Raman Spectroscopic Evidence for Cooperative C−H⋯O Interactions in the Acetaldehyde−CO$_2$ Complex

Marc A. Blatchford, Poovathinthodiyil Raveendran, and Scott L. Wallen*

Contribution from the Department of Chemistry, Kenan and Venable Laboratories, and the NSF Center for Environmentally Responsible Solvents and Processes, The University of North Carolina, Chapel Hill, North Carolina 27599-3290

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Recently, our laboratory reported that acetylation can be employed as a method for making otherwise CO_2-phobic carbohydrates more CO_2-philic, resulting in a new paradigm for the rational design of renewable CO_2-philes.[1] This work demonstrated that peracetylated sugars exhibit an unparalleled solubility in liquid and supercritical CO_2, with the acetate moieties on the periphery of the sugar ring appearing to be the primary sites for solute−solvent interaction. This type of solvation has previously been ascribed to the Lewis acid−Lewis base interaction between the electron-deficient carbon in CO_2 and the electron-rich carbonyl in the acetate.[2−4] However, our recent ab initio calculations of CO_2 complexes with simple model carbonyl compounds identified the possibility of a previously unknown, weaker C−H⋯O interaction that acts cooperatively with the Lewis acid−Lewis base interaction with carbonyl systems having hydrogen atoms attached to the α-carbon or the carbonyl.[5] The resulting geometries and binding energies of these complexes suggest the existence of a C−H⋯O interaction between a methyl proton of the acetate moiety and one of the CO_2 oxygen atoms. Also, in the case of acetaldehyde our results indicated the possibility of a cooperative C−H⋯O interaction with the aldehydic proton, which is illustrated in the optimized complex geometry given in Figure 1. The ab initio binding energy of the complex relative to the infinitely separated molecules at the MP2/aug-cc-pVDZ level for the geometry optimized at the MP2/6-31+G* level is −2.69 kcal/mol, including both the Lewis acid−Lewis base and weaker C−H⋯O interactions.[5] Due to their cooperativity it is difficult to assign separate energies to the individual interactions. We have previously proposed that similar cooperative, weak hydrogen bond (H-bond) interactions may explain the enhanced CO_2-solubility of acetate-containing compounds.[1]

H-bonding interactions have been previously shown to cause characteristic spectral changes upon complex formation, the most significant being the red-shifting and intensity increase of the A−H vibrational band due to electron distribution changes.[6] However, the discovery that carbon (C−H) could also participate as a donor in weak H-bonding schemes has shown that this spectroscopic "fingerprint" is not as definitive in characterizing H-bond interactions as previously thought. While there have been studies that have observed the traditional red-shift in the C−H stretching mode,[7−10] recent studies and ab initio calculations[11−17] have shown that in some cases, the C−H bond actually contracts, with a characteristic blue-shift in the observed C−H stretch frequency. Ab initio calculations have demonstrated that the carbon atom hybridization is also important in determining the effects a CH⋯X interaction will have on the C−H bond, affecting not only the H-bond strength, but also the degree to which various forces act on the bond, with
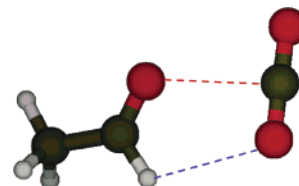

Figure 1. Optimized structure (MP2/6-31+G* level) of the CO_2−acetaldehyde complex resulting from proton side attack.[5]

the net result determining whether the C−H bond stretches or contracts.[18,19]

Acetaldehyde provides a unique case for analysis. As shown in Figure 1, one calculated geometry has the CO_2 interacting with the aldehydic proton. Since the C−H bond has a distinct vibrational mode at 2717 cm^{-1}, it is more readily observed and analyzed than the methyl vibrations. Our calculations for the acetaldehyde−CO_2 complex[5] predict that the aldehydic C−H bond contracts due to the cooperative CH⋯O interaction with one of the oxygen atoms of CO_2, with an accompanying blue-shift in the C−H stretching frequency. Simultaneously, the carbonyl bond is elongated due to the Lewis acid−Lewis base interaction, with a red-shift in the carbonyl stretching frequency. The goal of the present communication is to provide experimental evidence of these characteristic shifts in the Raman spectra of the gas-phase mixture, thereby demonstrating the relevance of the proposed cooperative CH⋯O interaction in the acetaldehyde−CO_2 complex and its potential importance to solvation in CO_2.

Pressure changes alone can cause shifts in peak positions, so any observed spectral changes are a convolution of both density effects and specific intermolecular interactions that are present. Therefore, to eliminate the changes caused by solvent density and thus determine the existence of specific interactions, the spectroscopic results for CO_2 should be compared to a gas in which no specific interactions are present under isodensity conditions. Helium was chosen as a standard, noninteracting gas since it is only capable of negligible intermolecular interactions. The general pressure setup and experimental procedure has been described previously.[20] He and CO_2 were pressurized to equivalent densities (2.38 mol/L), corresponding to pressures of 61.7 and 43.4 bar, respectively, and mixed with liquid acetaldehyde in an external pressure vessel. The resulting headspace gas was then bled into the spectroscopic cell for Raman measurements. Spectra were acquired by integrating each band for 10 min at 25.0 °C. The results of these experiments are presented in Figure 2.

