NMR - Determination of a Rotational Potential Energy Barrier

Joseph DiVerdi

Physical Chemistry Laboratory
Department of Chemistry
Colorado State University
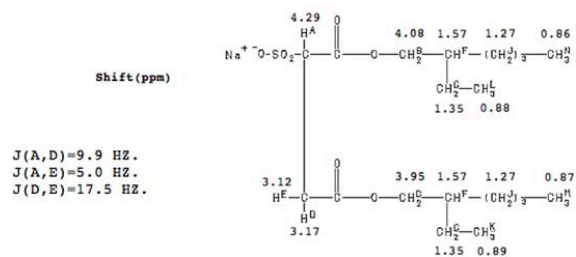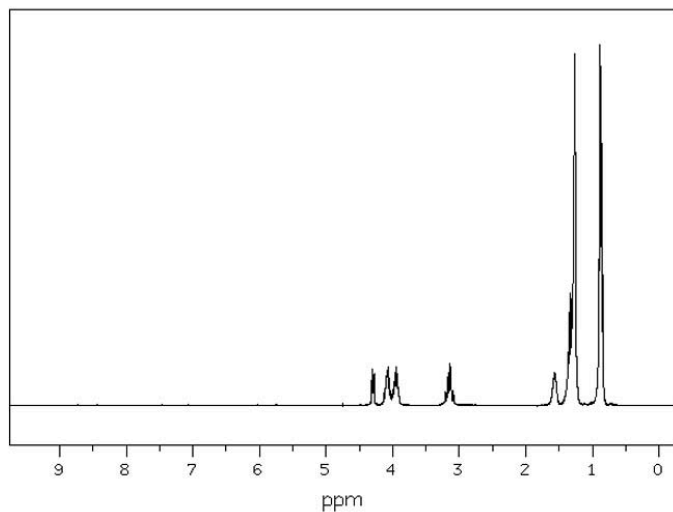Fort Collins, CO USA
April 2019

NMR Renowned for Structure Determination

SDBS-^{1}H NMR SDBS No. 7575HSP-41-199

$C_{20} H_{37} Na O_7 S$

sodium 1,4-bis(2-ethylhexyl) sulfosuccinate

SDBS-^{1}H NMR SDBS No. 7571HSP-02-122

$C_{20} H_{36} O_4$

bis(2-ethylhexyl) maleate

HSP-02-122

Shift (ppm)

$J(A,D) = 9.9$ HZ.
$J(A,E) = 5.0$ HZ.
$J(D,E) = 17.5$ HZ.
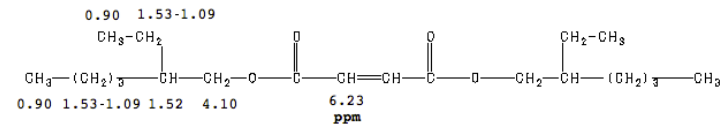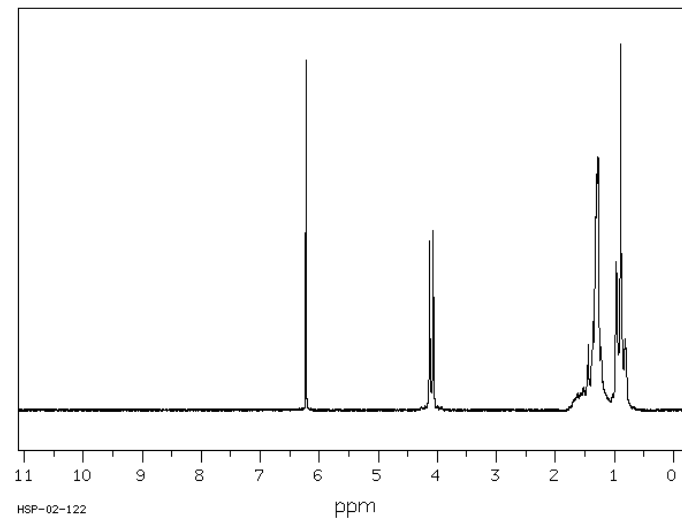
Also Capable of Dynamic Determinations

Colorado State University
Fort Collins, CO

Rate Processes and Nuclear Magnetic Resonance Spectra. II. Hindered Internal Rotation of Amides*

H. S. GUTOWSKY AND C. H. HOLM†
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois
(Received January 30, 1956)

Mathematical methods are presented for calculating rate constants of processes which narrow nuclear magnetic resonance absorption lines having discrete components. High resolution proton spectra show that the $R_1CO-NR_2R_3$ skeletons of N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) are planar and suggest that N-methylformamide, N-methylacetamide, N-methylformanilide and N-methylacet-anilide exist predominantly in one configuration. The presence of a significant amount of double bond character in the C—N amide bond is proved by the temperature dependent coalescence observed for the chemically shifted proton doublet of the $N(CH_3)_2$ groups in DMF and DMA, which gives values of about 22 and 19 kcal respectively for the free energy of activation required for reorientations about the bond.

Determination of Rate Processes from Earliest Days
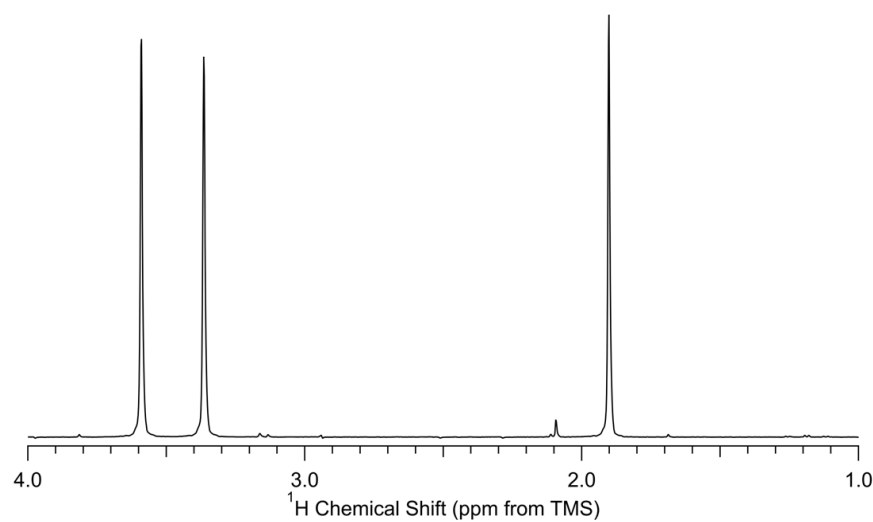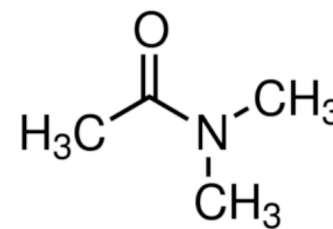
Explain a Simple NMR Spectrum

