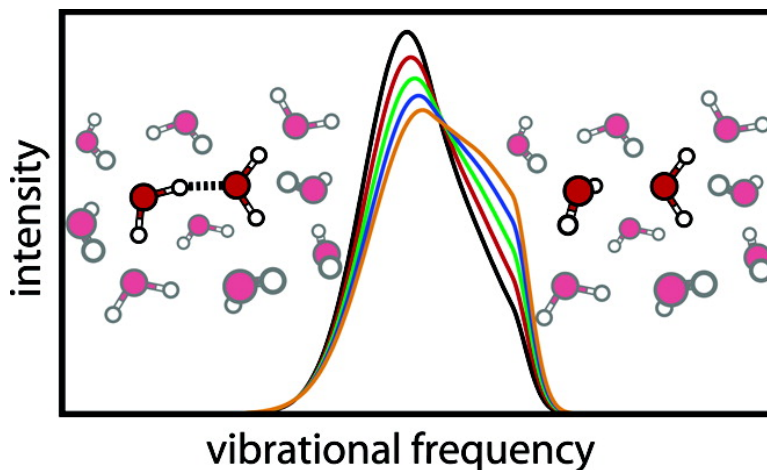


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J. Am. Chem. Soc., **2005**, 127 (42), 14930-14935 • DOI: 10.1021/ja0545214 • Publication Date (Web): 01 October 2005

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Temperature Dependence of Inhomogeneous Broadening: On the Meaning of Isosbestic Points

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Abstract: An isosbestic point in the temperature dependence of an absorption spectrum is commonly viewed as a sign of interconverting chemical or structural species. Here I explore an alternative microscopic origin of temperature-independent absorbance in inhomogeneously broadened spectra: While the equilibrium probability of observing a particular frequency generally changes with the magnitude of thermal fluctuations, the weight of at least one frequency is insensitive to small changes in temperature. The range of temperature accessible to aqueous solutions at ambient pressure is sufficiently small that such insensitivity would appear in experiments as an isosbestic point. This mechanism depends only on the continuity of equilibrium distributions, not on the presence of multiple components. Even the simplest model of a single solute species in a fluctuating environment exhibits isosbestic points, van't Hoff behavior, and, with appropriate dependence of transition frequency on configuration, multiple absorption peaks.

I. Introduction

Changes in spectroscopic absorbance as a function of external control parameters, such as temperature (T), pressure (p), or chemical potential (μ), provide clues to the microscopic structure of solutions. Isosbestic points, distinct frequencies where absorbance is insensitive to thermodynamic perturbations, are considered to be especially revealing. A popular interpretation focuses on the fact that different dilute solute species absorb additively. Any shift in the equilibrium between two interconverting species redistributes the weights of their contributions, modifying the net spectrum. However, if two species absorb with equal strength at a particular frequency, then the net absorbance at that frequency will not depend on their relative proportions. Changes in external conditions that shift equilibria between species but do not alter their intrinsic absorbance generate isosbestic points.¹

As an example, Raman spectra of HOD in liquid water exhibit an isosbestic point. (All discussion of absorptivity in this paper applies equally well to scattering intensity.) The scattering intensity at a frequency within the OD stretching band is nearly constant over much of the temperature range between freezing and boiling points at 1 atm.^{2–5} This fact has been cited for several decades as evidence for a two-state picture of liquid structure. Specifically, many have attributed a shoulder on the blue side of the line-shape to a distinct population of weak or broken hydrogen bonds between pairs of adjacent molecules.

A well-separated spectral feature in the X-ray absorption spectrum,⁶ as well as isosbestic behavior of more complicated spectroscopic observables,⁷ appears to bolster this view. Even those who interpret the vibrational spectrum as a continuum of intermolecular arrangements often decompose line-shapes or distributions into two or more components,⁸ putatively distinguished by hydrogen bonding strength, and imagine interconversion between them as “breaking and making of hydrogen bonds”.⁹ Whether explicit or implicit, two-state pictures are endemic in the modern literature on aqueous structure.

Inferring multi-state behavior from constant absorption over a range of temperature or pressure rests on the assumption that intrinsic absorbance of individual species is insensitive to thermodynamic perturbations. In this article, I scrutinize that assumption. Section II examines the general influence of thermal fluctuations on solutes' absorption line-shapes. Simple analysis and illustrative models, presented in Sections III and IV, indicate that isosbestic points in spectra obtained over a limited range of temperature or pressure are not compelling evidence for multi-component equilibrium. Instead, such points, and other apparent hallmarks of multi-state behavior, can arise trivially from the statistical thermodynamics of continuously distributed microscopic states. Here I demonstrate on microscopic grounds that isosbestic points can arise in one-component systems under very general circumstances, contrary to conventional expectations.² Section V discusses spectroscopic features that do distinguish multi-state equilibrium. In Section VI, I conclude with remarks on the specific case of liquid water.

