Relationship between Infrared Peak Maximum Position and Molecular Interactions

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We explored the interpretation of the well-accepted correlation between the apparent peak maximum position shift and extent of molecular interactions, like hydrogen bonding and dipole-dipole interactions, based on the overlapped multiple band model. The simulation of two overlapped Lorentzian bands was carried out to interpret how the maximum position of a composite peak relates to the relative contributions of two species representing the different levels of molecular interactions, i.e., free (or very weakly bound) *vs.* strongly bound. To demonstrate the validity of our interpretation of the origin of the peak position shift, the temperature-dependent IR spectra of ethylene glycol were also analyzed. It was found through the analysis of simulated and experimental spectra that the apparent peak shift in certain case can be safely interpreted as the measure of the strength of hydrogen bonding. The result of this study gives a new insight to interpret molecular interactions probed by vibrational spectroscopy.

Key Words : Frequency shifts, Overlapped bands, Self-modeling curve resolution (SMCR), Hydrogen bonding, Molecular interaction

Introduction

The extent of bathochromic shift of certain IR peaks under the influence of temperature or solution composition has been historically used as a convenient metric to characterize the degree or strength of specific molecular interactions, such as hydrogen bonding and dipole-dipole interactions. Pimentel and Sederholm published a classical paper on the "empirical correlation" between shift of stretching frequencies and hydrogen bond distances in solid crystals.[1] Similarly, the energy of hydrogen bonds has been estimated with the equation developed by Struszczyk based on the extent of peak position shift.[2] The success of such empirical correlation provided the support for the so-called single band position shift model, where the position of the vibrational frequency of a single absorption band associated with a specific species under the influence of molecular interaction gradually changes as temperature or concentration of a mixture is changed.

Recently, we have reported that many, if not most, of the bathochromic shift of IR peaks of liquid samples may be explained by the relative intensity changes of closely overlapped multiple bands, representing the relative population of discrete species in different state of interactions, which contribute to the absorption at fixed vibrational frequencies.[3-6] In this model, the individual vibrational frequency does not gradually shift with molecular environment, but their relative contribution changes as environmental factors, like temperature or concentration of a mixture is varied.

In this study, we explore the interpretation of the well-accepted correlation between the apparent peak maximum position shift and the extent of molecular interactions, like

hydrogen bonding and dipole-dipole interactions, based on the overlapped multiple band model. To see how the maximum position of a composite peak relates to the relative contributions of two species representing the different level of molecular interactions, i.e., free (or weakly bound) *vs.* strongly bound, we carry out the simulation of two overlapped Lorentzian bands. To demonstrate the validity of our interpretation of the origin of the peak position shift, experimental temperature-dependent IR spectra of ethylene glycol were also analyzed.

Background

Let us consider the case of two closely overlapped bands, both with Lorentzian band shape, comprising an apparent single composite peak,

$$A(\nu) = \frac{A_1}{1+(\nu-\nu_1)^2/w_1^2} + \frac{A_2}{1+(\nu-\nu_2)^2/w_2^2} \tag{1}$$

where A_1 and A_2 are the maximum intensities of the two bands, ν_1 and ν_2 are the corresponding frequency positions of the two peak maxima, and w_1 and w_2 represent the one half of the full band widths measured at the half height of the maximum intensity. For convenience, we assume $\nu_1 > \nu_2$. A very similar analysis (not included here) can also be carried out for the case involving overlapped bands with Gaussian band shapes to yield essentially the same result.

The maximum point of the composite peak, comprising the combined contributions of two separate bands, is found at the frequency ν_{max} by taking the first derivative of the peak profile $A(\nu)$ with respect to the frequency ν

$$\left.\frac{dA(\nu)}{d\nu}\right|_{\nu=\nu_{max}} = 0 \,. \tag{2}$$

We now have an explicit but somewhat complicated relationship, which defines the frequency ν_{max} of the peak maximum position.

$$\frac{-2A_1(\nu_{max}-\nu_1)/w_1^2}{\{1+(\nu_{max}-\nu_1)^2/w_1^2\}^2} + \frac{-2A_2(\nu_{max}-\nu_2)/w_2^2}{\{1+(\nu_{max}-\nu_2)^2/w_2^2\}^2} = 0 \,. \tag{3}$$

