Efficient Prediction of Mole Fraction Related Vibrational Frequency Shifts

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Abstract

While so far it has been possible to calculate vibrational spectra of mixtures at a particular composition, we present here a novel cluster approach for a fast and robust calculation of mole fraction dependent infrared and vibrational circular dichroism spectra at the example of acetonitrile/(R)-butan-2-ol mixtures. By assigning weights to a limited number of quantum chemically calculated clusters, vibrational spectra can be obtained at any desired composition by a weighted average of the single cluster spectra. In this way, peak positions carrying information about intermolecular interactions can be predicted. We show that mole fraction dependent peak shifts can be accurately modeled and that experimentally recorded infrared spectra can be reproduced with high accuracy over the entire mixing range. Since only a very limited number of clusters is required, the presented approach is a valuable and computationally efficient tool to access mole fraction dependent spectra of mixtures on a routine basis.

TOC Graphic



Infrared (IR) and vibrational circular dichroism¹⁻³ (VCD) spectroscopy are essential techniques for detecting the molecular structure of (chiral) compounds by determining functional groups, conformation and handedness of a molecule.^{4–7} Due to their high sensitivity to structures of atomic-scale resolution, the most widespread applications of IR and VCD are in qualitative analytical (bio)chemistry, including detailed investigations of reaction mechanisms^{8,9} and the determination of (chiral) products or intermediates in catalytic reactions.^{10,11} Furthermore, they are valuable techniques for probing atomic and molecular interactions, e.g. hydrogen bonds,^{12,13} intra- and intermolecular couplings in crystals^{14,15} or contacts between metals and (bio)molecules.¹⁶

However, both methods also serve as valuable tools in quantitative analytical chemistry, as they show a pronounced concentration dependence.¹⁷ Such quantitative spectroscopy analyses rely mostly on the Lambert–Beer law, that relates spectroscopic intensities to the concentrations of the absorbing species. While primarily used to determine the concentrations of molecules in samples, quantitative spectroscopy is also a powerful tool for studying diffusion coefficients¹⁸ and the aggregation behavior of molecules.¹⁹ IR and VCD have for instance been used by Stephens and coworkers to study the concentration dependent oligomerization of S-2,2'-dimethyl-biphenyl-6,6'-dicarboxylic acid, proving the existence of supramolecular cyclotetramers in solution.¹⁹

The interpretation of vibrational spectra generally requires an accurate theoretical modeling of the system of interest.^{3,6} This can be particularly challenging for the condensed phase, as an explicit treatment of the (non-idle) environment is often necessary.^{2,13,20–22} Common computational approaches for the calculation of liquid phase vibrational spectra are based on either molecular dynamics (MD) simulations^{2,20,23} or Boltzmann weighted ensembles of quantum chemically calculated clusters.²⁴ Both approaches have been successfully applied for the calculation of liquid phase spectra of neat substances and mixtures, but the need to run individual MD simulations¹⁷ or to construct different cluster sets for each composition of interest²⁴ limits their applicability for the calculation of mole fraction dependent spectra. To date, a low-cost computational method for a fast and robust calculation of mole fraction dependent vibrational spectra is still missing, yet the development of such a tool is highly desirable to support quantitative analyses and investigate the molecular structure of unknown mixtures.

Herein, we demonstrate that the IR and VCD spectra of acetonitrile/(R)-butan-2-ol mixtures can be accurately described at mole fractions of 0.2, 0.5 and 0.8 by treating the mixtures within the binary quantum cluster equilibrium (bQCE or cluster weighting) theory.^{25,26} This cluster ansatz provides an extension to Boltzmann weighting and allows for a simultaneous weighting of clusters of different sizes and compositions by deriving a mole fraction dependent system partition function from a set of quantum chemically calculated clusters. The requirement of Boltzmann weighting to construct different cluster sets for different compositions is thus circumvented and a single cluster set is sufficient to describe the entire mole fraction range,^{27,28} reducing the computational effort by far. By self-consistently solving a set of polynomial equations, the bQCE theory assigns populations (i.e., cluster weights) to the clusters. The system's IR and VCD spectra can then be obtained by a weighted average of the individual clusters' spectra. Detailed derivations of the bQCE theory can be found in earlier works^{25,26} and the Supporting Information. All bQCE calculations were carried out with our own Peacemaker software,^{26,29} for further details, the reader is referred to the Supporting Information.