N,N-dimethylacetamide
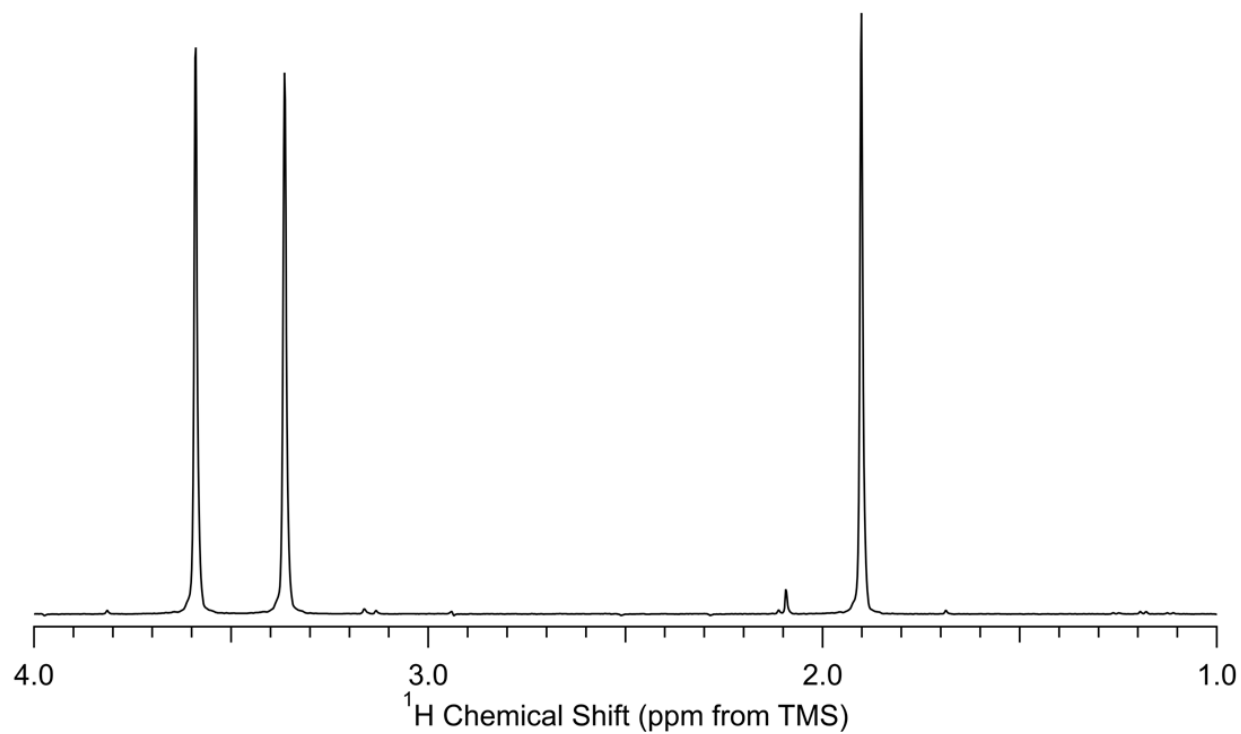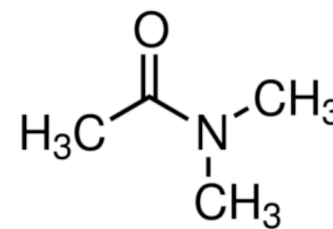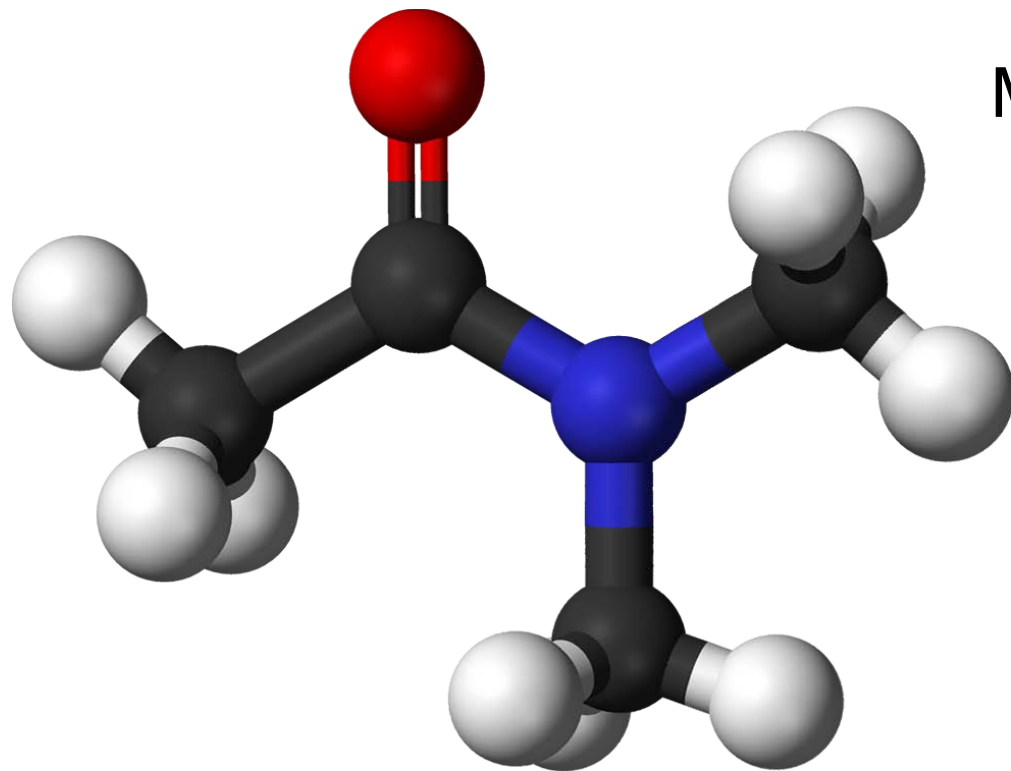
Explain two NMR Spectra