A simplifying assumption is now introduced to analytically solve the equation above. If ν_1 and ν_2 are sufficiently close to each other, such that $|\nu_1 - \nu_2| < w_1$ or w_2, the above equation can be solved to yield the approximate location of the peak maximum as

$$\nu_{max} \approx \frac{A_1/w_1^2}{A_1/w_1^2 + A_2/w_2^2}\nu_1 + \frac{A_2/w_2^2}{A_1/w_1^2 + A_2/w_2^2}\nu_2 \,. \tag{4}$$

The above approximate solution actually is reasonably accurate even for the case of two bands spread farther apart. Identical similar result can also be obtained for two overlapped bands with Gaussian profiles. A close examination of the above result shows that the maximum point of the composite peak comprising two overlapped bands is located closer to the band with a higher intensity and, more importantly, narrower band width.

Suppose the two overlapped bands represent spectral intensity contributions of two separate components comprising a binary mixture. The band intensity maxima, A_1 and A_2, are related to the mole fractions of two components, x_1 and x_2, by the Beer's law,

$$A_1 = a_1x_1 = a_1(1 - x_2) \text{ and} \tag{5}$$

$$A_2 = a_2x_2 \tag{6}$$

where a_1 and a_2 are the molar absorption intensity maxima of the two bands. The substitution of the above to the previous result (Eq. 4) yields

$$\nu_{max} \approx \frac{a_1(1-x_2)/w_1^2}{a_1(1-x_2)/w_1^2 + a_2x_2/w_2^2}\nu_1 + \frac{a_2x_2/w_2^2}{a_1(1-x_2)/w_1^2 + a_2x_2/w_2^2}\nu_2 \tag{7}$$

It is obvious that the extent of the peak position shift, $\Delta\nu = \nu_1 - \nu_{max}$, from the band position of the first (reference) component will not be a linear function of the mole fraction x_2 of the second component, unless the fortuitous condition

$$a_1/w_1^2 \approx a_2/w_2^2 \tag{8}$$

is satisfied. In this special case, we have

$$\Delta\nu \approx (\nu_2 - \nu_1)x_2 \tag{9}$$

and the extent of peak maximum shift indeed serves as a useful metric for the population increase of the second species.

Interestingly, this purely accidental matching condition

between two overlapped bands may actually happen in real life for some important cases, such as OH-stretching bands of free and hydrogen-bonded species. The band frequency for a hydrogen bonded species is shifted to a lower frequency (i.e., red shift) than that for the corresponding free (e.g., gas phase) species, with accompanying increase in the intensity and substantial broadening of the band profile. The former band for hydrogen-bonded species may have four times more intense molar absorptivity with twice as broad band profile compared to the unbounded free species. This situation can indeed satisfy the necessary condition for the linear relationship between the extent of peak maximum position shift and the amount of hydrogen-bonded species. However, it is important to note that such fortuitous outcome is based on the purely accidental matching of the line shapes and intensities of spectral bands associated with bound and free species.

Experimental Section

Simulations. The result obtained in Eq. (7) is valid for two overlapped bands located relatively close to each other. This assumption may not hold for some cases. The peak maximum position can be determined directly from the composite peak profile calculated numerically from Eq. (1) if individual band parameters are specified. We carry out the simulation of two overlapped Lorentzian bands to see how the maximum position of a composite peak relates to the relative contributions of two species representing the different level of molecular interactions, i.e., free (or weakly bound) *vs.* strongly bound. The simulated spectral dataset were generated by using MATLAB software (The MathWorks Inc.).

We start this simulation by picking more or less, arbitrarily the following parameters: ν_1, w_1, a_1, ν_2, w_2, and a_2. We assume $\nu_1 > \nu_2$; $w_1 < w_2$; and $a_1 < a_2$ to simulate the situation that species 1 is in the free state and species 2 is bound by a molecular interaction, like hydrogen bonding. Three separate scenarios will be explored: $(\nu_1 - \nu_2)/(w_1 \cdot w_2)^{1/2} = 0.5$, 1.0 and 2.0. This will cover different level of band overlap. Choose band profile parameters, such that $(a_1 w_2^2)/(a_2 w_1^2) = 0.5$, 1.0 or 2.0. For each case (nine of them so far), we calculate the composite peak profiles *via* Eq. (1) by incrementing values of the mole fraction x_2 of the bound species between 0.0 and 1.0, such that $A_1 = a_1 (1-x_2)$ and $A_2 = a_2 x_2$. We then estimate the frequency ν_{max} of the composite peak maximum from the calculated profile. We also construct the plot of the curves $(\nu_1 - \nu_{max})/(\nu_1 - \nu_2)$ *vs.* x_2 for three sets of profile parameters satisfying the conditions $(a_1 w_2^2)/(a_2 w_1^2) = 0.5$, 1.0 or 2.0 for the three scenarios $(\nu_1 - \nu_2)/(w_1 \cdot w_2)^{1/2} = 0.5$, 1.0 and 2.0.