The employed clusters were constructed to contain either only acetonitrile or (R)-butan-2-ol molecules (neat clusters) or a combination of both (mixed clusters). It is important to consider different conformers for each cluster size to account for different bonding motifs and interactions between the molecules. Some of the most important clusters in our cluster set are shown in Figure 1, together with relevant interactions found between the molecules. Acetonitrile is known to interact mainly by dipole-dipole and CH…N interactions (see Figure 1, top left and center). The dipole-dipole interactions of the nitrile groups are known to affect the C=N stretching vibration, greatly enhancing its IR intensity in the liquid phase as



Figure 1: Ball-and-stick images of some clusters showing the different kinds of interactions that are present in the neat acetonitrile and (R)-butan-2-ol liquids and in the mixtures of both. The color code for the atoms is: carbon: orange; nitrogen: blue; hydrogen: white; oxygen: red.

compared to the gas phase. The vibrational frequencies of acetonitrile are, however, hardly changed under aggregation. We applied the cluster weighting to acetonitrile and calculated the corresponding liquid phase IR spectrum, which shows an excellent agreement with the experimental reference, see Figure S1, Table S4 and the corresponding discussion in the Supporting Information. The main feature of the acetonitrile liquid phase spectrum, i.e., the high intensity of the C \equiv N stretching mode at 2252 cm⁻¹, is nicely captured by the calculated spectrum and can not be modeled by using an isolated acetonitrile monomer only (see Figure S4).

(R)-butan-2-ol molecules form homodromic structures and interact mainly through OH…O hydrogen bonds and dispersion interactions between the hydrocarbon chains (see Figure 1, top right). Liquid phase IR and VCD spectra of (R)-butan-2-ol have been investigated by cluster weighting before^{13,22} and we were able to reproduce these results with the cluster set employed herein (see Figures S2–S3, Table S4 and the corresponding discussion in the Supporting Information). These successful applications to the neat liquids justify the application of the cluster weighting approach for the calculation of mole fraction dependent liquid phase spectra of mixtures.

To obtain mole fraction dependent spectra of mixtures, we performed bQCE calculations of acetonitrile/(R)-butan-2-ol mixtures with mole fractions of $x_b = 0.2$, 0.5 and 0.8, with x_b being the mole fraction of (R)-butan-2-ol. In these calculations, the cluster weighting is applied to the complete ensemble of neat and mixed clusters simultaneously. The thereby obtained IR and VCD spectra are shown in Figure 2 together with the calculated spectra for the neat substances and experimental IR spectra at the same mole fractions (information about the experimental setup details are provided in the Supporting Information). Overall we observe a very good agreement between the calculated and experimental IR spectra, despite in the region around 1400 cm⁻¹ where no IR intensity occurs in the calculated spectra. We observe that increasing the (R)-butan-2-ol mole fraction from 0.0 to 0.2 results in the occurrence of peaks around 1080–1180 cm⁻¹ (C–C stretching, C–O stretching and C–C–H bending, peaks **2** and **3**) and between 1240–1350 cm⁻¹ (C–C–H bending, peaks **4–6**) and the intensities of these peaks further increase with increasing (R)-butan-2-ol mole fraction.

The most interesting spectral features are observed in the wavenumber regions where the IR spectra of the neat liquids overlap. In the experimental spectra, the symmetric CH_3 bending modes of both components are located at 1375 cm^{-1} (peak 7). The calculated spectra predict the correct peak position and it remains unchanged with varying composition of the mixtures.

The C-O-H bending of (R)-butan-2-ol occurs at 1460 cm⁻¹ (peak **9**). Increasing the mole fraction of (R)-butan-2-ol from 0.0 to 0.2 results in increased spectral intensity between 1450–1500 cm⁻¹ which manifests as a shoulder of the asymmetric CH₃ bending peak of acetonitrile (1440 cm⁻¹, peak **8**). Further increasing the (R)-butan-2-ol mole fraction leads



Figure 2: Vibrational spectra of acetonitrile/(R)-butan-2-ol mixtures with varying compositions. The composition is given by the mole fraction x_b of (R)-butan-2-ol. Top: Cluster weighted IR spectra at the BP86/def2-TZVP level of theory. Middle: Experimental IR spectra recorded in transmission mode. Note that for 1.0 and 0.8 the experimental data between 1060–1180 cm⁻¹ had to be excluded due to an oversaturation of the detector. Bottom: Cluster weighted VCD spectra at the BP86/def2-TZVP level of theory.

to an increasing intensity of this shoulder until it transforms into a distinct peak. This transformation is well captured by the cluster weighted spectra, although the peak width is overestimated.

One discrepancy is observed for the asymmetric CH_3 bending (peak 8), which is located

at around 1440 cm^{-1} for acetonitrile whereas it appears at 1420 cm^{-1} in the case of (R)butan-2-ol. This redshift is unfortunately not properly modeled by the cluster weighted IR spectra which is due to the lack of intensity around 1400 cm^{-1} . Another important redshift is, however, observed for the CH₃ rocking (peak **1**) which is located at 1040 cm^{-1} in the experimental acetonitrile spectrum but shifted to 1030 cm^{-1} in the experimental spectrum of (R)-butan-2-ol. A magnification of the corresponding wavenumber region is depicted in Figure 3 together with fitted experimental spectra obtained from a component data analysis. The redshift is modeled almost perfectly by the cluster weighted IR spectra and the deviations between the calculated and experimental peak maxima are in the range of 1 cm^{-1} with the exception of $x_b = 0.0$.

