

# NMR - Determination of a Rotational Potential Energy Barrier

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# Also Capable of Dynamic Determinations

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## 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*-methylacetanilide 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.

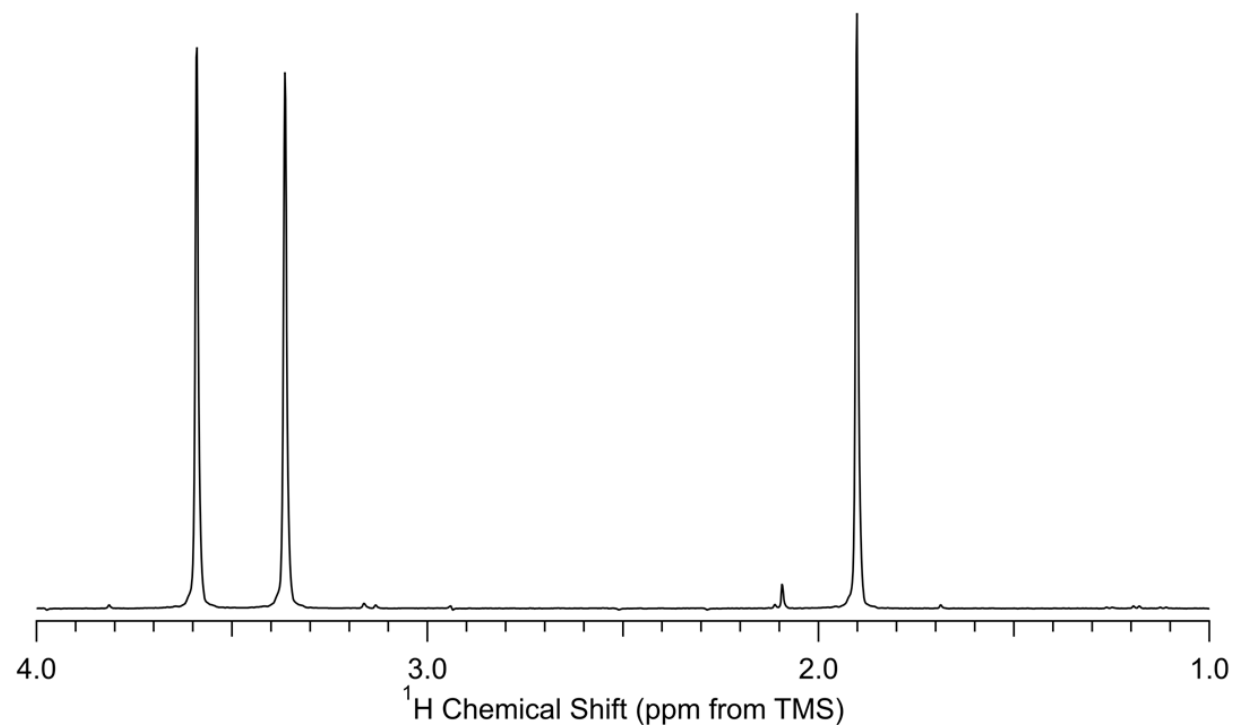
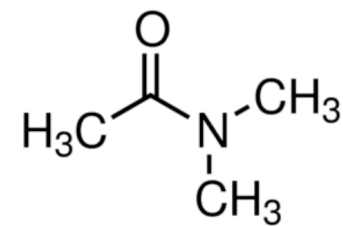
## Determination of Rate Processes from Earliest Days

# Explain a Simple NMR Spectrum

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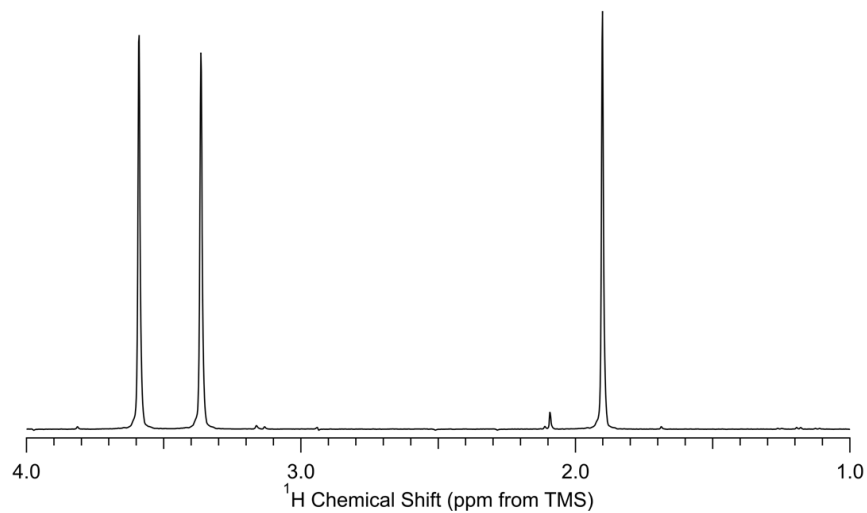
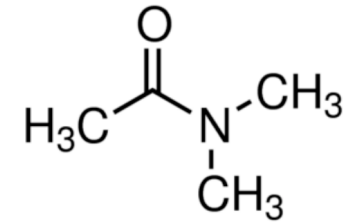
N,N-dimethylacetamide