N,N-dimethylacetamide

296 K
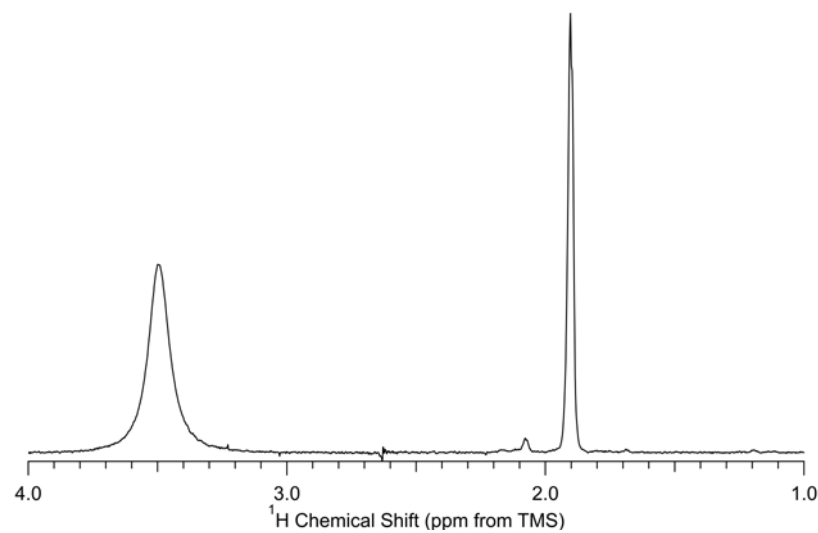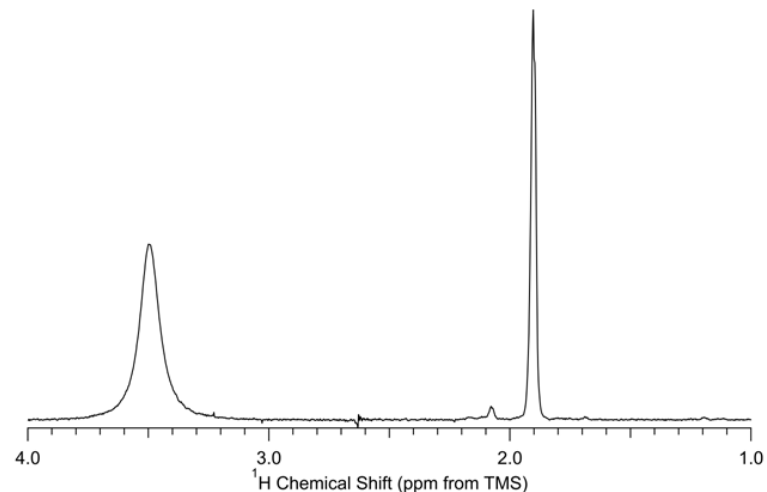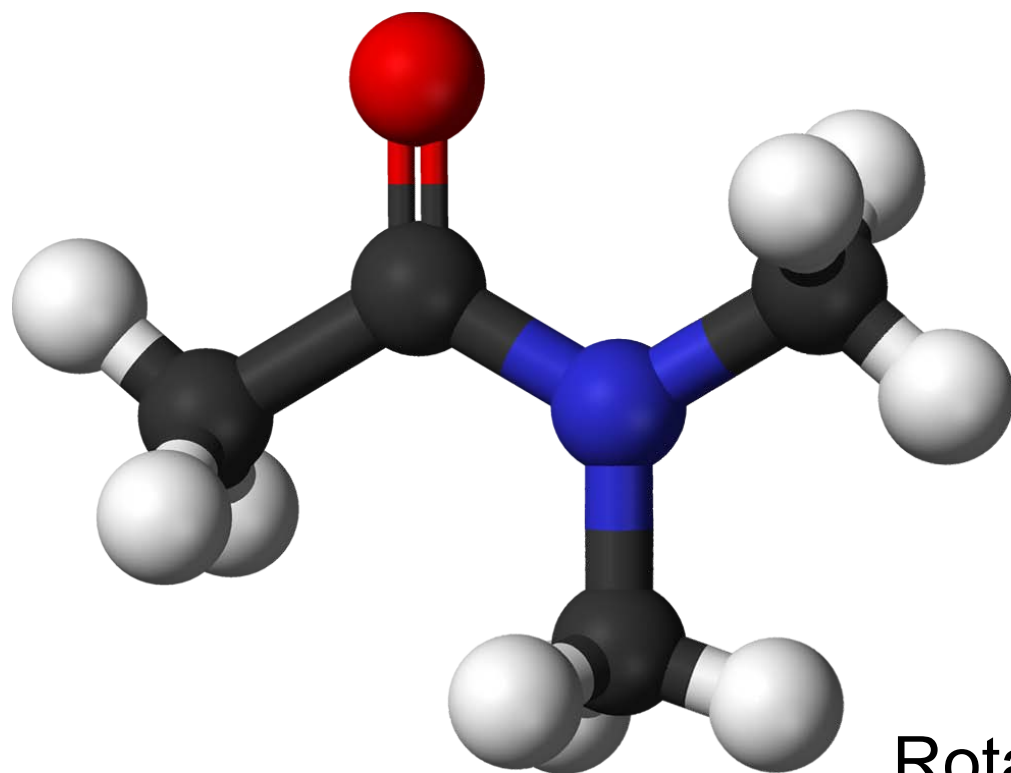
373 K

Effect of "No" Molecular Dynamics

Methyl near Oxygen
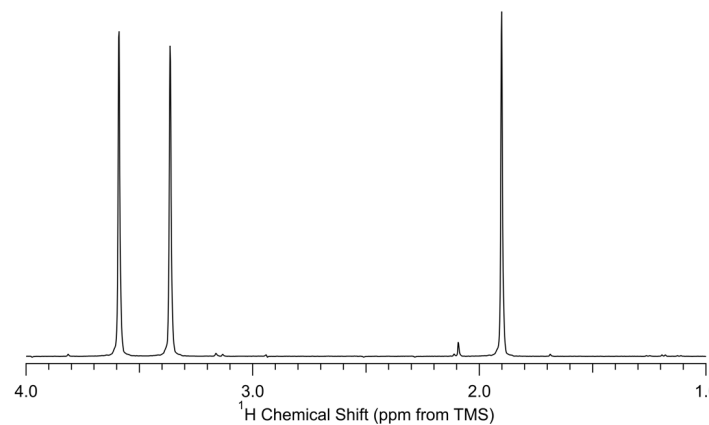
Methyl far from Oxygen

Resonance Frequency Depends Upon Chemical Environment

Effect of Fast Molecular Dynamics

Rotation About C–C Bond
Interchanges Chemical Environments

Fast Exchange Results in Observation of
Average of All Environments.

Motional Averaging – Optical Example

Stationary
Wheel

Rotating
Wheel

The "Average"
Color is
Observed

sp³-sp³ Bonds Rotate Relatively Freely

E

C

D

C

B

B

A

H₃C CH₃

H CH₃

H CH₃

CH₃

CH₃

CH₃

16 kJ/mol

19 kJ/mol

3.8 kJ/mol

180°   120°   60°   0°   60°   120°   180°
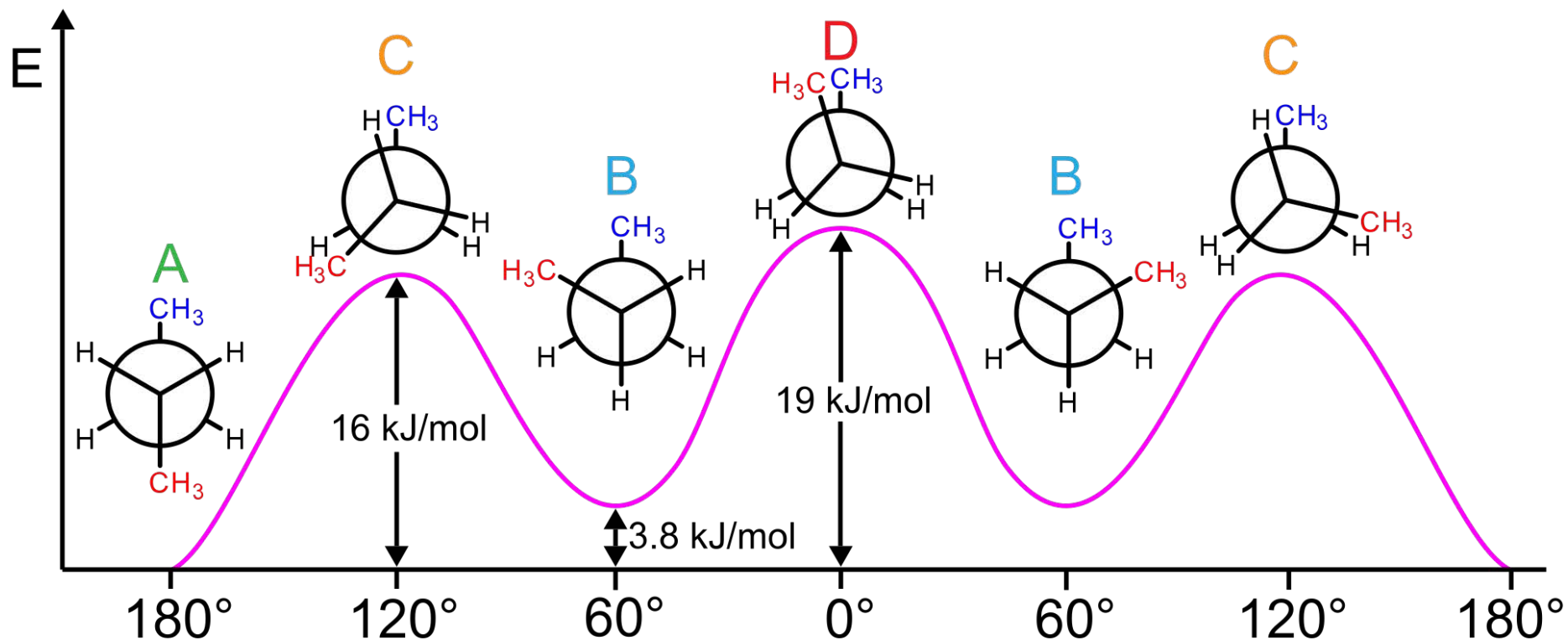
Rotation About C–C bond Changes Chemical Environments