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The notion that multi-state equilibrium uniquely explains isosbestic behavior has been challenged in the past.^{10–13} Previous counterarguments have leaned heavily on indirect empirical observations. Falk and Wyss noted that temperature-independent absorption due to OH stretching is common even in solids, where an appreciable population of broken hydrogen bonds seems unlikely. Cumutte and Bandekar showed numerically that explicit structural interconversion is not necessary to obtain an isosbestic point in distributions of OD stretching frequencies. These calculations, however, required as input atomic pair correlation functions, which themselves exhibit isosbestic points.¹⁴ The account of single-component isosbestic behavior I describe in this article is, to my knowledge, the first to proceed solely from intuitive microscopic ideas and well-known properties of equilibrium states.

II. Thermal Variation of Line-Shapes

Consider two electronic or vibrational states of a solute, “g” (ground) and “e” (excited), separated by an energy gap, $\hbar\omega_{\text{eg}}$. Coupling of these states to solvent fluctuations modulates the transition frequency, ω_{eg} , often producing broad absorption line-shapes. I will focus on one ubiquitous source of line broadening in dense, polar liquids, known as inhomogeneous broadening. In this mechanism, the instantaneous configuration, \mathbf{x} , of solvent and solute molecules (which I refer to collectively as the “bath”) determines the frequency, $\omega_{\text{eg}}(\mathbf{x})$, at which a solute absorbs.¹⁵ A diverse set of bath configurations yields a wide distribution of transition frequencies and, therefore, a broad line-shape.

Quantitatively, the inhomogeneously broadened line-shape $I(\omega)$ can be written in terms of the distribution function $\rho(\mathbf{x})$ for bath coordinates \mathbf{x} :

$$I(\omega) = \int d\mathbf{x} \rho(\mathbf{x}) \delta(\omega - \omega_{\text{eg}}(\mathbf{x})) \quad (1)$$

The possible sensitivity of transition dipole to bath fluctuations is neglected in eq 1 and hereafter. At thermal equilibrium, $\rho(\mathbf{x}) = Q^{-1} \exp[-U(\mathbf{x})/k_{\text{B}}T]$, where $U(\mathbf{x})$ is the potential energy function, Q is the canonical partition function, and k_{B} is Boltzmann’s constant. Under these approximations, $I(\omega)$ is simply a reduced Boltzmann distribution for the variable $\omega_{\text{eg}}(\mathbf{x})$.

Temperature dependence of $I(\omega)$ is controlled entirely by the equilibrium configurational distribution $\rho(\mathbf{x})$. Differentiating eq 1 at constant volume V and numbers of atoms $\{M_i\}$ yields

$$\left(\frac{\partial I(\omega)}{\partial T}\right)_{V, \{M_i\}} = \frac{I(\omega)}{k_{\text{B}}T^2} [\langle U \rangle_{\omega} - \langle U \rangle] \quad (2)$$

Angled brackets in eq 2 denote thermal averages over $\rho(\mathbf{x})$. The subscript ω indicates a restricted thermal average, including only configurations with a specific value of the transition frequency, $\omega_{\text{eg}}(\mathbf{x}) = \omega$. Relationships nearly identical to eq 2 have been presented before and have even been used to extract energy

functions from measured spectra.¹⁶ However, the implications of this simple result for isosbestic behavior have apparently been overlooked.

A local isosbestic point, where absorbance is insensitive to small changes in temperature, occurs wherever the derivative $\partial I/\partial T$ vanishes. According to eq 2, any frequency whose average energy equals that of the entire ensemble will exhibit constant absorbance over a suitably small range of temperature. Because $\langle U \rangle$ is a weighted average of $\langle U \rangle_{\omega}$, the mean value theorem guarantees that $\partial I/\partial T = 0$ for at least one frequency, ω^* , at any temperature. For the idealized spectra under consideration, isosbestic points always exist! This property is unrelated to the presence of distinct interconverting species, which would correspond to a particular form of $\rho(\mathbf{x})$.