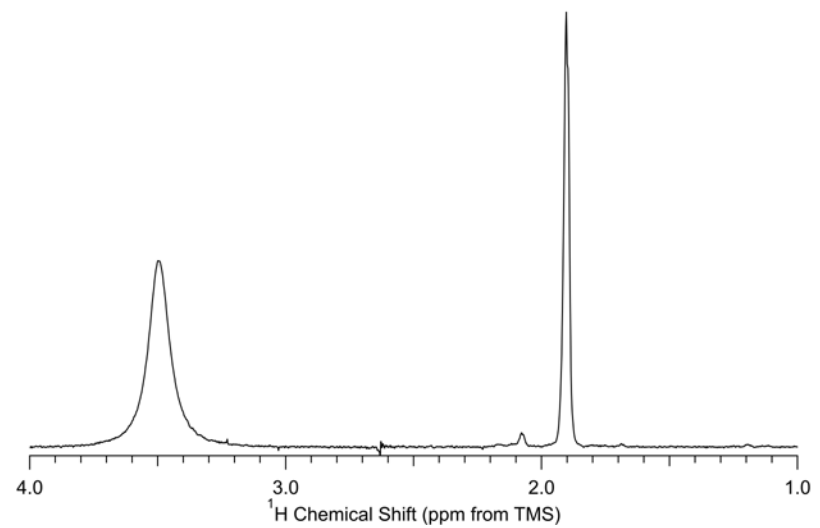
# Explain two NMR Spectra

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## N,N-dimethylacetamide



296 K

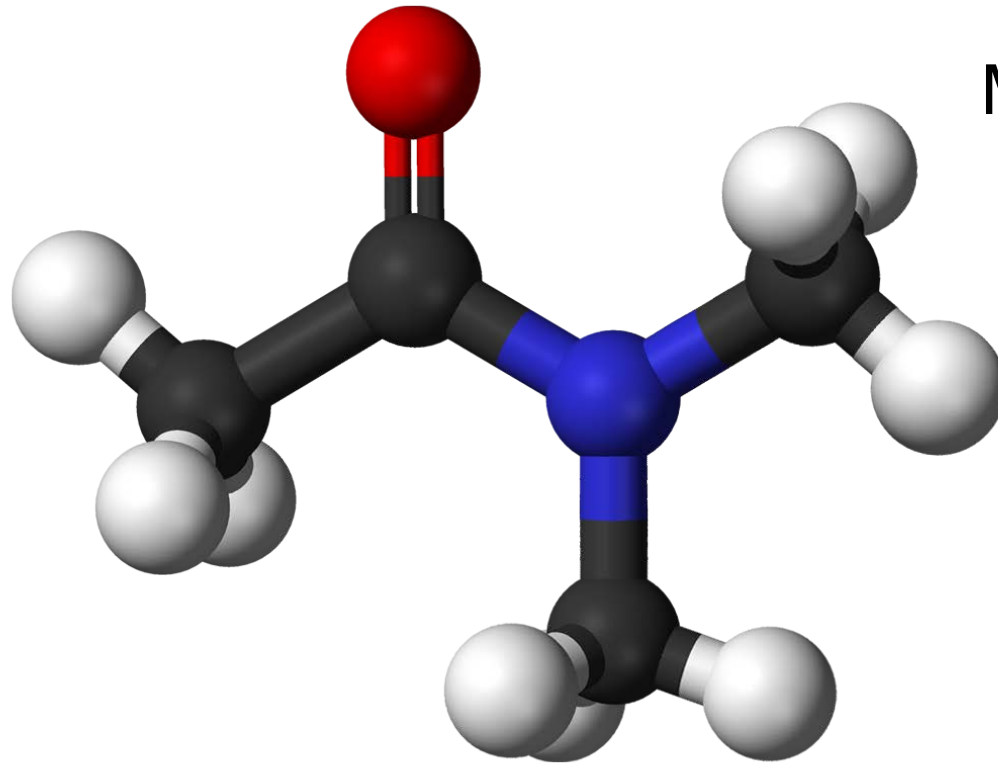


373 K

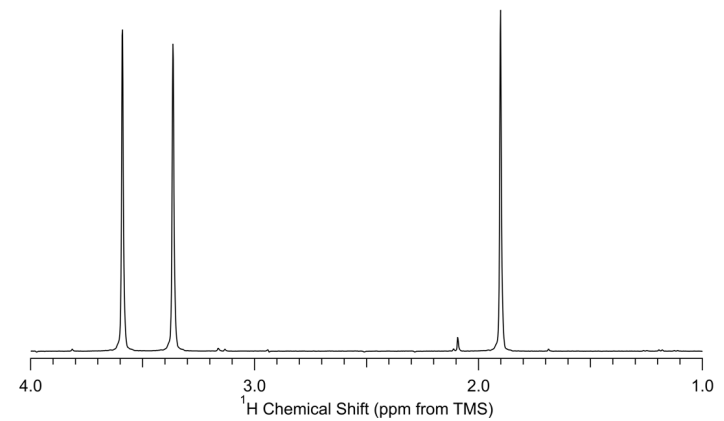
# Effect of “No” Molecular Dynamics

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Methyl near Oxygen