sp^2-sp^2 Bonds Rotate With Restraint

all atoms lie in the same plane
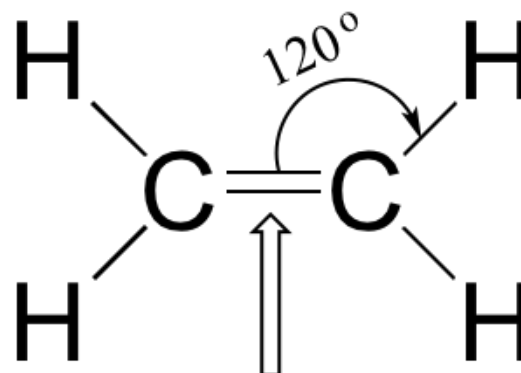
ethene

No Rotation about C–C bond
Preserves Chemical Environments

Temperature Affects Rotation Rate

N,N-dimethylacetamide
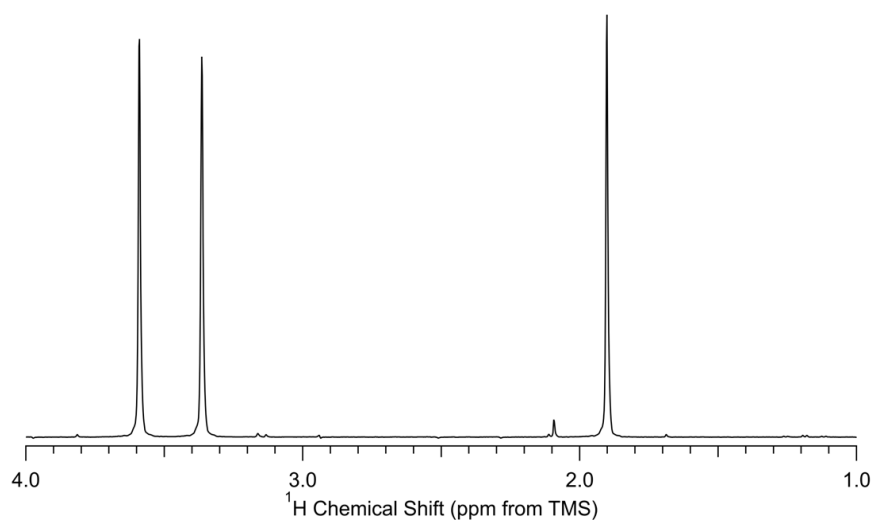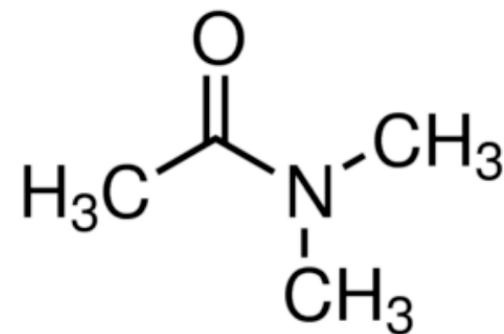
296 K
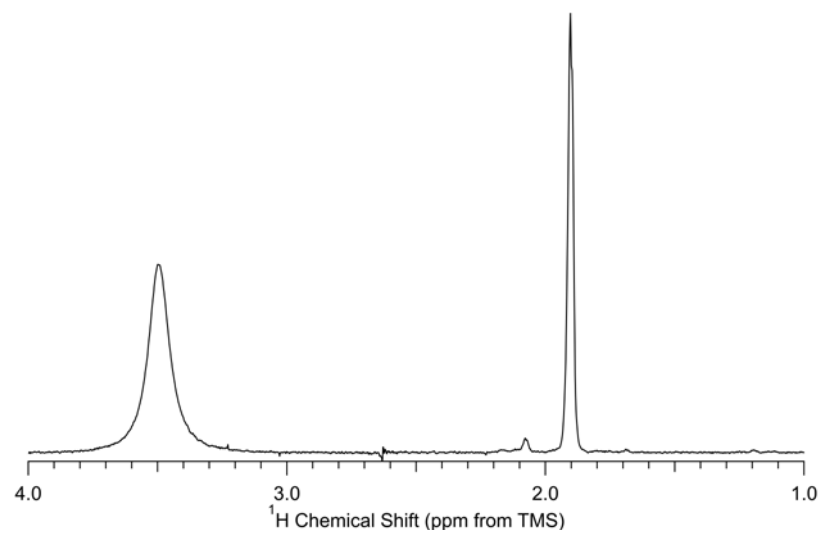
373 K

sp³-sp³ Bonds Rotate Relatively Freely
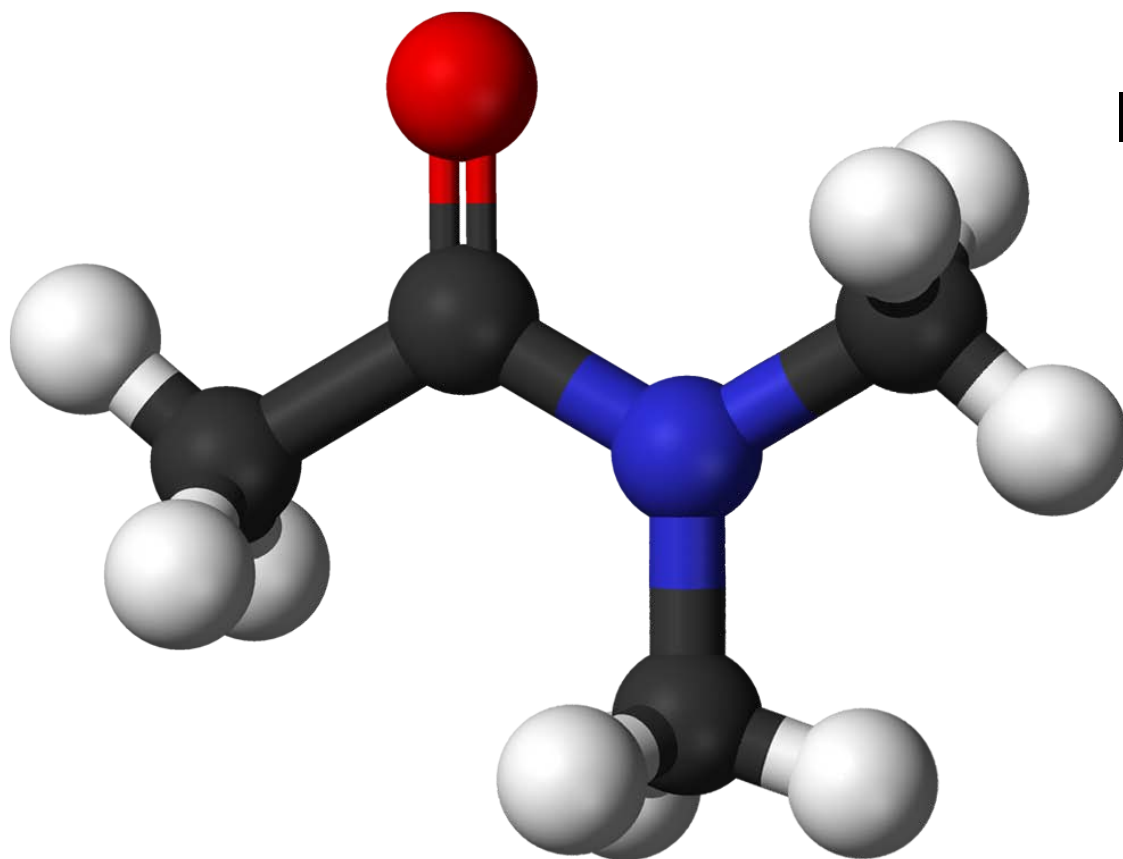
Isn't C-N Bond sp³-sp³?

