Characterization of pH-Dependent IR Spectra of Oxalic Acid: Comparison of Self-Modeling Curve Resolution Analysis with Calculation of IR Frequencies

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Self modeling curve resolution (SMCR) is a well-recognized technique for the analysis of evolving data sets.1,2 Jung et al.3 have introduced the use of two-dimensional (2D) correlation spectroscopy in conjunction with alternating least squares (ALS)-based SMCR analysis of spectral data set to obtain a set of concentration profiles C and spectra S of pure components from a set of unknown mixture spectra A without any prior knowledge about the system. Generalized 2D correlation spectroscopy has become one of standard analytical techniques to interpret spectral data sets obtained during the observation of a system under some external perturbation.9-13 The details of this technique are described elsewhere,9,11 so no further description is given here.

Since oxalic acid is one of most simple organic diprotic acid and only three different chemical species (that is, the neutral, anionic and dianionic forms) are expected to exist in aqueous solution, the aqueous oxalic acid solution is a good example to show the advantage of this 2D correlation spectra based SMCR analysis proposed by Jung et al.8 Thus, I apply this technique to pH-dependent FTIR spectra of oxalic acid to obtain the spectra for pure components. In addition, the calculation of IR spectra of oxalic acid in aqueous solution state is accomplished to confirm the accuracy of the obtained spectra by comparing them with the corresponding calculated spectra.

Experiments and Calculations

Oxalic acid and NaOH were of analytical reagent grade. 0.1 M oxalic acid and 0.1 M NaOH solutions were prepared with deionized water. The titration of oxalic acid was performed by adding small amounts of NaOH solution. FTIR spectra of oxalic acid were recorded every 0.5 pH units in the pH range of 0.5-8.0. All spectra were measured at a 2 cm⁻¹ resolution with Bomem DA8 FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector. To ensure a high signal-to-noise ratio, 512 scans were performed. A flow cell (CaF₂ window, Thermo Spectra-Tech. Inc.) was used in this study.

The analysis of the spectra of oxalic was analyzed after removing the component of absorption of water. To further analysis only range of 1100-1800 cm⁻¹ was used. 2D IR correlation spectra were calculated using an algorithm based on a numerical method developed by Noda.9 2D correlation spectra were obtained using the same software as those described previously.12,13 ALS-based SMCR method was performed using MATLAB software (Version 6, The Math Works Inc.).

All calculations of vibrational frequencies of oxalic acid in gas phase and in aqueous solution were performed with the Gaussian 98 package of programs.14 The density functional calculations were carried out with the Becke’s three-parameter hybrid functional with the Lee-Yang-Parr’s correlation functional and with the 6-31G** basis set. The molecular geometries of various isomers of oxalic acid were optimized and frequency calculations were made at the optimized geometries. The calculated frequencies were scaled by using a single scaling factor of 0.963 to get a better agreement with the experimental frequencies.15 The self-consistent reaction field (SCRF) calculations were performed with the SCIPCM model to account for the solvation effects of oxalic acid in aqueous solution.

Previous theoretical studies on neutral, anionic and dianionic forms of oxalic acid by employing high level ab initio and density functional theory calculations predict the existence of at least five conformers of the neutral oxalic acid and of two conformers of the anionic oxalic acid.16 Three conformers of neutral oxalic acid form were identified in matrix isolated experiment but the existence of the remaining conformers has not been confirmed until now.17 The relative populations of five different conformers of oxalic acid at the room temperature (298.15 K) were calculated by assuming a Boltzmann distribution among the isomers by using the zero-point vibrational energy corrected total energy of each conformer.

Results and Discussion

Figure 1 displays the pH-dependent IR spectra of oxalic acid. To obtain the pure component spectra of neutral (H₂A), anionic (HA⁻), and dianionic (A²⁻), and then the corresponding concentration profiles of these three components during the evaporation process, ALS regression was applied as reported previously.9 Synchronous and asynchronous 2D correlation spectra from pH-dependent IR spectra of oxalic acid will be described in more detail elsewhere.18
so no further in-depth discussion will be given here. As mentioned previously,\(^8\) of particular importance for the success of ALS iteration is the initial selection of the pure variables. As the initial pick of the pure variables, the dominant cross peaks in the asynchronous 2D correlation spectrum (figure not shown) representing the three pure variable bands: (1231, 1245), (1231, 1569), and (1569, 1623) cm\(^{-1}\) arising from (H\(_2\)A, HA\(^-\)), (H\(_2\)A, A\(^2-\)), and (A\(^2-\), HA\(^-\)), respectively, were selected. Intensity of pure variables was used as the initial guess for the score matrix comprising the information on concentration profile of pure component (T).