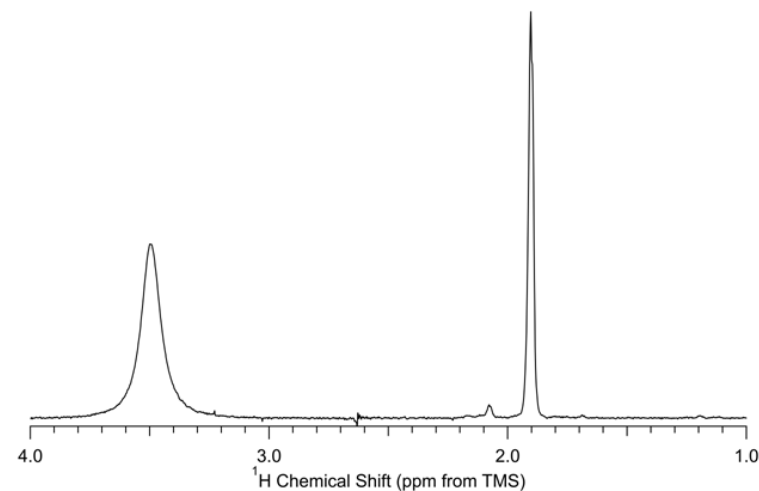
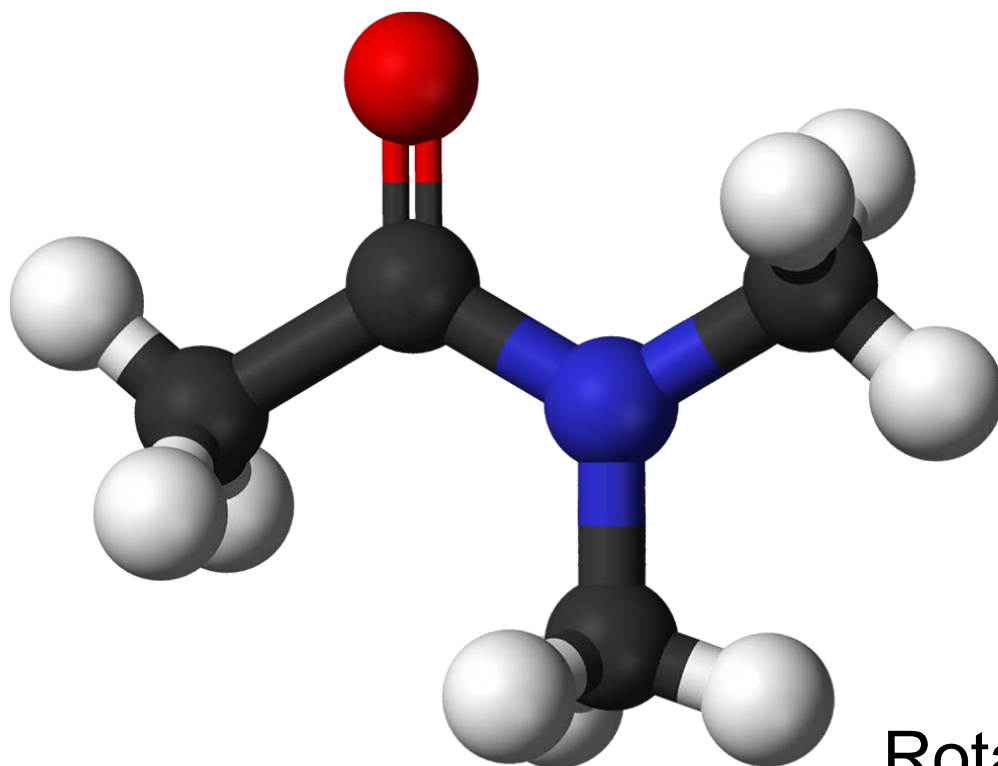
Methyl far from Oxygen

Resonance Frequency Depends Upon Chemical Environment

# Effect of Fast Molecular Dynamics

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Rotation About C–C Bond  
Interchanges Chemical Environments

Fast Exchange Results in Observation of  
Average of All Environments.