Any deviation of the $(\nu_1 - \nu_{max})/(\nu_1 - \nu_2)$ *vs.* x_2 curve from a straight line indicates that the apparent peak maximum shift cannot be used as an accurate measure of the amount of bound species.

Temperature-dependent FTIR Spectra of Ethylene Glycol. FTIR spectra were recorded at a spectral resolution
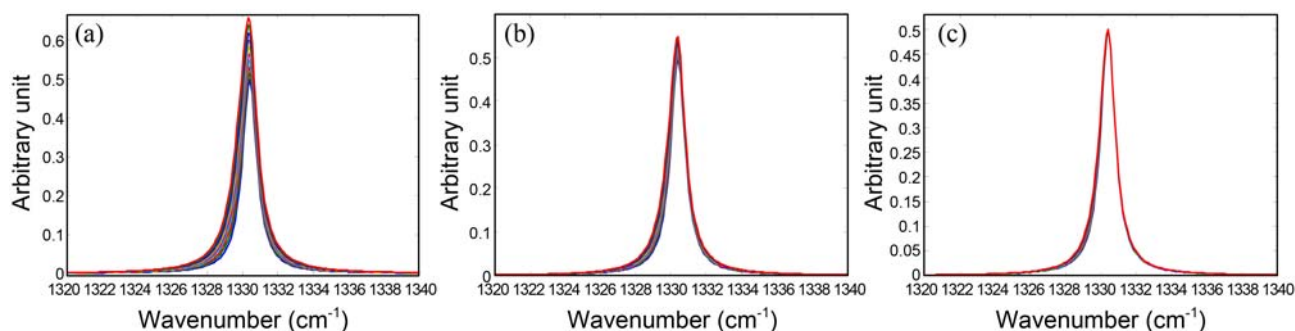
Figure 1. The spectral data sets of the simulated two overlapped Lorentzian bands at 1330.2 and 1330 cm^{-1}, respectively, with gradual increase or decrease with different rates in each step, changing in intensity in opposite directions. Here, $(\nu_1 - \nu_2)/(w_1 \cdot w_2)^{1/2} = 0.5$ and $(a_1 w_2^2)/(a_2 w_1^2) = 0.5$ (a), 1.0 (b), and 2.0 (c).

of 4 cm^{-1} with a Nicolet 6700 FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector. A total of 32 interferograms were co-added for each measurement. Attenuated total reflection (ATR) attachment, which includes a heating block attachment, was used for IR measurements. The temperature-dependent IR spectra of ethylene glycol were measured at an increment of 10 °C in the range of 25-155 °C.

Results and Discussion

Figure 1 shows three sets of the simulated two overlapped Lorentzian bands at 1330.2 and 1330 cm^{-1}, respectively, with gradual increase or decrease with different rates in each step, changing in intensity in opposite directions. There are a total of ten such steps. The choice of the wavenumber axis is quite arbitrary, and thus, it can be settled for any other spectral variable. Here, $(\nu_1 - \nu_2)/(w_1 \cdot w_2)^{1/2} = 0.5$ and $(a_1 w_2^2)/(a_2 w_1^2) = 0.5$, 1.0 and 2.0, respectively, for Figure 1(a), (b), and (c). Figure 2 shows the plot of the curves $(\nu_1 - \nu_{max})/(\nu_1 - \nu_2)$ *vs.* x_2 for three sets of profile parameters satisfying the conditions $(a_1 w_2^2)/(a_2 w_1^2) = 0.5$, 1.0 or 2.0 for the three scenarios $(\nu_1 - \nu_2)/(w_1 \cdot w_2)^{1/2} = 0.5$ for the simulated two overlapped Lorentzian bands shown in Figure 1.