If interactions between solute and solvent extend only over distances comparable to a molecular diameter, then the solute’s transition frequency depends on only a few bath coordinates. Even if these interactions span large distances, it is likely that the effect of constraining ω_{eg} is concentrated in a few collective modes of bath fluctuation or that each of many modes is perturbed weakly. As a result, the difference, $\langle U \rangle_{\omega} - \langle U \rangle$, is essentially equal in magnitude to the average energy of a small number of statistically independent degrees of freedom. This equivalence is exact in the case of a harmonic bath and linearly varying transition frequency:

$$U = \sum_{i=1}^n \frac{x_i^2}{2\alpha_i} \quad (3)$$

$$\omega_{\text{eg}} = \omega_0 + \sum_{i=1}^n a_i x_i \quad (4)$$

Here, x_i is the i th normal coordinate of the bath, and α_i is its associated susceptibility. The coefficient a_i determines the sensitivity of frequency shifts, about a reference value ω_0 , to fluctuations in x_i . In the absence of constraints, the equipartition principle dictates an average energy of $k_{\text{B}}T/2$ for each of the n normal modes. The temperature dependence of $\langle U \rangle_{\omega}$ is also easily determined for this model: The energetics of bath fluctuations remain harmonic when ω_{eg} is constrained, while the number of active normal modes is reduced by one. Consequently, $\langle U \rangle_{\omega} - \langle U \rangle = U_0(\omega) - k_{\text{B}}T/2$, where the function $U_0(\omega) = \omega^2/(2\sum_{i=1}^n \alpha_i a_i^2)$ is independent of temperature. Regardless of the diversity of contributing bath motions, the heat capacity associated with fluctuations in transition frequency is just a fraction of k_{B} . In such cases, eq 2 gives a change in relative absorption due to a small change in temperature ΔT

$$\left|\frac{\Delta I(\omega^*)}{I(\omega^*)}\right| \approx \left(\frac{\Delta T}{T}\right)^2 \quad (5)$$

at a local isosbestic point. Temperature ranges explored in most experiments are, in fact, small in this context. The maximum relative change in temperature for aqueous experiments bounded by freezing and boiling transitions at ambient pressure is $\Delta T/T \approx 0.37$. One should not expect the relative change in absorbance at a local isosbestic point to much exceed 10% over this range.

III. Spectroscopic Model

A schematic one-dimensional model is sufficient to illustrate these ideas. Relevant bath degrees of freedom are represented

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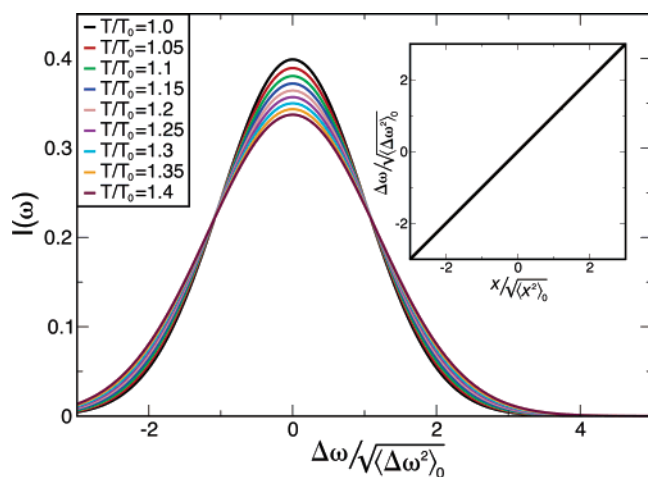


Figure 1. Absorption line-shape $I(\omega)$ at several temperatures for a single solute species coupled to a Gaussian bath. Here, frequency shift $\Delta\omega$ is linear in the bath variable x , as shown in the inset. $\Delta\omega$ has been scaled by its root-mean-squared value, $\sqrt{\langle\Delta\omega^2\rangle_0}$, at an arbitrary reference temperature T_0 . The bath coordinate has similarly been scaled by its root-mean-squared value, $\sqrt{\langle x^2\rangle_0}$, at the same temperature. The bath susceptibility, α , was presumed temperature-independent for this calculation.