With Low Barrier?

Why Aren't Signals *Always* Averaged?

Resonance Structures

Carbonyl resonance contributing structure

Third resonance contributing structure important for amides
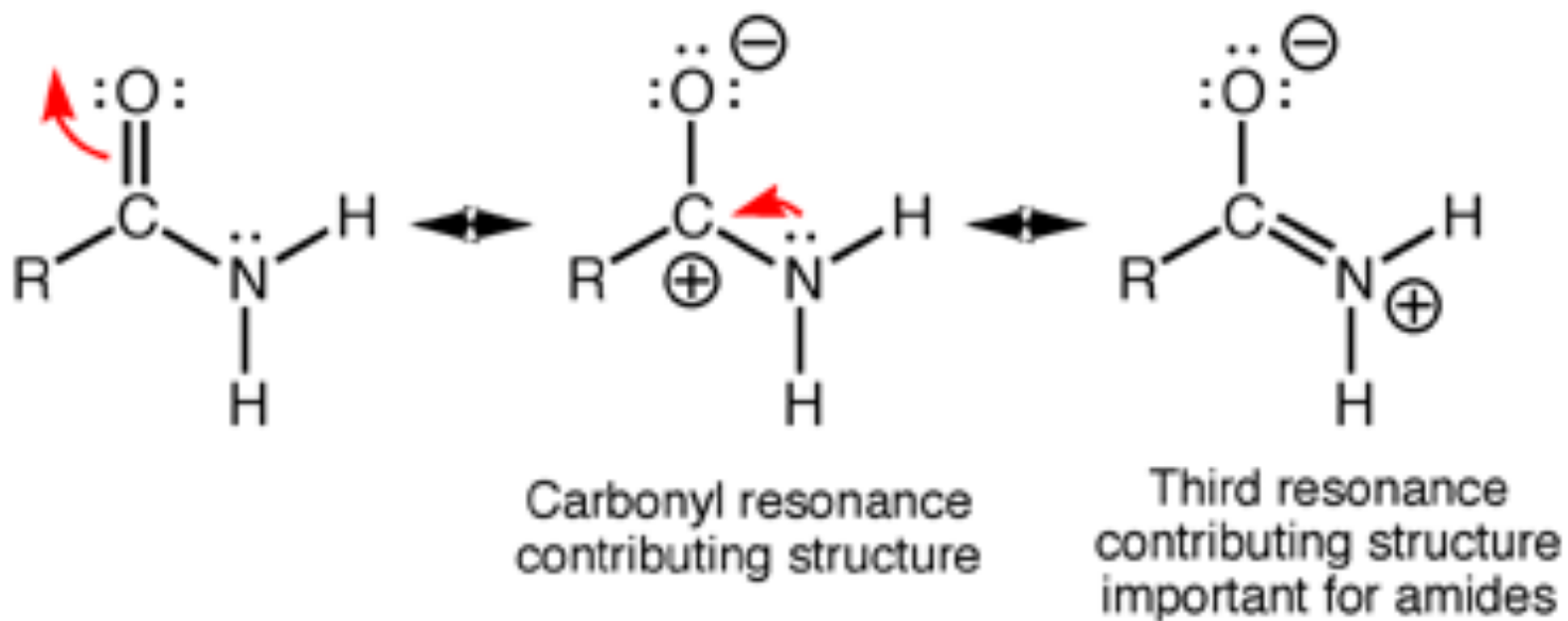
C-N Bond Exhibits Mixed sp^2-sp^2 and sp^3-sp^3 Character

Partial "Double Bond" Character

Amides protonated here

Less electrophilic than other carbonyls

Large rotation barrier due to partial double bond

N atom is sp^2 hybridized and non-basic

All of the atoms in the box are in the same plane
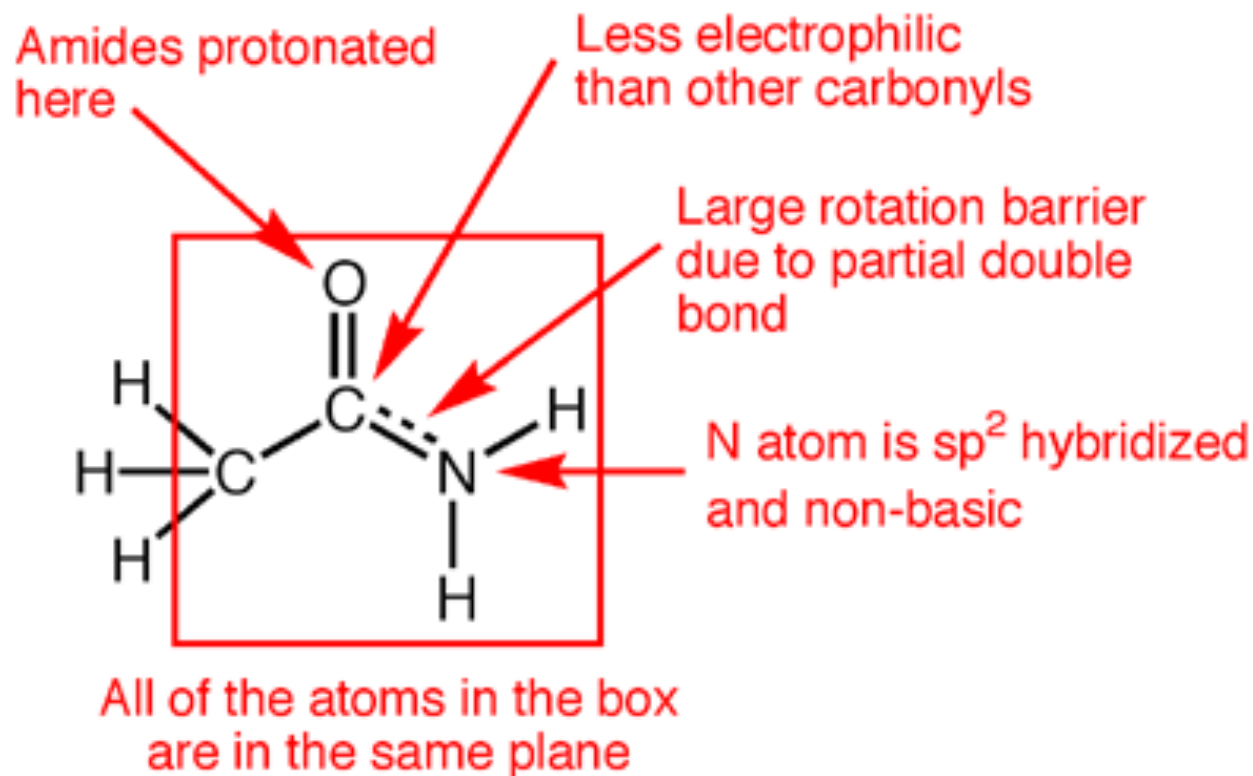
C-N Bond Exhibits Mixed sp^2-sp^2 and sp^3-sp^3 Character

