Motional Collapse of Methyl Group Vibrational Bands

Sir:

N-Alkanes such as hexadecane form clathrate crystals with urea in which the alkane chains are held in their fully extended all-trans conformation in channels formed by the urea matrix.[1] The chains are arranged end to end in the channels with adjacent methyl groups. The neat alkane crystals also have extended chains which are arranged in a similar manner, although of course the lateral surroundings of the chains are quite different.

The C–H stretching bands of the alkanes are easily observable in both the infrared and the Raman spectra even in the clathrate, since urea has essentially no bands in this region. The C–H bands are similar in the clathrate and in the neat crystal and the normal modes corresponding to the major bands are fairly well characterized. In the infrared spectrum at room temperature, the hexadecane–urea clathrate shows the doubly degenerate asymmetric stretch with a half-width at half-maximum of ~11 cm^{-1} at 2956.6 cm^{-1}.[2] At 9 K the spectrum is dramatically different: the asymmetric stretch appears as two bands at 2946.1 (with a half-width of 4 cm^{-1}) and 2958.4 cm^{-1} (with a half-width of 8 cm^{-1}). As the temperature is raised from 9 K, the asymmetric stretching bands gradually collapse in a manner qualitatively the same as the collapse of an exchanging nuclear magnetic resonance doublet.

The spectra can be analyzed using the Bloch equations with exchange, modified for the fact that the low-temperature doublet consists of two bands of unequal intensity and width. These Bloch equations give

$$I(\omega) = \mathrm{Im}\,\frac{i\tau[I_+(\alpha_-\tau + 1) + I_-(\alpha_+\tau + 1) + 2(I_+I_-)^{1/2}]}{(\alpha_+\tau + 1)(\alpha_-\tau + 1) - 1}$$

using the notation familiar from NMR.[3] Here $I(\omega)$ is the intensity of the line, ω_0 is the center of the spectrum, τ is the reciprocal rate of exchange, $\alpha_\pm = 1/T_\pm - i(\omega - \omega_0 \mp \delta\omega/2)$ and $I_\pm$, $T_\pm$, and $\delta\omega$ are the intensities, the dephasing times (taken as the inverse widths), and the splitting of the two bands in the absence of exchange, respectively. The cross term $(I_+I_-)^{1/2}$ is due to the "overlap" contributions;[4] similar formulas for exchange collapse of spectral lines have been derived before.[5] The infrared spectra were analyzed by fitting each spectrum with a set of Lorentzian bands and then comparing the peak splittings of the asymmetric methyl stretching bands with those calculated from the equation for different values of τ. Values of $I_\pm$, $T_\pm$, and $\delta\omega$ were taken from the 9 K spectrum which is assumed to represent the no exchange situation. The values of τ can be fit to an Arrhenius expression $\tau = A \exp(-\Delta E/kT)$ which gives $A = 0.88 \pm 0.15$ ps and $\Delta E = 55 \pm 9$ cm^{-1}. We have measured Raman spectra from 130 K to room temperature and, over this range, these spectra look similar to the infrared spectra.

The infrared spectra of a neat polycrystalline sample of n-$C_{20}H_{42}$ show narrower bands at low temperature but otherwise behave in a similar manner to the clathrate spectra. They have been analyzed in the same way with the result $A = 1.46 \pm 0.10$ ps and $\Delta E = 60 \pm 5$ cm^{-1}.

It is known that the bands which we are considering are split by intramolecular effects[6] and that the higher frequency one is due to the mode symmetric with respect to the plane of the carbon skeleton.[7] NMR studies of neat alkane crystals suggest that at temperature of ~150 K, the methyl groups reorient freely while the backbone methylene groups are held rigidly.[8] In contrast, the methylene backbone seems to be considerably more mobile in the clathrate crystals.[9]

The motional collapse we observe is similar in the two systems and is almost certainly due to the rotation of the methyl groups. The high temperature rate (the A factor) of ~1 ps is reasonable for this motion. The activation energy of ~60 cm^{-1} is apparently low for a barrier which is thought to be 910 cm^{-1} in the neat crystal.[8] The rotational tunneling or other exchange mechanism is certain to be dependent on the torsional state and thus on the temperature. Thermally weighted tunneling times show rather low activation energies at low temperatures[10] and this may be the qualitative explanation of our low values.

The motional collapse of vibrational lines should generally be observable for rapidly rotating methyl groups, librating water molecules and other hydrides. Indeed, spectra of the water of hydration of a variety of alkali and alkaline earth salts show similar collapsing bands.[11] In these crystals, the water sits in one of two asymmetric sites at low temperature, and moves between them as the temperature is increased.

The existence of these collapsing bands is of interest to the general theory of motional narrowing of vibrational bands[4,12] and provides a way to determine the fast motions of small groups in solids. We are in the process of studying both the alkane and water of hydration systems further to better characterize these processes.

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References and Notes

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Richard A. MacPhail, Robert G. Snyder
Herbert L. Strauss*
Department of Chemistry, University of California
Berkeley, California 94720

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Electron Transfer in Nickel-Catalyzed Addition Reactions

Sir:

We recently noted that $Ni(acac)_2$ treated with 1 equiv of Dibah efficiently catalyzed conjugate addition of alkenyl[1] and alkynyl[2] organometallics to α,β-unsaturated ketones. Based on product analysis arguments, House has made a case for an electron-transfer mechanism for cuprate conjugate additions to α,β-enones.[3] In the light of his correlations, we have attempted to determine if the $Ni(acac)_2$/Dibah system could serve as a one-electron reducing agent and if conjugate addition using this system occurred by electron transfer. We now report our results, based on chemical and electrochemical studies, which substantiate these contentions.

As a preamble to our studies we measured the catalytic activity of the $Ni(acac)_2$/Dibah system per unit of time over a period of 24 h. The catalyst mixture was prepared in the usual manner and was allowed to stir at 0 °C. At various time intervals, aliquots were withdrawn and were tested for relative ability to catalyze the conjugate addition of alkenylzirconium reagent **1** to cyclohexen-1-one (as measured by yield of adduct produced in a given 15-min period). We noted that catalytic

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