The Raman spectra, which have been normalized in intensity for clarity, show significant shifts for both bands of interest in the presence of CO_2 compared to their positions in He. As CO_2
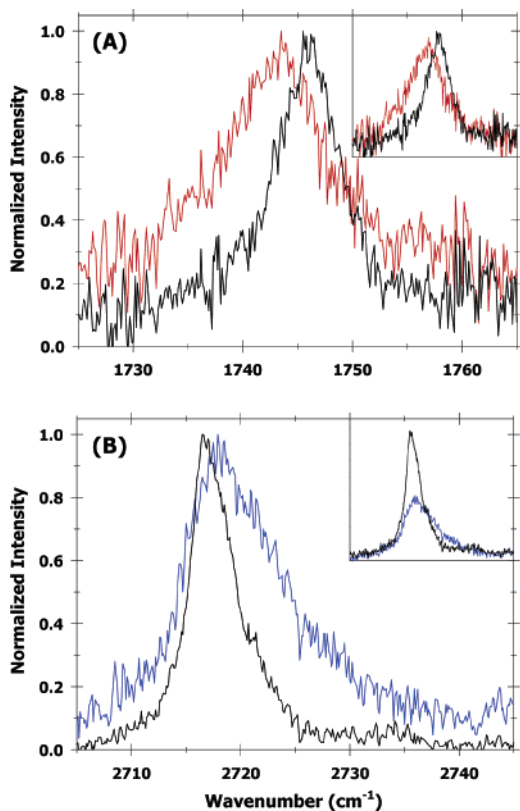
Figure 2. Normalized Raman spectra of acetaldehyde in: (A) the carbonyl stretch region in pressurized He (black) and CO_2 (red) and (B) the aldehydic C−H stretch region in pressurized He (black) and CO_2 (blue). The insets show broadening and intensity changes of modes upon CO_2 complexation.

complexes with the acetaldehyde, the population distribution of states is shifted, with the net effect of the interaction causing the band to decrease in intensity and shift in one particular direction. Both bands of interest show signs of characteristic interactions with CO_2 as predicted by the calculations.[5] Figure 2A shows that the carbonyl band maximum red-shifts from 1746.0 to 1743.5 cm^{-1}, a shift of -2.5 cm^{-1} and increases in width from 6.8 to 9.2 cm^{-1}, an increase of 2.4 cm^{-1}. These observations are consistent with the existence of a Lewis acid−Lewis base interaction between the carbonyl and CO_2. More noteworthy with respect to the present question, however, is the shift observed in the aldehydic proton. Figure 2B shows that the aldehydic proton band maximum blue-shifts from 2717.0 to 2718.3 cm^{-1}, a shift of $+1.3$ cm^{-1} and broadens significantly, increasing in width from 4.5 to 8.9 cm^{-1}, an increase of 4.4 cm^{-1}. Both observations are consistent with the predicted C−H···O interaction involving the CO_2 oxygen, resulting from the proton side approach (Figure 1). These spectroscopic measurements of the acetaldehyde−CO_2 complex provide strong evidence corroborating our ab initio results that predicted a cooperative, C−H···O interaction as a significant stabilization mechanism for solvation in CO_2 systems. The insets of A and B in Figure 2 show the unnormalized spectra of the carbonyl and aldehyde C−H stretching modes, respectively. One can see that there is a difference in the relative changes in the intensity of the carbonyl versus the C−H stretch for acetaldehyde interacting with CO_2. This decrease in the C−H stretching intensity is also indicative of the C−H···O interaction.[21,22]

The blue-shifting and changes in the band profile of the aldehyde C−H stretching band are consistent with the existence of one of the geometries predicted by our ab initio calculations. Confirmation of the other geometry is more complex due to the presence of

several overlapping bands in the methyl C−H stretching region. Although spectroscopic studies of the clusters in molecular beams may be able to provide better comparisons with calculated frequency shifts, the present data is relevant to understand the role of these interactions at room temperature. The ramifications of this interaction are quite significant with respect to the identification of a novel mechanism for enhancing the enthalpic contribution to solubility of compounds in CO_2. While the cooperative C−H···O interaction is relatively weak and may seem inconsequential, it may help to explain the higher CO_2-solubility of acetates relative to other carbonyl compounds.[1,23,24] This interaction may prove to be quite general with respect to placing a Lewis base group in a position that could allow a simultaneous C−H···O (or stronger) interaction with CO_2. The present work suggests a new paradigm for synthetic chemists to consider when integrating CO_2-philic functionalities in molecular systems for the rational design of CO_2 soluble materials.

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