by a single coordinate, x , with a linear restoring force, i.e., $U(x) = x^2/2\alpha$. Physically, x could describe the fluctuating electric field of a polarizable solvent, coupled to a solute dipole whose magnitude differs in ground and excited states. In that case, the one-dimensional caricature, with a suitable choice of α , is equivalent to a dielectric continuum approximation.^{17,18} A model for inhomogeneous broadening must also specify how bath fluctuations modulate the solute's energy gap. If $\omega_{\text{eg}}(x)$ is a linear function of the bath coordinate, as in a standard Brownian oscillator model,¹⁵ then the absorption spectrum is Gaussian, with a characteristic width proportional to $\sqrt{\alpha k_{\text{B}}T}$. This line-shape is plotted in Figure 1 at several temperatures between an arbitrary reference temperature, T_0 , and $T_0 + \Delta T = 1.4T_0$, a range comparable to 0–100 °C. Together with the principle of equipartition, eq 2 implies local isosbestic points at $\Delta\omega^*(T) = \pm\sqrt{\langle\Delta\omega^2\rangle}$, where $\Delta\omega(x) = \omega_{\text{eg}}(x) - \omega_0$ is the instantaneous frequency shift away from the band center ω_0 . Although $\Delta\omega^*(T_0)$ and $\Delta\omega^*(T_0 + \Delta T)$ differ by roughly 20% of the half bandwidth, changes in absorbance at $\Delta\omega^*(T_0 + \Delta T/2)$ are barely detectable within this temperature range. To distinguish $\Delta\omega^*(T_0 + \Delta T/2)$ from a true isosbestic point, one would need to confidently resolve differences in absolute absorbance of less than 1%.

The occurrence of two symmetric isosbestic points is unavoidable in this particular model, where positive and negative frequency shifts are equally likely. Nonlinearities, either in the forces governing bath fluctuations or in the dependence of $\Delta\omega$ on x , will break this symmetry. It is unlikely that realistic nonlinearities will reduce the number of locally temperature-invariant points in an inhomogeneously broadened spectrum. Very large frequency shifts, whether in the positive or negative direction, typically correspond to molecular arrangements with very high energy. The restricted average $\langle U \rangle_\omega$, varying continuously with $\Delta\omega$, should therefore cross the average energy $\langle U \rangle$

an even number of times. However, one of these crossings could well occur in the wings of the line-shape. (See, for example, Figure 4.) In that case, one isosbestic point would be much less prominent than the other and could even escape experimental detection. Effects of dynamics or changes in transition dipole, which are omitted in my analysis, might also remove one or more local isosbestic points.

The local isosbestic points I have identified for a single solute species exhibit temperature-insensitive absorbance only over a sufficiently small range of temperature. In this sense, they are not strict, or “exact”, isosbestic points. I emphasize, however, that temperature invariance is no more exact when interconverting species are present. Two dilute absorbing components could be represented by a bimodal distribution of bath coordinates $\rho(\mathbf{x}) = n^{(1)}\rho^{(1)}(\mathbf{x}) + n^{(2)}\rho^{(2)}(\mathbf{x})$. Here $n^{(1)}$ and $n^{(2)} = 1 - n^{(1)}$ are the probabilities of finding a given solute as species “1” and “2”, respectively, and $\rho^{(i)}(\mathbf{x})$ is the distribution of bath variables within state i . In this case

$$\left(\frac{\partial I(\omega)}{\partial T}\right)_{V,\{M_i\}} = \left(\frac{\partial n^{(1)}}{\partial T}\right)_{V,\{M_i\}} [I_1(\omega) - I_2(\omega)] + \frac{1}{k_{\text{B}}T^2} [n^{(1)}I^{(1)}(\omega)(\langle U \rangle_\omega^{(1)} - \langle U \rangle^{(1)}) + n^{(2)}I^{(2)}(\omega)(\langle U \rangle_\omega^{(2)} - \langle U \rangle^{(2)})] \quad (6)$$

where $I^{(i)}(\omega) = \int d\mathbf{x} \rho^{(i)}(\mathbf{x}) \delta(\omega - \omega_{\text{eg}}(\mathbf{x}))$ is the line-shape of species i and $\langle \dots \rangle^{(i)}$ denotes an average over $\rho^{(i)}(\mathbf{x})$. Note that a local isosbestic point is not necessarily located where $I^{(1)}(\omega) = I^{(2)}(\omega)$ since energy fluctuations described by the final two terms in eq 6 confer temperature dependence on both components' line-shapes. Because $I^{(1)}$ and $I^{(2)}$ are each subject to inhomogeneous broadening, local isosbestic points will shift with temperature just as in the single species example.