Modeled With Activated Process Model
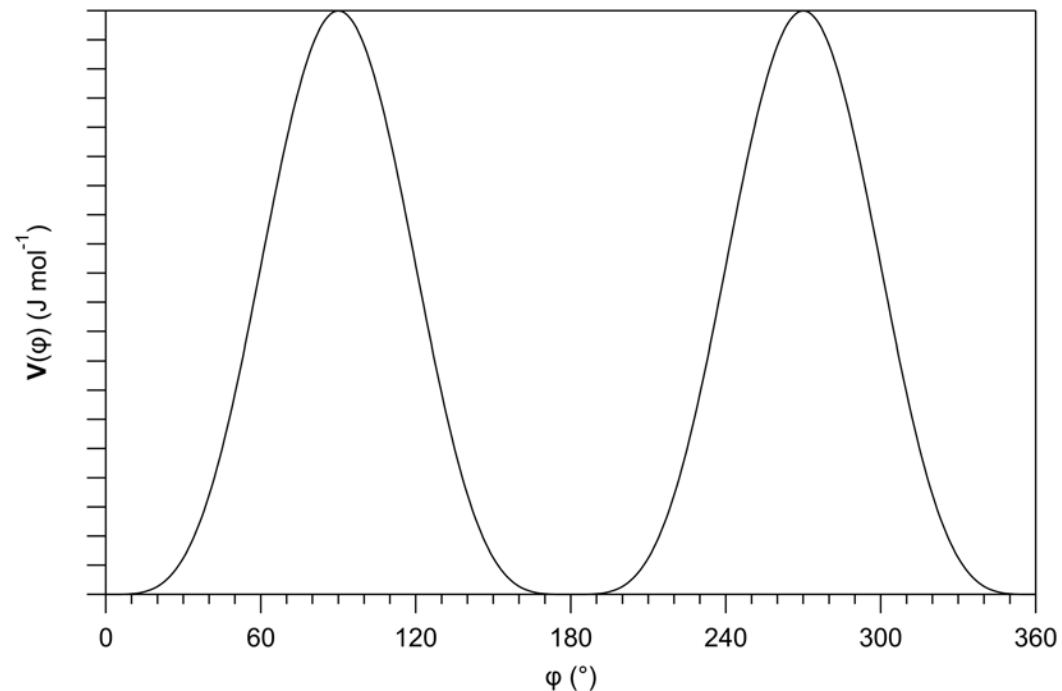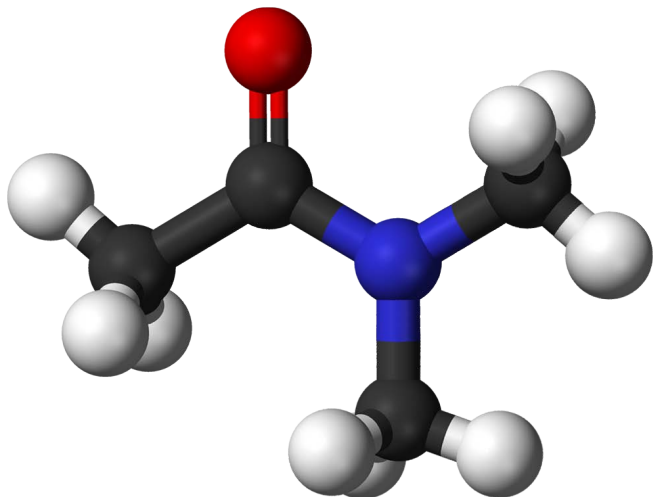
$$k = \nu_0 e^{\frac{-E_a}{RT}}$$
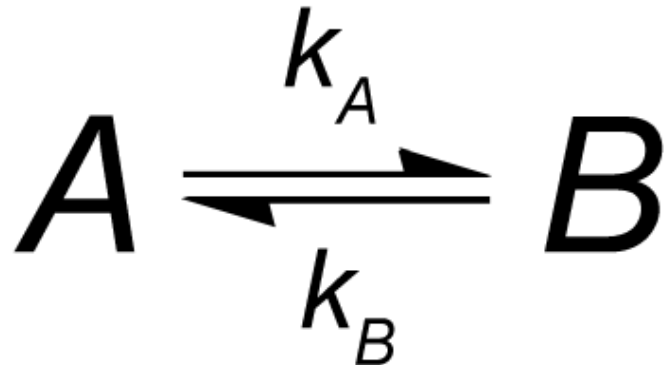
Arrhenius Behavior –
exchange rate varies
with activation energy
and temperature

Modeled With Activated Process Model

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B$$

We consider a liquid where there are two sites with different local fields giving resonance with two components A and B shifted by $+\delta\nu/2$ and $-\delta\nu/2$ from their average resonant frequency.

Modeled With Activated Process Model

The relative intensities of these components are directly proportional to the proton fractions p_A and p_B contributing to each component.

The process interchanges protons between sites *A* and *B*.

So if the protons N_A and N_B at each site are labeled $N_A{}^*$ and $N_B{}^*$ at some instant