Figure 2 also depicts cluster weighted VCD spectra. As acetonitrile is achiral, the chiral (R)-butan-2-ol is the only VCD active molecule in the mixtures. Therefore, there should be no VCD intensity observable for neat acetonitrile which is the case for the cluster weighted spectrum of $x_b = 0.0$. As soon as some (R)-butan-2-ol molecules are present, the mixtures show VCD activity and the intensity increases with increasing (R)-butan-2-ol mole fraction. However, the peak shapes and positions remain basically unchanged with varying composition (see also Figure S10). The VCD spectra of the mixtures therefore resemble the calculated VCD spectra of neat (R)-butan-2-ol $(x_b = 1.0)$ and the VCD intensities are roughly proportional to the concentration (mole fraction) of the chiral compound (see Table S5). These results may indicate that acetonitrile–(R)-butan-2-ol interactions are only weakly pronounced in the mixtures.

Interactions between (R)-butan-2-ol and acetonitrile can occur by hydrogen bonding, dipole–dipole interactions and dispersion interactions (see Figure 1, bottom). However, a relevant amount of mixed clusters will only form if these heteromolecular interactions are strong enough to break the dipole–dipole interactions between acetonitrile molecules and the hydrogen bonds between (R)-butan-2-ol molecules. Although the pronounced dipole moments μ and polarizabilities α of acetonitrile ($\mu = 3.93$ D, $\alpha = 4.4 \times 10^{-24}$ cm³)³⁰ and



Figure 3: Vibrational spectra of acetonitrile/(R)-butan-2-ol mixtures with varying compositions between 1010–1060 cm⁻¹. The composition is given by the mole fraction x_b of (R)-butan-2-ol. Top: Cluster weighted IR spectra at the BP86/def2-TZVP level of theory. Middle: Fitted experimental spectra obtained from component data analysis. The raw experimental data are shown in gray. Bottom: Positions of the peak maxima as function of x_b .

(*R*)-butan-2-ol ($\mu = 1.80$ D, $\alpha = 8.9 \times 10^{-24}$ cm³)³⁰ may promote the formation of dipole– dipole and dispersion interactions, the large size difference between both molecules limits this heteroassociation.³¹ The tendency toward a hydrogen bond formation can be estimated from the electronic binding energies of hydrogen bonded dimers.^{32,33} From the calculations of



Figure 4: Summed cluster weights of neat and mixed clusters of the acetonitrile/(R)-butan-2-ol mixtures at 298.15 K.

such clusters we observe binding energies of $-29.08 \text{ kJ mol}^{-1}$ for a (R)-butan-2-ol dimer and only $-20.61 \text{ kJ mol}^{-1}$ for a mixed acetonitrile/(R)-butan-2-ol dimer. The same trends are observed for larger cluster sizes and suggest that hydrogen bonds between acetonitrile and (R)-butan-2-ol are not strong enough to break the hydrogen bonds between (R)-butan-2-ol molecules.

These findings suggest that the binary acetonitrile/(R)-butan-2-ol system is dominated by self-association of the neat compounds. This assumption is supported by Figure 4 which shows that the mixed clusters are populated only to a minor extent in the bQCE calculations. A maximum population of 3.33 % is reached at $x_b = 0.4$. The most populated mixed cluster is shown in Figure 1, bottom right, and illustrates the problems of the heteroassociation as described above, i.e., the hydrogen bonds between (R)-butan-2-ol molecules can not be broken by acetonitrile. The ring-shaped (R)-butan-2-ol pentamer thus retains its structure and the acetonitrile monomer is located on top of the ring.

In summary we have introduced a novel approach for the prediction of mole fraction dependent IR and VCD spectra at the example of acetonitrile/(R)-butan-2-ol mixtures. By assigning weights to a set of simple and easily accessible quantum chemically calculated clusters, the mole fraction dependent spectra are obtained as a weighted average of the individual cluster spectra. The simultaneous weighting of differently sized clusters makes it possible to investigate the entire mole fraction range of a mixture with only one single cluster set. This simplicity makes this novel approach computationally very efficient and allows for routine investigations of mole fraction dependent vibrational spectra of mixtures. We have shown that mole fraction related vibrational frequency shifts can be modeled with high accuracy and that the obtained cluster weights provide detailed information about the molecular structure and interactions present in the mixtures.

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Supporting Information Available

Derivation of the bQCE theory; methodological details on the cluster generation, quantum chemical calculations, bQCE calculations and experimental measurements; experimental reference data used for the bQCE calculations; optimized bQCE parameters; discussion about the cluster weighted spectra of neat acetonitrile and (R)-butan-2-ol; cluster weighted spectra of the investigated acetonitrile/(R)-butan-2-ol mixtures at additional levels of theory; cluster populations at additional levels of theory; electronic energies of the clusters (PDF)

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