In a model where frequency shifts depend linearly on a Gaussian bath coordinate, the number of absorption peaks, rather than isosbestic points, distinguish systems with and without interconverting species. However, multiplicity of spectral features can also be a misleading gauge of multi-state equilibrium. Only a slight modification of the one-dimensional model is needed to generate spectra with more than one peak from a single species in a Gaussian bath. Specifically, the solute transition frequency might depend on bath coordinates in a substantially nonlinear way. Some spectroscopic observables, such as energies of core electron excitations probed by X-ray absorption, are very sensitive to local symmetry.¹⁹ Small displacements in solvent near a locally symmetric configuration could then switch ω_{eg} between two characteristic values. Such a sharp division of a smooth bath distribution into two classes could give the appearance of physically distinct, stable species. Figure 2 illustrates this possibility. The nonlinear function $\Delta\omega(x)$ plotted in the inset of Figure 2 yields a two-peaked line-shape from a single species coupled to a Gaussian distribution of bath fluctuations. Indeed, spectra of arbitrary complexity can be rendered from such a trivial one-state model through appropriate choice of $\Delta\omega(x)$. I stress that the distributions of microscopic states underlying Figures 1 and 2 are identical. The models differ only in the way the spectroscopic observable ω_{eg} reports on this distribution.

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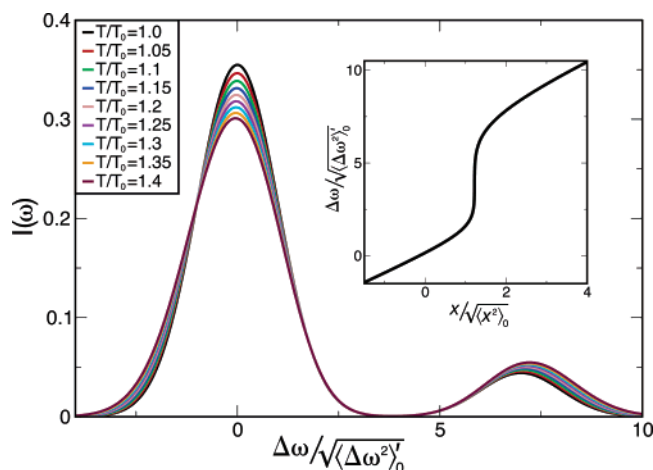


Figure 2. Absorption line-shapes at several temperatures for a single solute species responding nonlinearly to a one-dimensional Gaussian bath. The specific dependence of frequency shift on bath coordinate, plotted in the inset, was constructed to give a line-shape $I_0(\omega)$ at reference temperature T_0 that is a superposition of two Gaussian peaks, both with variance $\langle \Delta \omega^2 \rangle_0$. In detail, for each value of $\Delta \omega$, a value of x was located (via bisection) to equate cumulative probabilities, $\int_{-\infty}^{\Delta \omega(x)} I_0(\omega) d\omega = \int_{-\infty}^x \exp(-x^2/2\alpha k_B T_0) / \sqrt{2\pi\alpha k_B T_0} dx$.

When distinct spectral features do arise from interconverting species, the integrated absorbance of each feature should reflect the corresponding component's population. Specifically, if energies of the two states are temperature-independent, then the logarithm of the ratio between integrated absorbances will be a linear function of T^{-1} . Such van't Hoff behavior is another widely accepted sign of multi-state equilibrium. The features of aqueous X-ray and Raman spectra assigned to broken and intact hydrogen bonds exhibit van't Hoff behavior, consistent with a two-state picture.⁶ Remarkably, however, a single species coupled to a Gaussian bath satisfies the van't Hoff equation as an excellent approximation over temperature ranges accessible for aqueous systems. To demonstrate this fact, I define two "species" artificially by dividing the spectrum at a cutoff frequency ω_c

$$\tilde{n}^{(1)} = \int_{-\infty}^{\omega_c} d\omega I(\omega) \quad (7)$$

and $\tilde{n}^{(2)} = 1 - \tilde{n}^{(1)}$. These integrated absorbances vary with temperature according to

$$\left(\frac{\partial \ln(\tilde{n}^{(1)}/\tilde{n}^{(2)})}{\partial(1/k_B T)} \right)_{V, \{M_i\}} = \langle U \rangle_{\omega > \omega_c} - \langle U \rangle_{\omega < \omega_c} \quad (8)$$

Subscripts in the right-hand side of eq 8 indicate average quantities of the two "species", that is, restricted averages over configurations with transition frequencies greater or less than the cutoff. As with the energy difference in eq 2, if fluctuations in ω_{eg} are dominated by a few bath modes, then the right-hand side of eq 8 will depend weakly on temperature. Figure 3 shows the nearly linear relationship between $\ln(\tilde{n}^{(1)}/\tilde{n}^{(2)})$ and inverse temperature for the single species models considered in Figures 1 and 2. A slight curvature is discernible but would be difficult to resolve experimentally. Furthermore, the origin of this curvature, namely, differing heat capacities in two subensembles, is generally pertinent for mixtures of chemically distinct, interconverting species as well.