$$dN_A^\star/dt = -k_A N_A^\star \ and \ dN_B^\star/dt = -k_B N_B^\star$$

where: $\qquad k_A p_A = -k_B p_B$

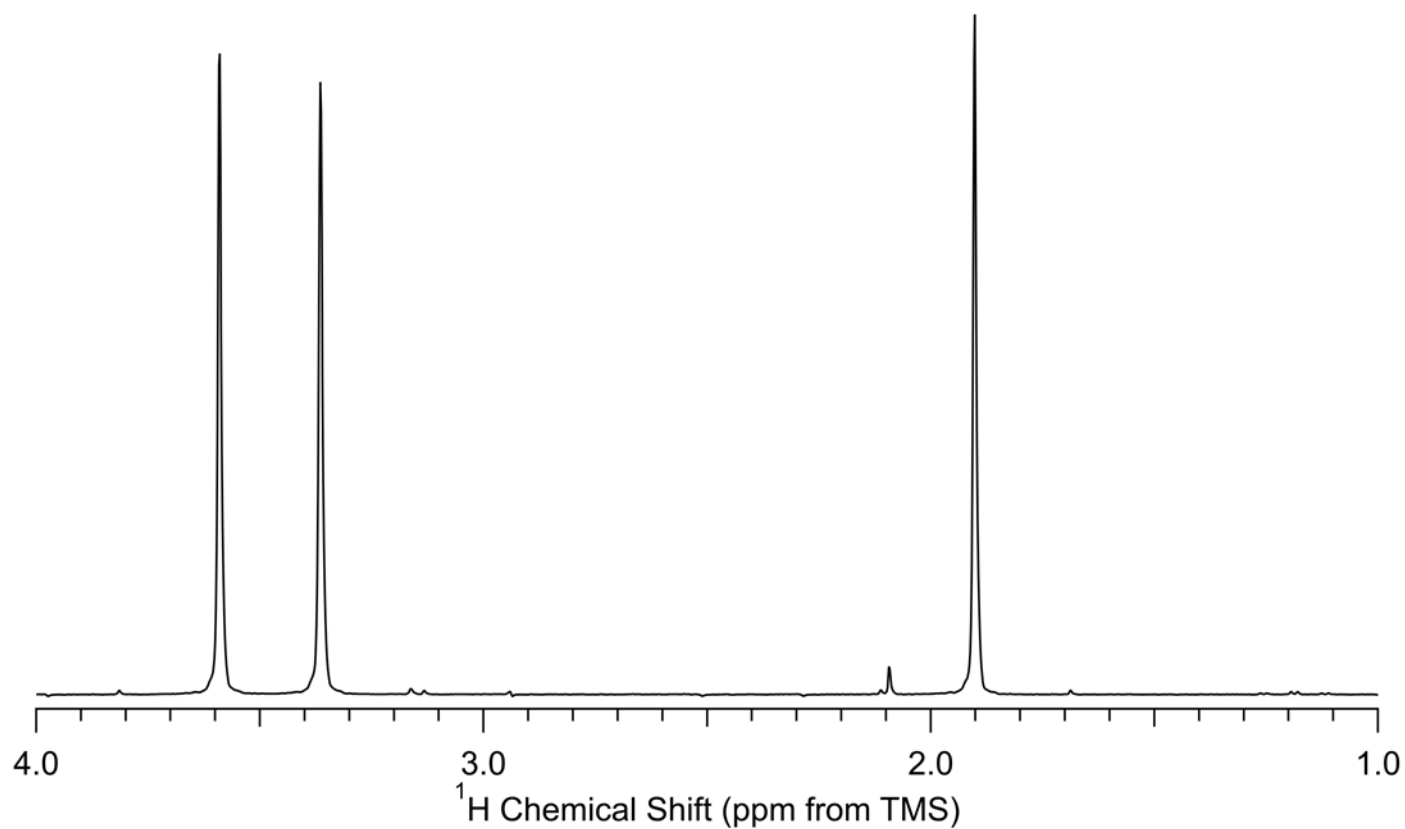The average lifetime of protons at each site is:

$$\tau_A = 1/k_A = \tau/p_B \ and \ \tau_B = 1/k_B = \tau/p_A$$

where: $\qquad \tau = \dfrac{\tau_A \tau_B}{\tau_A + \tau_B}$
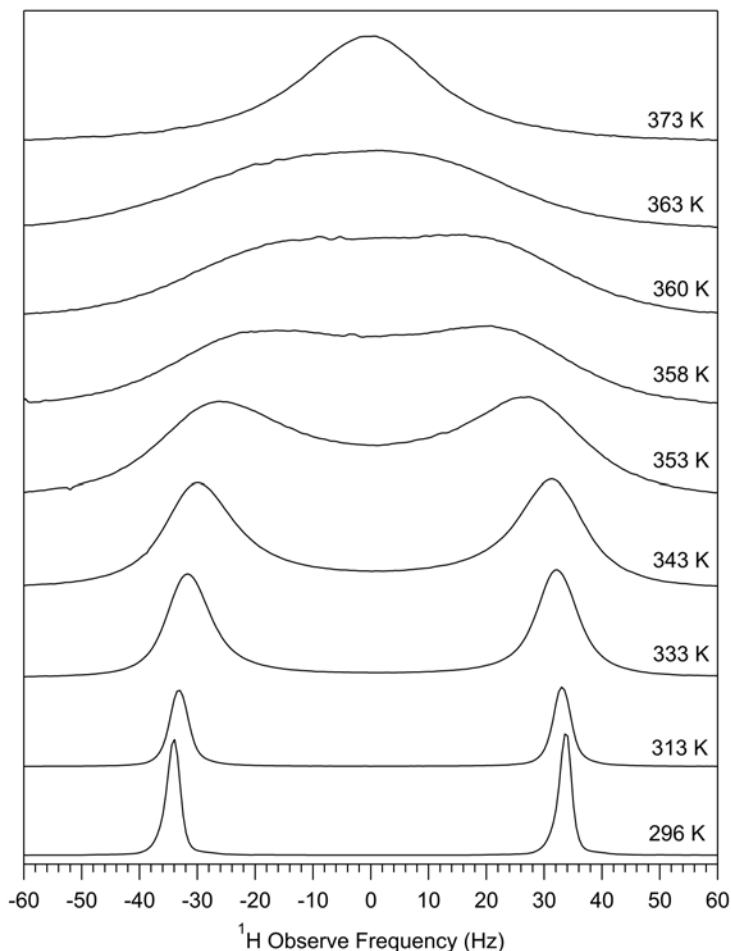
Simulation of NMR Spectra

$$g(\nu) = \frac{K\tau(\nu_A - \nu_B)^2}{(\frac{1}{2}(\nu_A - \nu_B) - \nu)^2 + 4\pi^2\nu^2(\nu_A - \nu)^2(\nu_B - \nu)^2}$$

^{1}H Chemical Shift (ppm from TMS)

Experimental NMR Spectra
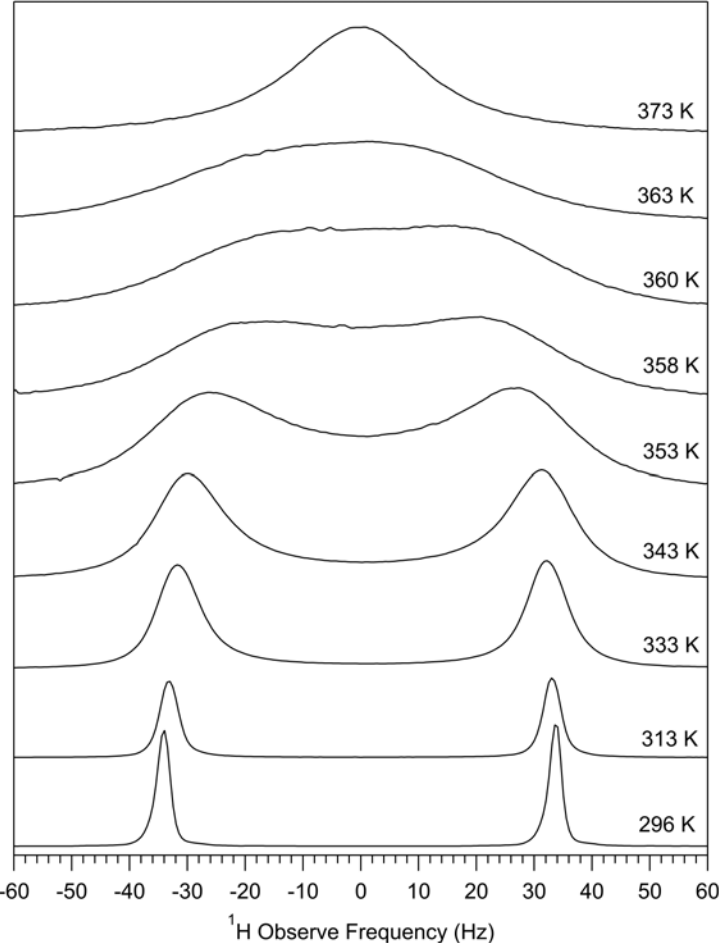
Expanded Region of
N-methyl Signals
With Re-centered Scale