# Motional Averaging – Optical Example

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Stationary  
Wheel



Rotating  
Wheel

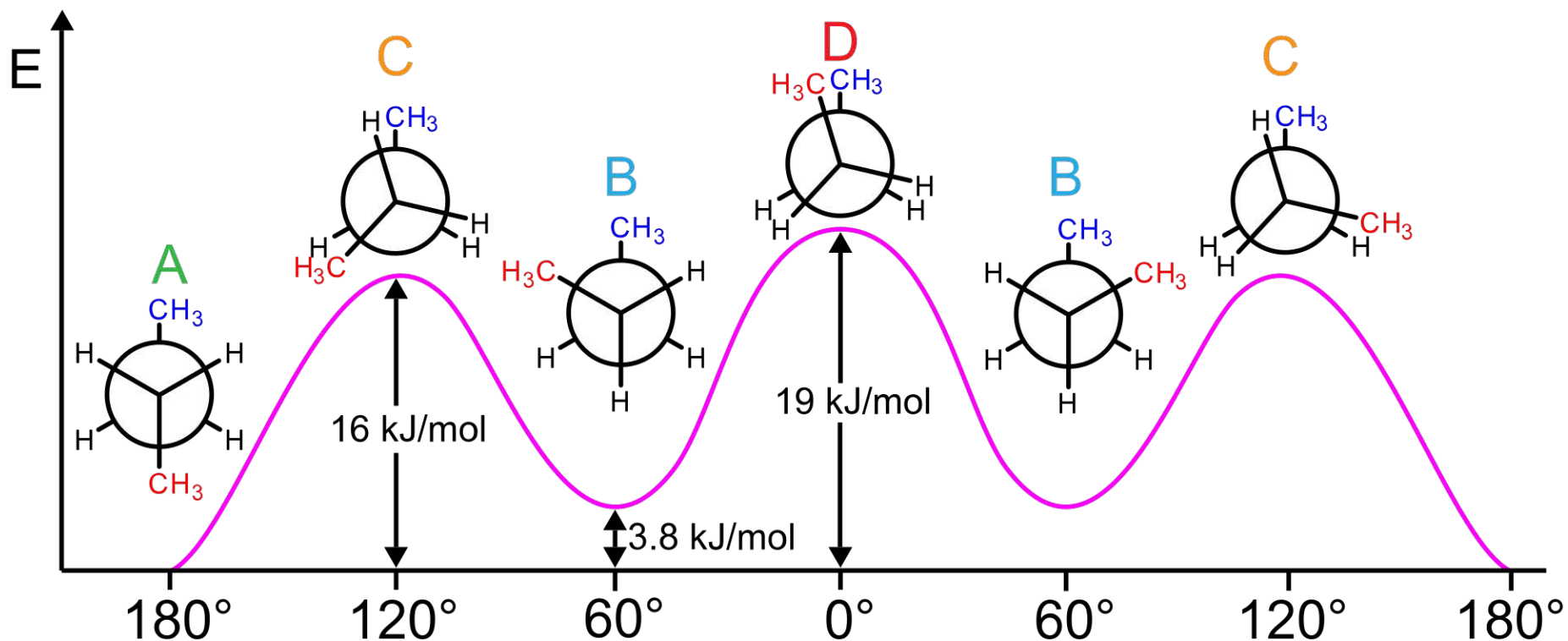


The “Average”  
Color is  
Observed



# $sp^3$ - $sp^3$ Bonds Rotate Relatively Freely

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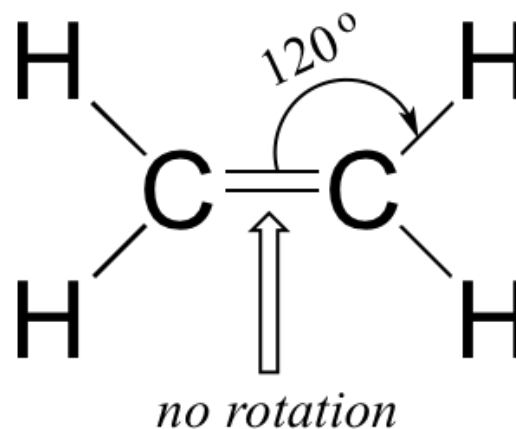
Rotation About C–C bond Changes Chemical Environments