Corresponding cases for $(\nu_1 - \nu_2)/(w_1 \cdot w_2)^{1/2} = 1$ and 2 are shown, respectively, in Figure 3 and 4. Figure 5 and 6 show the plot of the curves $(\nu_1 - \nu_{max})/(\nu_1 - \nu_2)$ *vs.* x_2 for three sets of profile parameters satisfying the conditions $(a_1 w_2^2)/(a_2$

Figure 2. Plot of the curves $(\nu_1 - \nu_{max})/(\nu_1 - \nu_2)$ *vs.* x_2 for three sets of profile parameters satisfying the conditions $(a_1 w_2^2)/(a_2 w_1^2) = 0.5$ (■), 1.0 (●) and 2.0 (▲) for the simulated two overlapped Lorentzian bands shown in Figure 1.

$w_1^2) = 0.5$, 1.0 or 2.0 for the three scenarios $(\nu_1 - \nu_2)/(w_1 \cdot w_2)^{1/2} = 1$ and 2 for the simulated two overlapped Lorentzian bands shown in Figure 3 and 4, respectively.
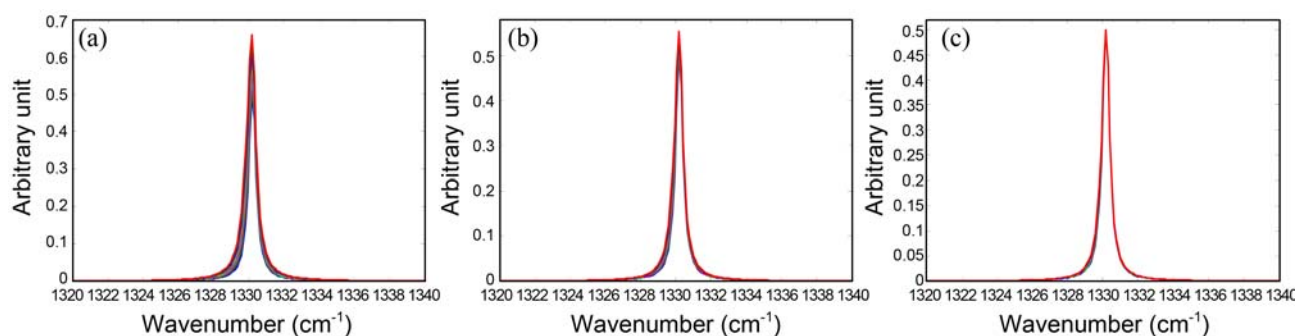
These results clearly show the peak maximum position can be used as a reasonable measure of the strength of hydrogen bonding, not because it reflects the gradual weakening of a unique hydrogen bonding but because it corresponds to the population of two different hydrogen bonding states.