Measured at 7.0 T
300 MHz for ^1H

Measured in Solution
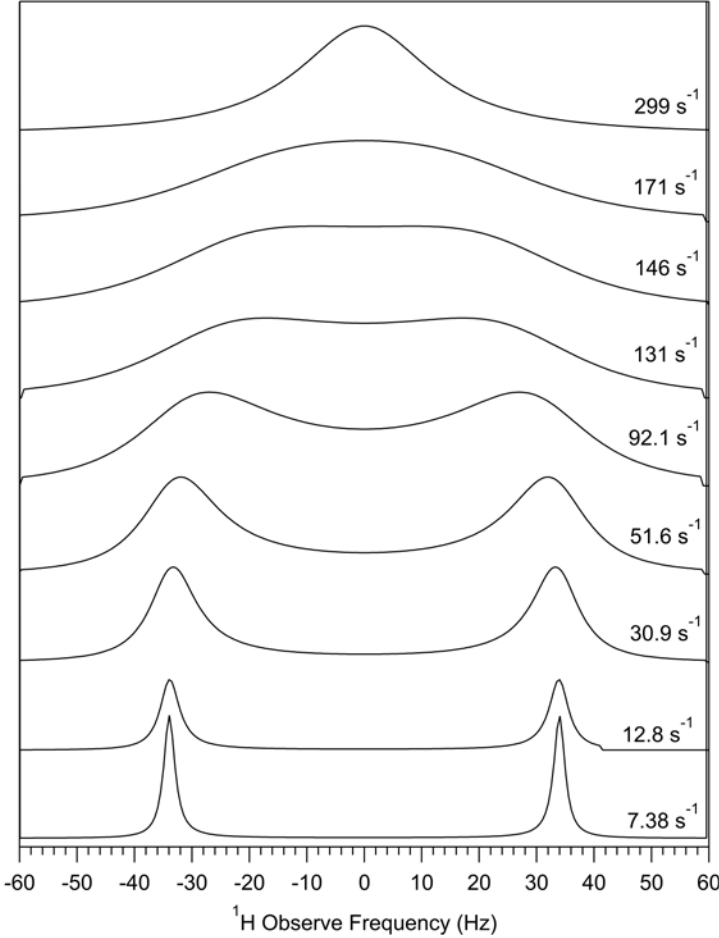$C_2Cl_{4(l)}$ - 393 K BP
In Flame-Sealed
Glass Tube

Experimental & Simulated NMR Spectra

Experiment

373 K
363 K
360 K
358 K
353 K
343 K
333 K
313 K
296 K

^{1}H Observe Frequency (Hz)

Simulated

299 s^{-1}
171 s^{-1}
146 s^{-1}
131 s^{-1}
92.1 s^{-1}
51.6 s^{-1}
30.9 s^{-1}
12.8 s^{-1}
7.38 s^{-1}

^{1}H Observe Frequency (Hz)

Arrhenius Plot for Activation Energy
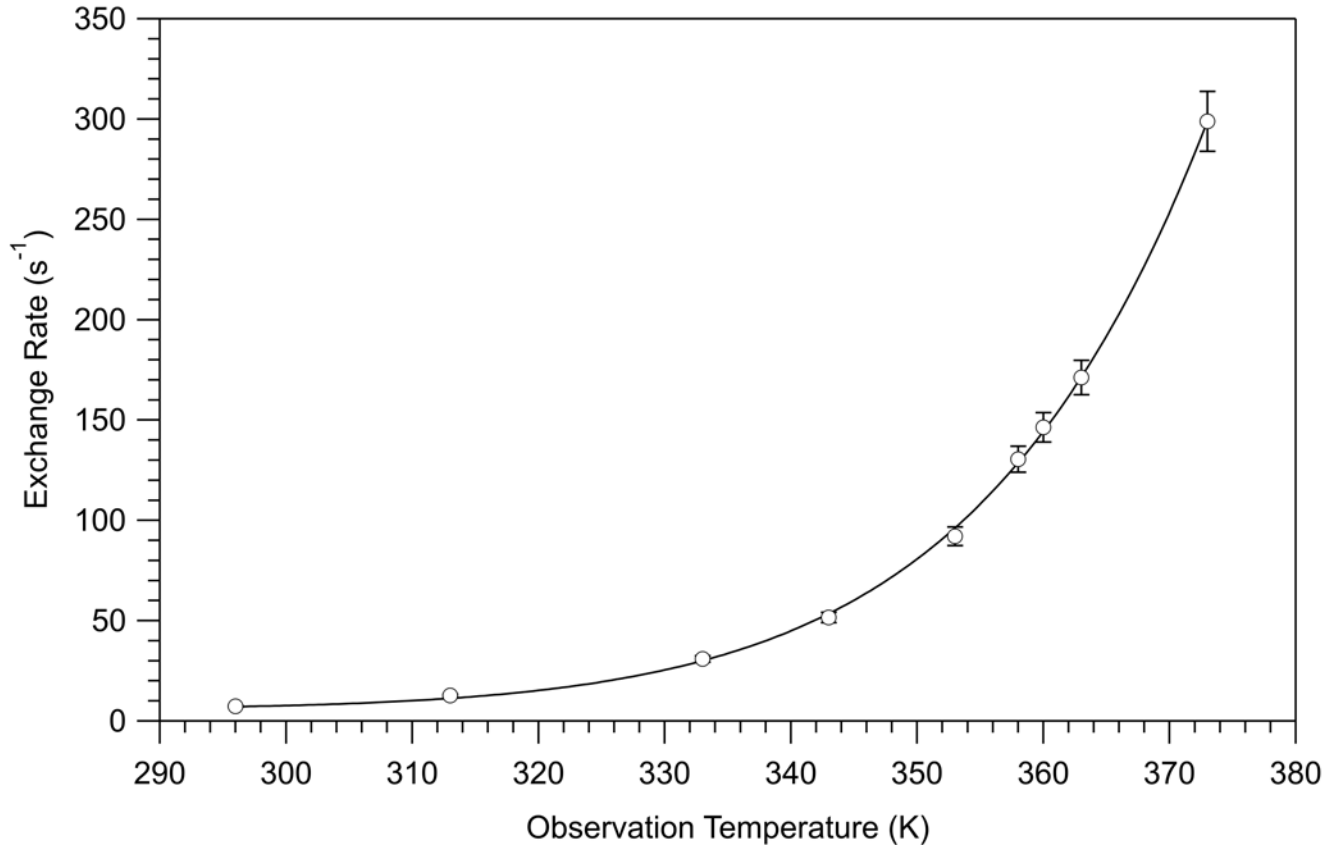
Experimental:
64370 ± 3 kJ mol^{-1}

Literature:
70290 kJ mol^{-1}

$$k = \nu_0 e^{\frac{-E_a}{RT}}$$

Acknowledgements

Professor Tenaya Newkirk for Spectrometer Access

Mr. Ross Gadde for Experimental Technique