Remarkable Changes in the (N)CH_3 Stretching Wavenumbers of Amines on Protonation

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Remarkable changes in the (N)CH_3 stretching wavenumbers have been observed for amines on protonation. These C–H stretching wavenumbers are related linearly to the corresponding C–H bond lengths calculated by the ab initio method. The (N)CH_3 stretching bands are useful for distinguishing between free and protonated amines.

As a result of concern about global warming, the removal of carbon dioxide from natural and refinery gases is industrially important. CO_2 is removed, in general, by reversible absorption methods employing a variety of chemical or physical solvents.[1] Aqueous alkanolamine solution is one of the major chemical solvents for this purpose. Kinetics and NMR studies have revealed that amines act as a Lewis base as follows:[2,3]

$$R_3N + CO_2 + H_2O \rightarrow R_3NH^+ + HCO_3^-. \qquad (1)$$

NMR spectroscopy has failed, however, to distinguish between free and protoneted amines because of rapid exchanges between them on a time scale of 10^{-8}–10^{-6} s.[3] Raman spectroscopy, on the other hand, is a powerful tool for detecting on a time scale of 10^{-14}–10^{-13} s each chemical species such as the free and protonated amines, and allows observations of the spectral changes in situ. The N–H stretching bands in the 3100–3500 cm^{-1} region for primary and secondary amines are greatly shifted to lower wavenumber on protonation and have been used as the key for distinguishing between the free and protonated amines.[4] For tertiary amines, however, no such useful key bands have been available.

In this letter, we report on the use of the stretching bands of the C–H bond adjacent to a nitrogen atom for distinguishing between free and protonated amines and on the origin of the wavenumber shifts of these C–H stretching bands. For Raman measurements, 30% aqueous or HCl amine solutions were used. CO_2 was absorbed into the amine solutions at 23 °C under atmospheric pressure. Figure 1 shows the Raman spectra in the 2730–3100 cm^{-1} region of 2-(*N,N*-dimethylamino)ethanol (DMAE) and 2-(*N*-methylamino)ethanol (MAE) in the aqueous, CO_2, and HCl solutions. Remarkable high-wavenumber shifts of the (N)CH_3 stretching vibrations are observed when DMAE or MAE (a or d of Figure 1) changes to its protonated amine (c for DMAEH$^+$ or f for MAEH$^+$). The spectrum of DMAEH$^+$ or MAEH$^+$ (c or f) is almost the same as that of the aqueous solution saturated with CO_2 (b or e), indicating that the amine is protonated in the CO_2 solution. In the aqueous solution saturated with CO_2, the Raman bands of HCO_3^- are observed at 632, 672, and 1017 cm^{-1} and the band of CO_3^{2-} is observed at 1066 cm^{-1}.[5] The reaction (1) is thus confirmed by Raman spectroscopy.

For 2-aminoethanol (AE), Raman bands are observed at 2952, 2940, and 2884 cm^{-1} in the aqueous solution and are shifted to 3005, 2971, and 2898 cm^{-1} on protonation. Similar bands are also observed for DMAE and MAE (Figure 1). On the basis of the assignments of dimethylethylamine[6] and propylamine,[7] the (N)CH_2 antisymmetric and symmetric stretching vibrations are assigned to the bands at 2952 or 2940 (3005) and at 2884 (2898) cm^{-1}, respectively, for AE (protonated AE). The (N)CH_3 asymmetric and symmetric stretching vibrations are assigned to the bands at 2985 cm^{-1} and at 2844 and 2796 cm^{-1}, respectively, for the two (N)CH_3 groups of DMAE and to the bands at 2983 and at 2814 cm^{-1}, respectively, for the (N)CH_3 group of MAE.

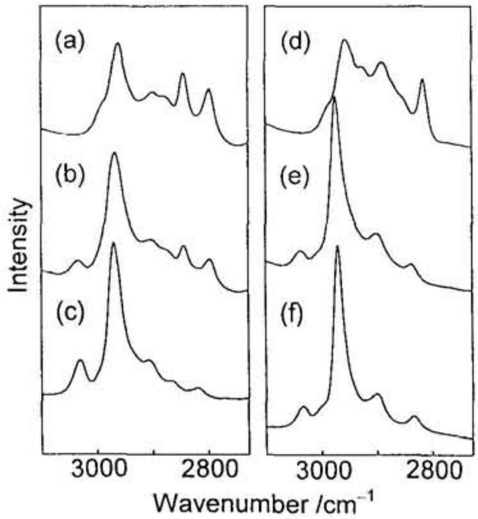

Figure 1. Raman spectra of DMAE: (a) aqueous solution, (b) aqueous solution nearly saturated with CO_2, and (c) HCl solution (DMAEH$^+$), and of MAE: (d) aqueous solution, (e) aqueous solution saturated with CO_2, and (f) HCl solution (MAEH$^+$).