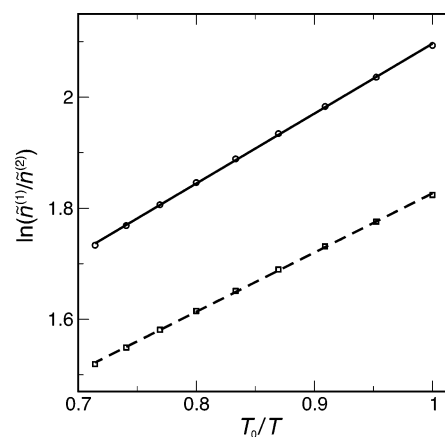


Figure 3. van't Hoff plots for the model systems considered in Figures 1 and 2 over a temperature range comparable to 0–100 °C. For the single species linearly coupled to a Gaussian bath (squares), two populations were defined by choosing the rightmost isosbestic point as the cutoff frequency. For the model with nonlinear coupling (circles), populations were divided by the local minimum of $I_0(\omega)$ (i.e., between the two peaks in Figure 2). Solid and dashed lines are best-fit straight lines through the two data sets. In both cases, temperature has been scaled by an arbitrary reference value T_0 .

IV. Other Thermodynamic Variables

Intensive fields, such as temperature or pressure, play equivalent thermodynamic roles with respect to their conjugate extensive variables. The conclusions we have drawn for temperature isosbestic points thus have natural extensions. In particular, when varying pressure, one should expect nearly constant absorbance wherever the derivative

$$\left(\frac{\partial I(\omega)}{\partial p} \right)_{T, \{M_i\}} = - \frac{I(\omega)}{k_B T} [\langle V \rangle_{\omega} - \langle V \rangle] \quad (9)$$

vanishes. As with eq 2, relationships similar to eq 9 have appeared before,²⁰ but their bearing on isosbestic behavior has escaped attention.

Imagine that changes in volume due to constraints on transition frequency have a characteristic scale, ν_0 , and an isothermal compressibility, κ . The relative change in absorbance at a local isosbestic point over a small range, Δp , is then approximately

$$\left| \frac{\Delta I(\omega^*)}{I(\omega^*)} \right| \approx \left(\frac{\kappa \nu_0}{k_B T} \right) \Delta p^2 \quad (10)$$

Assuming ν_0 to be some fraction of a molecular volume and κ to be the bulk compressibility of liquid water, the pressure scale over which local isosbestic points are well-defined ($|\Delta I/I| \ll 1$) at room temperature is $\sqrt{(k_B T / \kappa \nu_0)} \approx 10^4$ atm. This range is comparable to what has been explored in aqueous experiments.²⁰

Similarly, changes in chemical potential or concentration of $H^+(aq)$ will generate local isosbestic points at frequencies where

$$\left(\frac{\partial I(\omega)}{\partial \text{pH}} \right)_{T, p, \{M_i\}} = - (\ln 10) I(\omega) [\langle N_{H^+} \rangle_{\omega} - \langle N_{H^+} \rangle] \quad (11)$$

changes sign. In deriving eq 11, I have assumed that the concentration of $H^+(aq)$ is low enough that its density fluctuations are simply those of an ideal solution. What constitutes a

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small pH change in this context depends on how strongly the spectroscopic observable is coupled to acid–base chemistry, that is, how the average number of hydronium ions changes when ω_{eg} is constrained.

A single solute species coupled to a fluctuating bath generates isosbestic points in inhomogeneously broadened spectra over small ranges of *any* external parameter that influences the equilibrium distribution of microscopic states. These points occur at frequencies where restricted averages of extensive variables are equal to unrestricted ensemble averages, as exemplified by eqs 2, 9, and 11. It is illuminating to consider the average numbers N_1 and N_2 of two genuine, interconverting chemical species as external parameters that can be constrained. Shifting the equilibrium between these species at fixed T and p clearly modifies microscopic distributions, and a local isosbestic point will appear. Since the components generally absorb with different strengths at a particular frequency, constraining ω_{eg} generally biases their relative proportions. Isosbestic points occur where such a constraint does not bias the chemical equilibrium on average, $\langle N_1 - N_2 \rangle_{\omega} = \langle N_1 - N_2 \rangle$. They correspond precisely to frequencies where the two components absorb with equal strength. This classic isosbestic scenario is the result of variations along a particular direction in the space of thermodynamic parameters. Isosbestic points accompany variations along other directions as well, but with different quantities, such as energy or volume, playing the role of $N_1 - N_2$. As I have shown, it is not even necessary for the thermodynamic space to include a parameter characterizing the position of a chemical equilibrium. Attributing temperature or pressure isosbestic points to underlying two-state equilibria amounts to asserting a simple relationship between energy or volume and population differences. These assertions are reasonable when the position of a chemical equilibrium establishes a nearly unique thermodynamic state. In general, however, energy, volume, and solutes' relative concentrations can vary independently.