Illustrative example of experimental data to interpret the

Figure 3. The spectral data sets of the simulated two overlapped Lorentzian bands at 1330.2 and 1330 cm^{-1}, respectively, with gradual increase or decrease with different rates in each step, changing in intensity in opposite directions. Here, $(\nu_1 - \nu_2)/(w_1 \cdot w_2)^{1/2} = 1$ and $(a_1 w_2^2)/(a_2 w_1^2) = 0.5$ (a), 1.0 (b), and 2.0 (c).
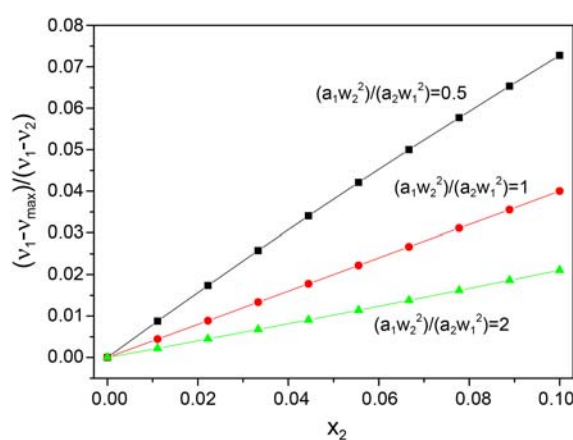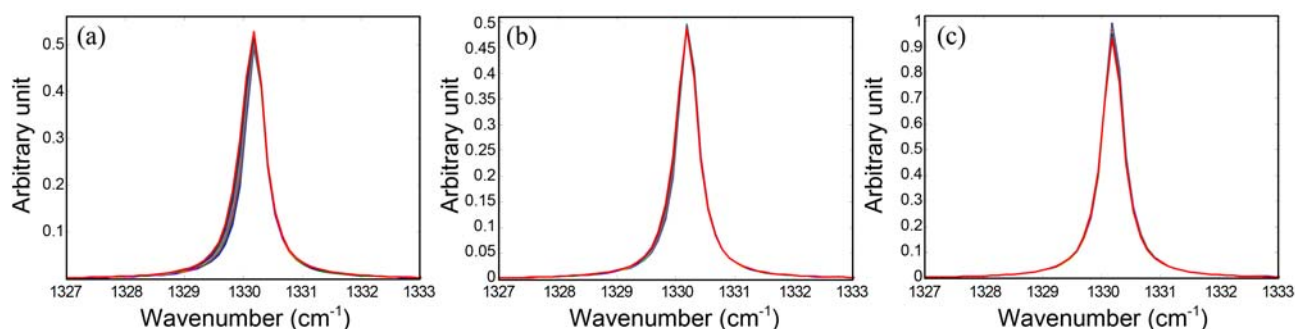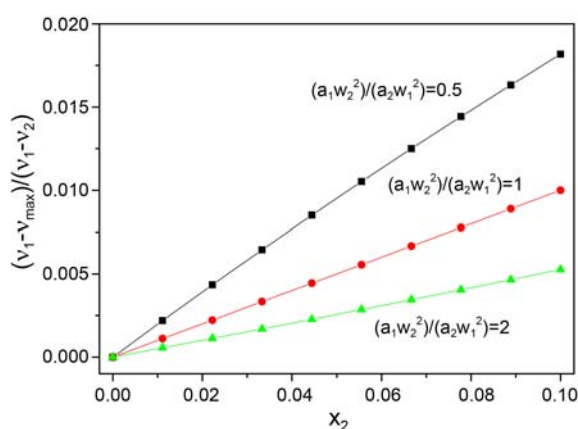
Figure 4. The spectral data sets of the simulated two overlapped Lorentzian bands at 1330.2 and 1330 cm^{-1}, respectively, with gradual increase or decrease with different rates in each step, changing in intensity in opposite directions. Here, $(\nu_1 - \nu_2)/(w_1 \cdot w_2)^{1/2} = 2$ and $(a_1 w_2^2)/(a_2 w_1^2) = 0.5$ (a), 1.0 (b), and 2.0 (c).

Figure 5. Plot of the curves $(\nu_1 - \nu_{max})/(\nu_1 - \nu_2)$ *vs.* x_2 for three sets of profile parameters satisfying the conditions $(a_1 w_2^2)/(a_2 w_1^2) = 0.5$ (■), 1.0 (●) and 2.0 (▲) for the simulated two overlapped Lorentzian bands shown in Figure 3.
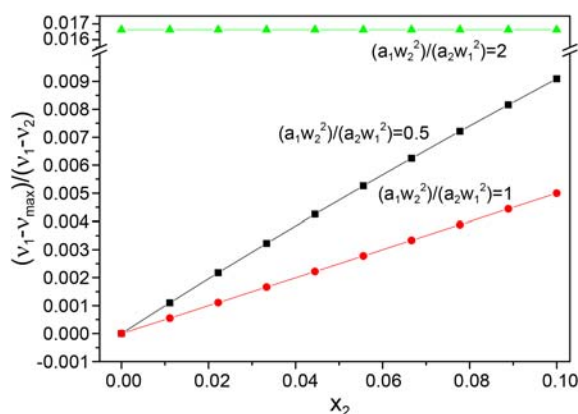

Figure 7. The temperature-dependent IR spectra of ethylene glycol obtained during the heating process from 25 to 155 °C at an increment of 10 °C.

Figure 6. Plot of the curves $(\nu_1 - \nu_{max})/(\nu_1 - \nu_2)$ *vs.* x_2 for three sets of profile parameters satisfying the conditions $(a_1 w_2^2)/(a_2 w_1^2) = 0.5$ (■), 1.0 (●) and 2.0 (▲) for the simulated two overlapped Lorentzian bands shown in Figure 4.