The origin of the shift of the C–H stretching wavenumbers was examined by utilizing ab initio molecular orbital calculations. The calculations were performed on possible conformers (14 for DMAE, 7 of 14 for DMAEH$^+$, 27 for MAE, and 14 for MAEH$^+$) with the GAUSSIAN 94 program by the restricted Hatree–Fock method using the 6-31G** basis set (HF/6-31G**).[8] The conformers calculated to be more stable are actually present in the aqueous and HCl solutions,[9] namely, $G^-G^+g^-$ and G^-Tx (x = t, g^+, or g^-) for DMAE, G^-G^+t for DMAEH$^+$, TG^+g^-, $G^-G^-g^+$, and TG^-t for MAE, and TG^+t for MAEH$^+$. The normal coordinate calculations indicate that for DMAE and MAE the higher-wavenumber bands at about 2985 cm^{-1} are associated with the C–H stretching vibration of two shorter C–H bonds of the (N)CH_3 group (or the (N)CH_3 asymmetric stretching vibration, $\nu_a CH_3$) and the lowest-wavenumber bands at about 2805 cm^{-1} are associated with the C–H stretching vibration of one longer C–H bond (or the (N)CH_3 symmetric stretching vibration, $\nu_s CH_3$). For DMAEH$^+$ and MAEH$^+$, the highest-wavenumber bands at about 3035 cm^{-1} are associated with the $\nu_a CH_3$ vibration and the

Table 1. Observed and calculated highest and lowest (N)CH_3 stretching wavenumbers

Compound	ν_{obs}(high) / cm^{-1}	ν_{calc}(high)[a] / cm^{-1}	ν_{obs}(low) / cm^{-1}	ν_{calc}(low)[a] / cm^{-1}
DMAE	2985[b]	2950,[c] 2942,[c] 2947,[d] 2939[d]	2796[b]	2811,[c] 2799,[c] 2798,[d] 2791[d]
$DMAEH^+$	3031,[e] 3036[f]	3025,[g] 3011[g]	2906,[e] 2903[f]	2920,[g] 2913[g]
MAE	2983[b]	2937,[h] 2940,[i] 2929[j]	2814[b]	2817,[h] 2819,[i] 2807[j]
$MAEH^+$	3033,[e] 3037[f]	3015[k]	2902,[e] 2902[f]	2917[k]

[a] Calculated by the HF/6-31G** method. The wavenumbers given have been scaled by a factor of 0.9.[10] [b] Aqueous solution. [c] $G^-G^+g^-$. [d] G^-Tt. [e] HCl solution. [f] Aqueous solution saturated with CO_2. [g] G^-G^+t. [h] TG^+g^-. [i] $G^-G^-g^+$. [j] TG^-t. [k] TG^+t.

lower-wavenumber bands at about 2905 cm^{-1} are associated with the ν_sCH_3 vibration. These observed and calculated (N)CH_3 stretching wavenumbers are given in Table 1. The calculated wavenumbers well reproduce the observed wavenumbers.

For alkanes, the highest-wavenumber band at about 2960 cm^{-1} has, in general, been assigned to the (C)CH_3 asymmetric stretching vibration.[4] The (N)CH_3 symmetric stretching vibration is observed in a region around 2805 cm^{-1}, which is significantly lower than the region for the (C)CH_3 symmetric stretching vibration around 2870 cm^{-1}.[4] It is obvious that hyperconjugative interactions occur between the lone pair of nitrogen and the adjacent C–H bond *trans* to the lone pair. This leads to a lengthening of the C–H bond and to the occurrence of the characteristic bands in the 2700–2850 cm^{-1} region, known as "Bohlmann bands".[11] It has also been reported that the isolated C–H stretching bands associated with the *trans* and *gauche* conformation with respect to the lone pair of nitrogen are observed at 2799 and 2952 cm^{-1}, respectively, for monoprotonated deuterotrimethylamine and at 2834 and 2962 cm^{-1}, respectively, for monoprotonated deuterodimethylamine.[12] The present calculations correctly predicted this effect; for DMAE and MAE, the lengths of the C–H bond *trans* to the lone pair of nitrogen are calculated to be about 1.094 Å, while the lengths of the other two C–H bonds of the (N)CH_3 group are calculated to be about 1.084 Å; for $DMAEH^+$ and $MAEH^+$, on the other hand, the calculated C–H bond lengths of the (N)CH_3 group are shortened and are similar to each other (about 1.080 Å).[13] The stretching wavenumbers increase with decreasing corresponding bond lengths in accordance with the Badger rule.[14] A precise linear relationship has been reported between the isolated C–H stretching wavenumbers and the corresponding ab initio calculated C–H bond lengths for monoprotonated deuteroalkanes[15] and has also been obtained between the isolated C–D stretching wavenumbers and the calculated C–D bond lengths for monodeuterated *N*-alkyl chains.[16] The relationship between the averaged (N)CH_3 stretching wavenumbers calculated for each of the conformers and the averaged lengths calculated for the corresponding C–H bonds is shown in Figure 2, where the results for pentane are also given. The good linear relationship obtained indicates that the diagonal force constants for the C–H bonds are primarily responsible for the (N)CH_3 stretching wavenumbers.

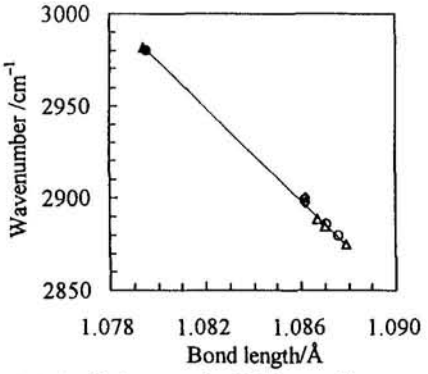

Figure 2. Relationship between the (N)CH_3 stretching wavenumbers and the corresponding C–H bond lengths calculated by the HF/6-31G** method. ○, $G^-G^+g^-$ or G^-Tt for DMAE; ●, G^-G^+t for $DMAEH^+$; △, TG^+g^-, $G^-G^-g^+$, or TG^-t for MAE; ▲, TG^+t for $MAEH^+$; ◇, TT or TG for pentane.

In conclusion, the (N)CH_3 stretching wavenumbers are related linearly to the corresponding ab initio calculated C–H bond lengths, and the (N)CH_3 stretching bands are useful for distinguishing between free and protonated amines.

References and Notes

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