V. Discussion

The calculations I have presented are purely illustrative. They demonstrate that the appearance of isosbestic points in inhomogeneously broadened spectra can have little to do with the existence of distinct, interconverting species. Specific calculations exemplifying this principle for vibrational spectroscopy of HOD in liquid water will be presented elsewhere.²¹ Extensive evidence suggests that the OD stretching band is strongly shaped by inhomogeneous broadening, with a dominant contribution from a single hydrogen bonding degree of freedom.^{8,9} Recent work indicates that the associated transition polarizability varies weakly among pertinent configurations.²² The assumptions made in this paper are therefore quite reasonable for Raman spectroscopy of the OD stretch. The observed temperature isosbestic point can indeed be easily rationalized as the result of straightforward changes in a continuous distribution of hydrogen bonding geometries, with no need to invoke distinct classes of solvation structure. Two-state pictures inspired by the appearance of isosbestic points in a variety of systems, including other solutes in water^{23–25} and other liquids such as methanol,^{26,27} should be similarly reconsidered.

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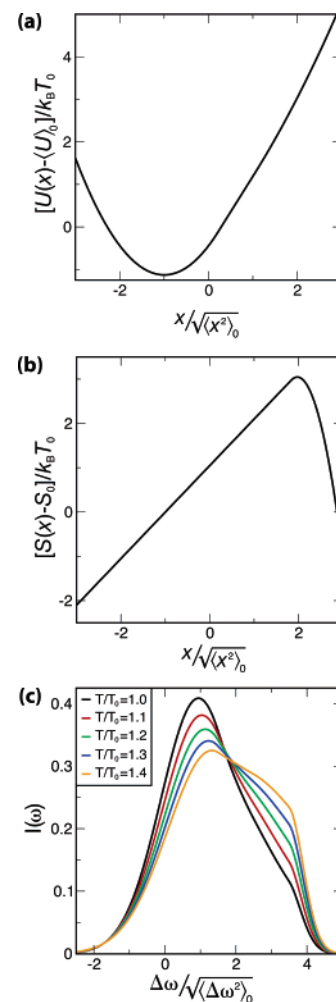


Figure 4. Example line-shapes arising from non-Gaussian, single-state bath fluctuations. The energy and entropy functions governing a bath distribution $\rho(x) \propto \exp[S(x)/k_B - U(x)/k_B T]$ are plotted in (a) and (b), respectively. Line-shapes are shown in (c) for temperatures between an arbitrary reference value T_0 and $1.4 T_0$. Entropy is meaningful and relevant here only within an additive constant S_0 . As in Figure 1, $\langle \dots \rangle_0$ denotes an equilibrium average at the reference temperature T_0 .

Factors I have neglected entirely, such as entropy of bath fluctuations, homogeneous broadening, and variations in transition dipole, only enrich the possible spectroscopic behavior of systems with very simple underlying distributions of microscopic states. Figure 4 demonstrates this fact. I have plotted line-shapes corresponding to a non-Gaussian, but nonetheless single-component, bath distribution. In this model, both entropy $S(x)$ and energy vary anharmonically along a one-dimensional bath coordinate x . I have chosen frequency shifts and bath displacements to be proportionate, $\Delta\omega \propto x$, for the sake of simplicity. Nonlinear forces might reflect details of intermolecular potentials at short distances (e.g., forces which stabilize hydrogen bonds). Indeed, the shape of $U(x)$ in Figure 4a is similar to that extracted from Raman spectra of HOD in D_2O ,¹⁶ and the line-shapes in

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Figure 4c strongly resemble measured spectra. Although the bath in this case is not a linearly responding medium, it need not have any bistable or multi-state character.