# $sp^2$ - $sp^2$ Bonds Rotate With Restraint

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*all atoms lie in the same plane*



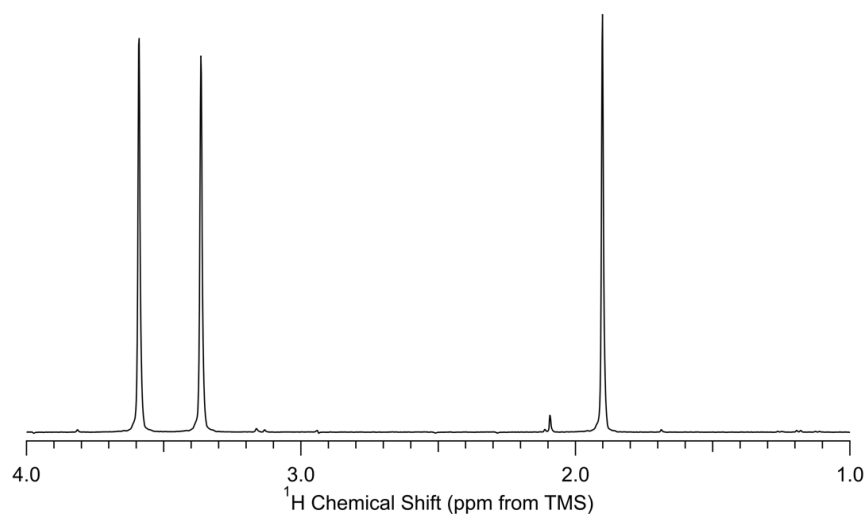
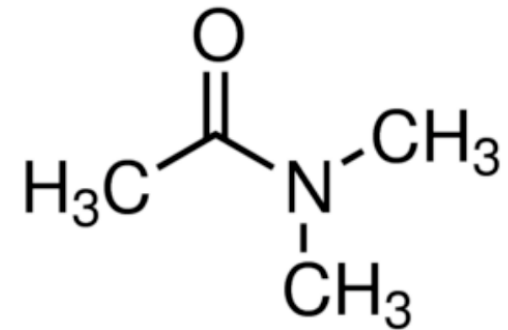
ethene

