity electronic transitions are represented as displaced harmonic oscillators with $\Delta = 2$ and an excited-state frequency of 950 cm^{-1}. The ground-state frequency is 1050 cm^{-1}. The homogeneous line width is 400 cm^{-1}, and the inhomogeneous line width is 500 cm^{-1}. The resulting absorption spectra are shown as solid and dashed curves. The top panel includes an absorption spectrum drawn with a total line width of 100 cm^{-1}. The separation of the electronic origins are, from top to bottom, 5750, 500, and 0 cm^{-1}. The upper curve in each panel marked with triangles is for the case of anti-correlated inhomogeneous fluctuations, $C_{\mathrm{AB}} = -0.99$. The lower curve marked with circles is for the fully correlated inhomogeneous fluctuations, $C_{\mathrm{AB}} = +0.99$.

be easily measurable. The bottom panel shows the behavior expected for a degenerate pair of transitions. The case of $C_{AB} = +0.99$ retains the degeneracy for all microscopic environments and thus results in $\rho = 1/8$ for all excitation wavenumbers. If the inhomogeneous broadening fluctuations are negatively correlated then individual molecules exhibit environmental "site" splittings. The resulting asymmetry then results in a significant deviation of ρ from the value of 1/8. In this case, of course, it is clear that the anti-correlated fluctuations are equivalent to anti-symmetric perturbations that lift the molecular symmetry. Positively correlated fluctuations are symmetric.

Discussion

The main conclusion of this work is that the value of the depolarization ratio changes significantly when one changes the degree of correlation of the inhomogeneous distribution for this reasonably realistic case. This influence of the correlation of inhomogeneous broadening effects on Raman depolarization dispersion can be viewed as a necessary extra consideration in the evaluation of models aimed at the extraction of excited-state parameters from Raman depolarization data or, alternatively, as a methodology for probing the degree of correlation of solvent-induced inhomogeneous broadening. In this last respect it is clear that this method is of greatest relevance for closely spaced states with similar intensities. Noncollinear orientations for the transition dipoles are required. Molecules with degenerate or nearly degenerate excited states would appear to be most interesting for such studies.

A specific model of solvent−solute interactions can be introduced that serves to illustrate the alternatives of correlated and anti-correlated behavior. In this model the solvent is treated as an elastic medium with normal modes. The solute couples to these modes such that their equilibrium position is dependent on the electronic state of the molecule.[8] One such mode coupled to the ground and two excited states is illustrated in Figure 2. The equilibrium position of this solvent phonon must depend on the electronic state of the solute in order to contribute to the absorption and resonance Raman processes. In the case shown this shift is opposite in direction for the two excited states. These solvent modes are envisioned as being distributed over a range of low frequencies and as being over-damped. In this way they do not contribute to the observed resonance Raman line-shape as they would if they were not over-damped. The small but finite relaxation of the solvent phonon position following optical excitation (during which the major motion is along high-frequency internal degrees of freedom) will result in a solvent-induced contribution to the homogeneous line width such that the value of Γ deduced from an analysis of the Raman intensity will be larger than that intrinsic to the molecule. At thermal equilibrium each of the solvent phonons will be highly populated. Because these phonons are over-damped this thermal population is equivalent to sampling the solvent phonon coordinate at discrete points in configuration space. For each position along each solvent coordinate the optical excitation results in Raman processes along the internal degrees of freedom with minor solvent relaxation contributions to the homogeneous relaxation. The continuous distribution of solvent phonon coordinates becomes equivalent to the inhomogeneous distribution. Solvent phonon relaxation is equivalent to interconversion between the discrete microscopic environments of the inhomogeneous distribution. For the example shown in Figure 2 with the solvent phonons shifted in opposite directions, the effect of solvent phonon displacement is to shift one electronic excitation up and the other one down. This is equivalent to anti-correlated fluctuations in the inhomogeneous distribution.

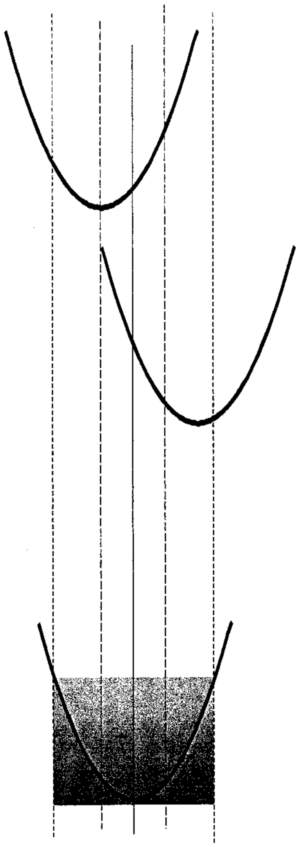

Figure 2. A schematic illustration of a solvent phonon mode showing the equilibrium position in the ground electronic state and a band representing thermal energy and the corresponding equilibrium positions in two excited electronic states. The vertical lines represent particular initial configurations of the molecular surroundings corresponding to particular displacements along this particular solvent phonon.

Acknowledgment. This research was supported by NSF Grants CHE-9207380 and CHE 9803058 and NIH Grant GM323233.

References and Notes

(1) Sevian, H. M.; Skinner, J. L. *Theor. Chim. Acta* **1992**, *82*, 29. This paper contains many references relevant to this subject.

(2) Wynne; K.; Hochstrasser, R. M. *Chem. Phys.* **1993**, *171*, 179; Galli, C.; Wynne, K.; Le Cours, S. M.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1993**, *206*, 493.

(3) Penner, A. P.; Siebrand, W. *Chem. Phys. Lett.* **1976**, *39*, 11.

(4) Myers, A. B.; Harris, R. A.; Mathies, R. A. *J. Chem. Phys.* **1983**, *79*, 603; Myers, A. B.; Trulson, M. O.; Mathies, R. A. *J. Chem. Phys.* **1985**, *83*, 5000.

(5) Harhay, G. P.; Hudson, B. S. *J. Phys. Chem.* **1993**, *97*, 8158.

(6) Muiño, P. L.; Harris, D.; Berryhill, J.; Hudson, B.; Callis, P. In *Time-Resolved Laser Spectroscopy in Biochemistry III*; Lakowicz, J. L., Eftink, M. R., Fugate, R. D., Gafni, A., Gratton, E., Ross, J. B. A., Eds.; SPIE Conf. Proc. **1992**, *1640*, 240; Muino, P. L.; Callis, P. R. *J. Chem. Phys.* **1994**, *100*, 4093.

(7) For example: Shang, Q.-y.; Hudson, B. S. *Chem. Phys. Lett.* **1991**, *183*, 63; Sension, R. J.; Strauss, H. L. *J. Chem. Phys.* **1986**, *85*, 3791.

(8) Myers, A. B. *Annu. Rev. Phys. Chem.* **1998**, *49*, 267.