Note that the leftmost isosbestic point in Figure 4c resides in the line-shape's low-frequency wing. In this model, entropy is responsible for its inconspicuousness. The larger multiplicity of configurations with $x > 0$ shifts the peak of $I(\omega)$ away from the energy minimum. The ensemble average energy is therefore higher than it would be for uniform multiplicity [$S(x) = \text{const}$]. The convex energy function $U(x)$ crosses $\langle U \rangle$ twice. One crossing corresponds to the set of configurations that dominate the thermal average, generating an isosbestic point near the peak of $I(\omega)$. The second crossing corresponds to high-energy configurations on the opposite side of the energy minimum. These latter configurations are disfavored both energetically and entropically. Their associated isosbestic point is thus well-removed from the center of the line-shape. This mechanism is a generic, but not unique, way for isosbestic points to, in effect, disappear into the wings of a spectrum.

A more complete, and therefore more flexible, spectroscopic model should strengthen the argument that certain conventional signatures of multi-state equilibrium (temperature or pressure isosbestic points, multi-peaked spectra, and van't Hoff behavior) are not sufficient to infer the presence of chemically or structurally distinct solute species. What criteria should compel one to make such an inference? Distinct species should be separated by free energy barriers that render the dynamics of interconversion much slower than basic molecular motions. Time-resolved nonlinear spectroscopy allows the observation of populations enriched in one species as they relax to equilibrium. The time scale of this relaxation provides a much more stringent test of two-state pictures than variations of linear spectra over a limited thermodynamic range. Femtosecond two-dimensional infrared spectroscopy of the OH stretch in liquid D_2O indicates that purportedly distinct populations of broken and intact hydrogen bonds, in fact, interconvert quite rapidly.²⁸ The results presented here demonstrate that such observations of fast spectral diffusion,^{29,28} and the barrierless landscape they imply, are consistent with the existence of an isosbestic point in the one-dimensional Raman spectrum.

The continuous bath distributions employed in this paper could be viewed as an equilibrium between very many microscopically distinct species. From this perspective, fluctuations within a single basin of attraction amount to an extreme limit of the multi-component picture. While technically correct, this view can be misleading. Specifically, it undermines distinctions that do exist when a molecule or intermolecular arrangement adopts a small number of genuinely distinct forms. In loose terms, for two species to be meaningfully distinct, they must be separated by a region of configuration space where the density of low-energy microscopic states is much smaller than

for either species. Fluctuations within a single basin of attraction do not satisfy this criterion. Slow interconversion between components, on the other hand, virtually ensures structural segregation. At first glance, a multi-peaked reduced distribution function would seem to imply a similar distinction, but the small weight of transition frequencies between peaks in Figure 2 reflects only the fact that $\Delta\omega(x)$ is a rapidly varying function in this interval. Without knowing how frequency shifts depend on configuration, one can extract little structural information from the shape of an inhomogeneously broadened spectrum.

VI. Conclusions

The likelihood of single species isosbestic points arises from the fact that fluctuations modulating a solute's transition frequency are *microscopic* in character. Associated heat capacities and compressibilities are commensurately microscopic. Variations in ambient conditions of less than 100 K or 10^4 atm, despite their significance for phase transitions of a liquid such as water, exert small perturbations on the equilibrium distribution of relevant coordinates. Over such small ranges, a vanishing derivative in the line-shape would appear as an isosbestic point in most currently feasible spectroscopic measurements. In the limit of inhomogeneous broadening, statistical mechanics guarantees the existence of such local isosbestic points in any smooth spectrum. Since broad, continuous distributions are the rule in dense polar liquids, conclusions regarding distinct solvation structures require more detailed dynamical information than one-dimensional spectra can provide.

Implications for intermolecular structure in liquid water are especially interesting. Rationalizing isosbestic behavior in the Raman and IR spectra of HOD in $H_2O(l)$ has been a long-standing challenge for continuum pictures. This work shows how a smooth distribution of hydrogen bonding geometries, lacking qualitatively distinguishable species, could plausibly generate temperature and pressure isosbestic points. Rather than demarking distinct populations of solvation structures, isosbestic points in this scenario simply discriminate frequencies whose energies (or volumes) are below average from those with higher energies (or larger volumes). Two populations can certainly be defined according to such a dividing point, and they would likely exhibit van't Hoff behavior over accessible temperature ranges, but this division is arbitrary. Different cutoff frequencies could be chosen, and the corresponding populations would satisfy van't Hoff's equation just as well. Marked insensitivity to the choice of cutoff frequency thus calls into question the multiple species interpretation of an isosbestic point. The variety of divisions employed in two-state analyses of liquid water⁵ suggests such an arbitrariness. It will be interesting to see if detailed measurements confirm this consequence of inhomogeneous broadening.

Acknowledgment. I thank Jared Smith and Rich Saykally for many useful discussions.

JA0545214

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