No Rotation about C–C bond  
Preserves Chemical Environments

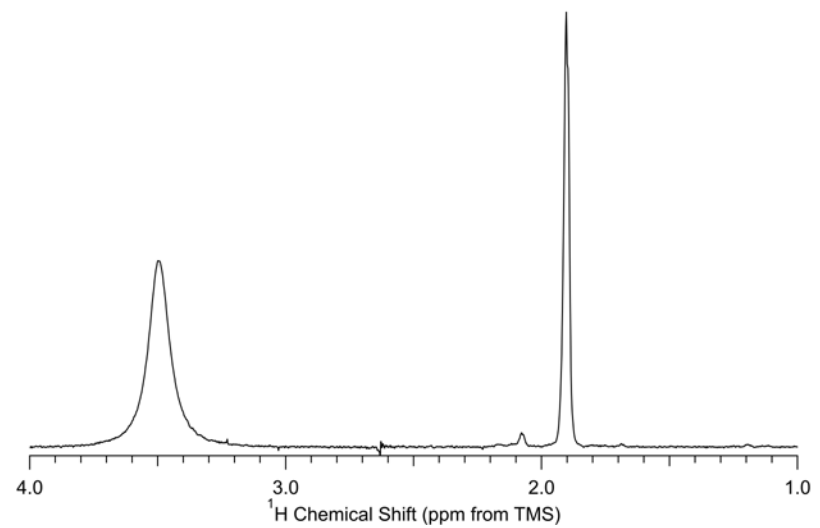
# Temperature Affects Rotation Rate

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N,N-dimethylacetamide



296 K

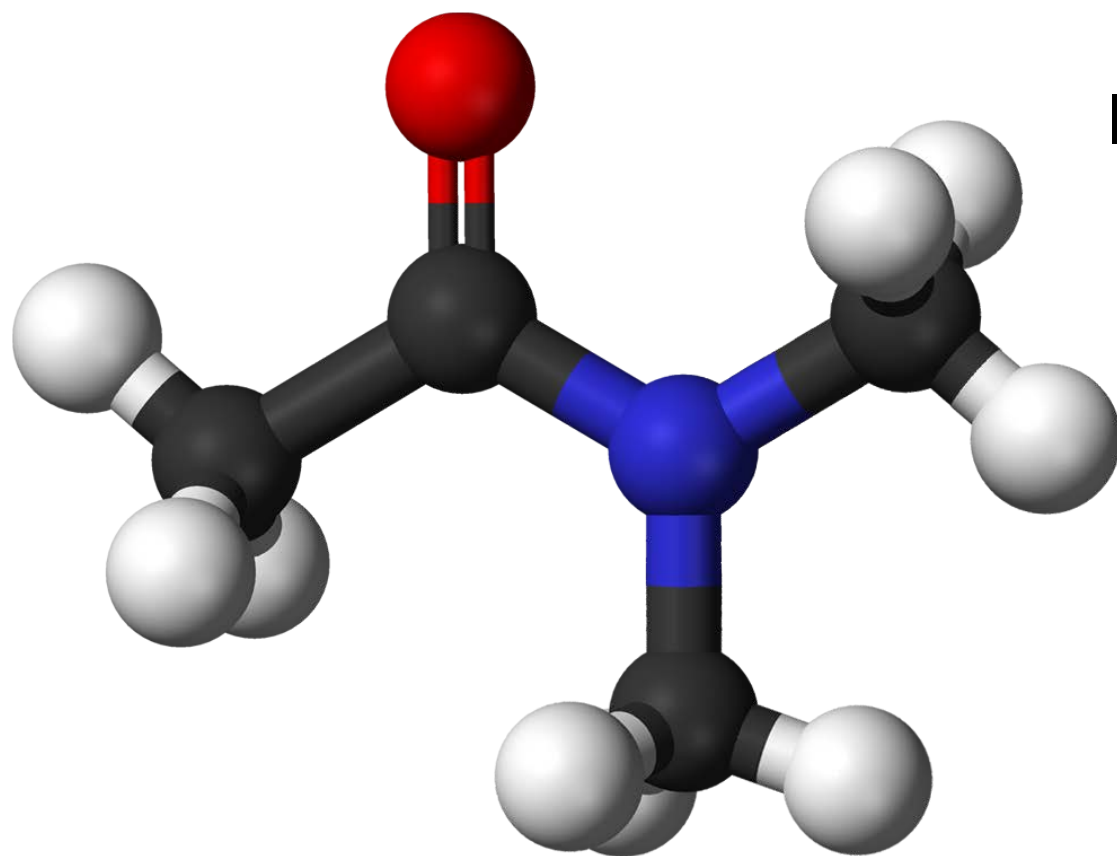


373 K

# $sp^3$ - $sp^3$ Bonds Rotate Relatively Freely

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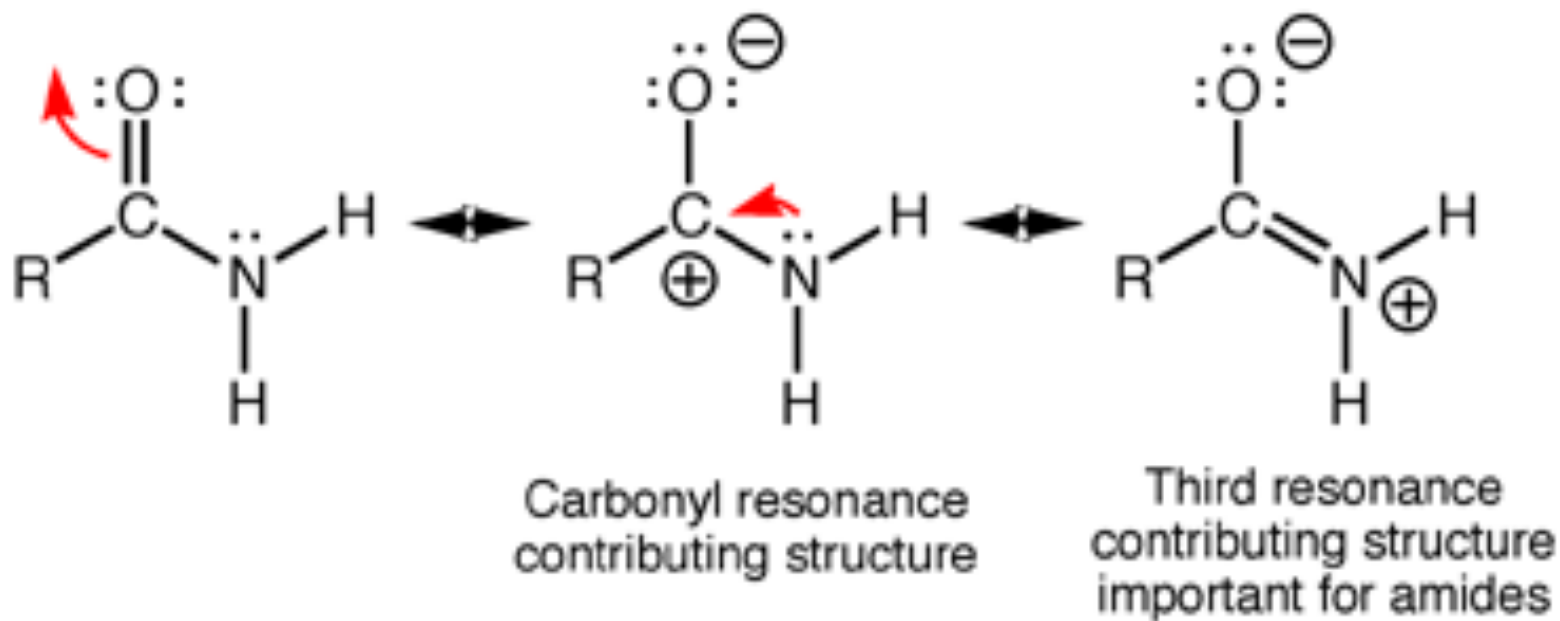