Figure 8. Plot of the curves $(\nu_1 - \nu_{max})/(\nu_2 - \nu_1)$ *vs. temperature* for the temperature-dependent IR spectra of ethylene glycol shown in Figure 7.

peak position shift of two overlapped bands is also demonstrated in this study. Figure 7 shows the temperature-dependent IR spectra of ethylene glycol obtained during the heating process from 25 to 155 °C at an increment of 10 °C. In this study, we only focused on the OH stretching band of ethylene glycol in the region of 3000-3650 cm^{-1}, which is
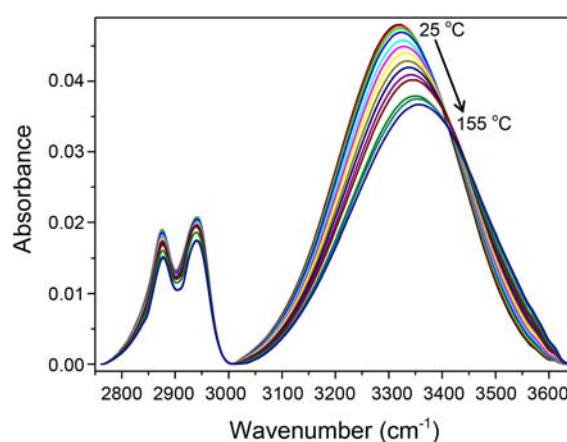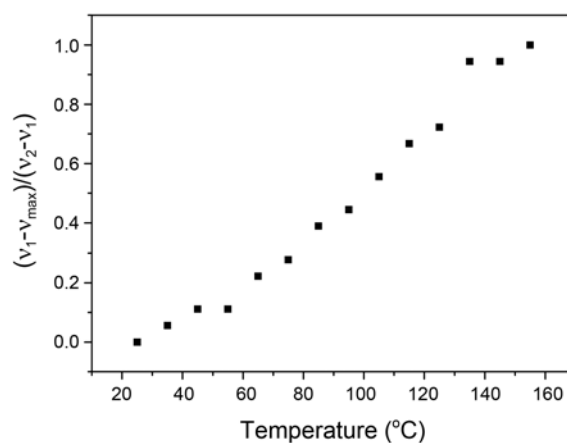
associated with hydrogen bonding interactions. This OH stretching band of ethylene glycol shows the characteristic positional shift toward higher frequencies with increasing temperature, as indicated by the arrow. It has been widely believed that the strength of the hydrogen bond of ethylene glycol is weakening so that the band intensity associated

with the absorption coefficient will diminish and band frequency will gradually shift.[7] However, we have recently reported that the so-called frequency shift of hydrogen bonding of OH band of ethylene glycol with temperature may be due to the change in population of two overlapped bands with fixed frequencies, instead of the gradual change in the vibational frequency of a hydrogen bond of ethylene glycol.[3-5]

We can resolve the band profiles and mole fractions of the free and bound species of the temperature-dependent IR spectra of ethylene glycol by applying the self-modeling curve resolution (SMCR)[8,9] technique with the binary system assumption. SMCR result of the temperature-dependent IR spectra of ethylene glycol was previously reported[3] The maximum position ν_{max} of the composite peak can be obtained from the experimentally observed spectra. Combined with the band positions ν_1 and ν_2 of the pure component spectra obtained from SMCR, $(\nu_1 - \nu_{max})/(\nu_1 - \nu_2)$ was calculated. This result can be plotted against the resolved concentration profile of bound species x_2 to see how good the position shift of the composite peak can be used to estimate the extent of molecular interactions.

Figure 8 shows the plot of the curves $(\nu_1 - \nu_{max})/(\nu_2 - \nu_1)$ *vs. temperature* for the temperature-dependent IR spectra of ethylene glycol obtained during the heating process from 25 to 155 ^{o}C. It clearly shows that the peak maximum position does indeed closely represent the relative population (thus, strength) of hydrogen bonding. It is in good agreement with our previous results that there are two distinct species, probably the hydrogen bonded and either nonhydrogen bonded or substantially weakly bonded ethylene glycol, which change their relative populations with temperature.[3]

Conclusion

We have demonstrated the new interpretation of the well-accepted correlation between the apparent peak maximum position shift and extent of molecular interactions, like hydrogen bonding and dipole-dipole interactions, based on the overlapped multiple band model. We carried out the simulation of two overlapped Lorentzian bands, to see how the maximum position of a composite peak relates to the relative contributions of two species representing the different level of molecular interactions, i.e., free (or weakly bound) vs. strongly bound. The temperature-dependent IR spectra of ethylene glycol to interpret the peak position shift of two overlapped bands are also demonstrated.

The results of simulation data sets and experimental temperature-dependent IR spectra of ethylene glycol clearly show that the apparent peak shift in certain case can be used as the measure of the strength of hydrogen bonding. Interestingly the results under a cursory observation all look as if the peak shift is associated with a single band with continuously changing frequency, even though it actually is a linear combination of two overlapped bands.

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