The iterative ALS regression process is then applied as described previously.\(^8\) Finally, the scores and loading vectors of ALS representing the concentration profiles (C) and spectra of individual chemical components (S), respectively, are obtained. The plots of individual chemical components from the ALS regression process described above for FTIR spectra of oxalic acid are shown in Figure 2. To confirm the spectra of oxalic acid obtained from 2D correlation spectroscopy based SMCR analysis, theoretical spectra are calculated and compared with the SMCR-estimated spectra.

The existence of six conformers of neutral oxalic acid is reconfirmed from the B3LYP calculations. But only the five energetically lowest conformers are considered in the construction of the theoretical IR spectra because the sixth conformer in gas phase is less stable than the most stable conformer by 63.5 kJ/mole and thus the contribution from the sixth conformer to the theoretical spectra is estimated to be less than 1 ppb.

The calculated spectrum of neutral oxalic acid is obtained by summing the relative population weighted scaled calculated spectra of each conformer. The relative populations of oxalic acid in gas phase at 298.15 K are 0.981, 0.016, 0.002 and 0.001 for the cTc, cTt, tTt and tCt conformers, respectively where the C and T characters designate the cis and trans conformation of O=C-C=O dihedral angle, respectively and the c and t characters designate the cis and trans conformation of C-C-O-H dihedral angle, respectively. But those in aqueous solution at 298.15 K are 0.597, 0.237, 0.008, 0.069 and 0.017 for the cTt, tTt, tCt and cCt conformers, respectively.

The calculated spectrum of the neutral form of oxalic acid in aqueous solution is displayed in Figure 3 (solid line). The calculated spectra of the anionic and dianionic forms of oxalic acid will be present elsewhere. The comparison between the theoretical spectrum and the SMCR-estimated spectrum of oxalic acid shows good agreements. The calculated peaks at 1230 and 1267 cm\(^{-1}\) correspond to the broad band around 1224 cm\(^{-1}\) in the SMCR-estimated spectrum and the calculated peaks at 1736, 1777, and 1798 cm\(^{-1}\) correspond to the broad band around 1745 cm\(^{-1}\) in the SMCR-estimated spectrum. But the long tail in the range of 1270-1360 cm\(^{-1}\) of the broad band around 1224 cm\(^{-1}\) and a band at 1615 cm\(^{-1}\) do not appear at the calculated spectrum.

**Figure 1.** pH-dependent FTIR spectra of oxalic acid. Arrows in the inlet indicate the direction of the pH increase.

**Figure 2.** Spectra of individual chemical components of oxalic acid obtained from 2D correlation spectra based SMCR results for pH-dependent FTIR spectra of oxalic acid. Solid, dashed, and dotted lines represent neutral (H\(_2\)A), anionic (HA\(^-\)), and dianionic (A\(^2-\)), respectively.

**Figure 3.** The calculated IR spectra of neutral (H\(_2\)A) form of oxalic acid in gas and solution. Solid, and dotted lines represent in solution and in gas, respectively.
These differences between the theoretical spectrum and the SMCR-estimated spectrum may be originated from the correction of solvent effect in the spectra of aqueous solution by the spectrum of deionized water. The correction assumes that the bands originated from water are identical in the spectrum for deionized water and in the spectra for aqueous oxalic acid. But introduction of oxalic acid into pure water is expected to invoke some change of the water structure around solute molecule owing to interaction between solvent and solute molecules. This change induces some changes on the bands due to water in the experimental observed spectra, and thus the bands due to water in the solution spectra are different from the corresponding ones in the spectrum of deionized water. Similar phenomena are expected for the bands due to oxalic acid in the solution spectra. Comparison between the calculated spectra of neutral form (H₂A) of oxalic acid in gas and solution displayed in Figure 3 does clearly show the solvent effect.

Considering the origin of these differences between the calculated spectrum and the SMCR-estimated spectrum for oxalic acid and the accuracy of the calculated spectra, the SMCR-estimated spectra can be regarded as being surprisingly accurate for H₂A. The same accuracies are expected for the spectra of HA⁻ and A²⁻. Thus, it can be concluded that this 2D correlation spectra based SMCR technique will provide more insight into the complex spectral changes.

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