Isn't C-N Bond  $sp^3$ - $sp^3$ ?

With Low Barrier?

Why Aren't Signals *Always* Averaged?

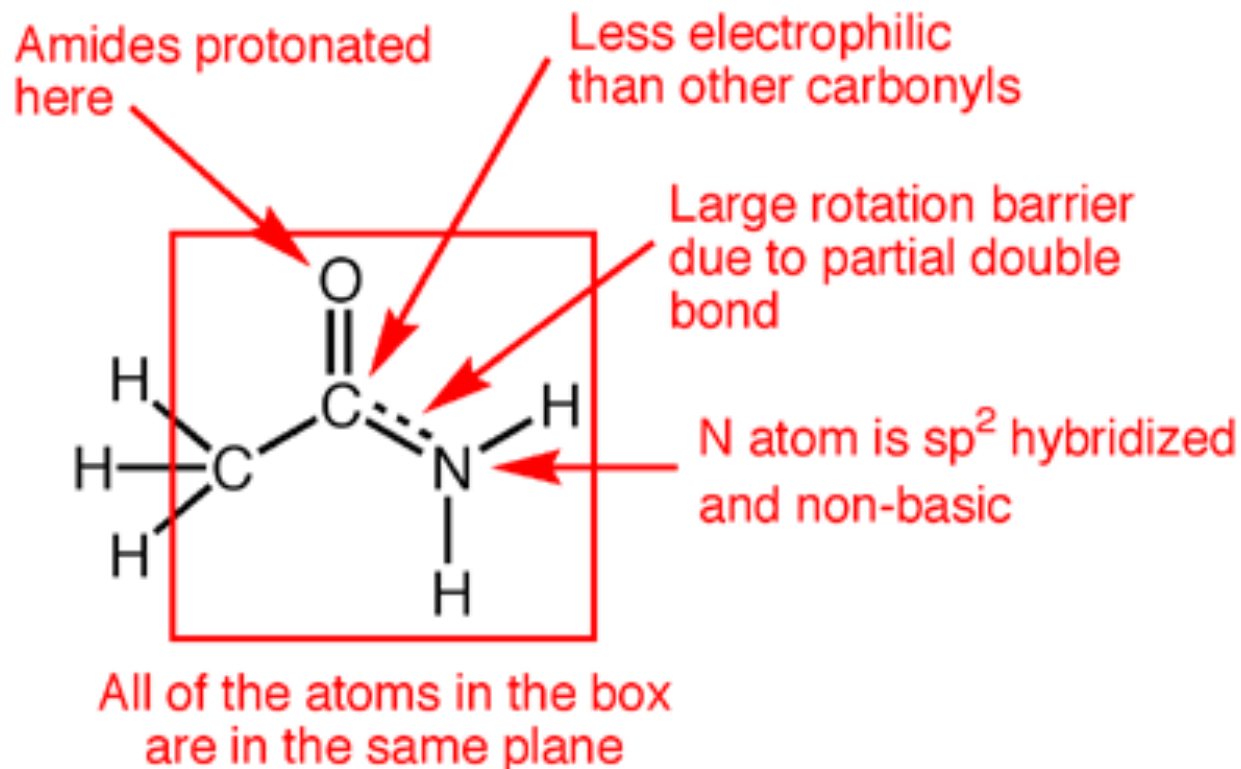
# Resonance Structures



C-N Bond Exhibits Mixed  $\text{sp}^2\text{-sp}^2$  and  $\text{sp}^3\text{-sp}^3$  Character

# Partial "Double Bond" Character

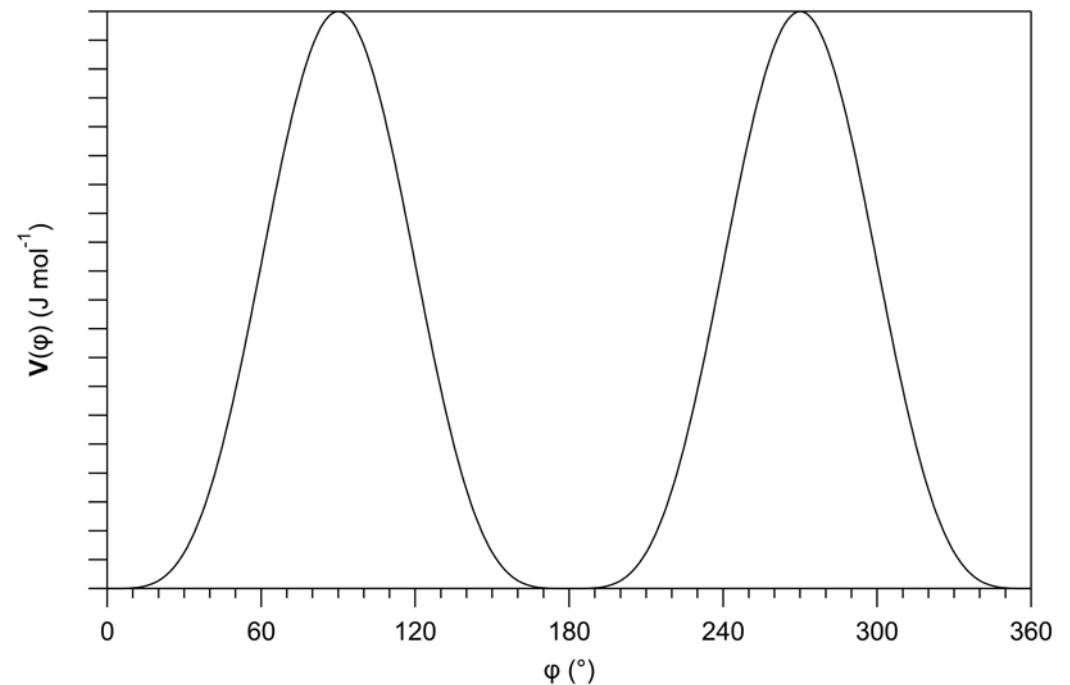
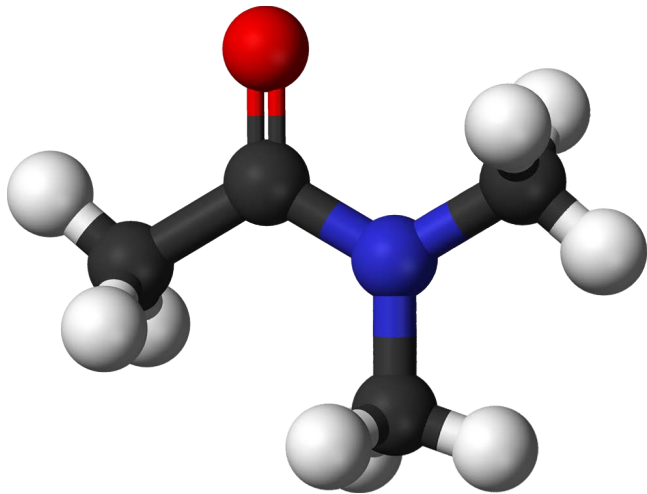
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C-N Bond Exhibits Mixed  $sp^2$ - $sp^2$  and  $sp^3$ - $sp^3$  Character

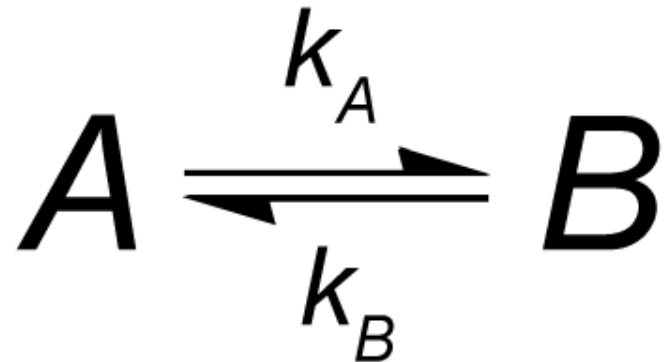
# Modeled With Activated Process Model

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

Arrhenius Behavior –  
exchange rate varies  
with activation energy  
and temperature



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.



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

$$dN_A^*/dt = -k_A N_A^* \text{ and } dN_B^*/dt = -k_B N_B^*$$

where:  $k_A p_A = k_B p_B$

The average lifetime of protons at each site is:

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

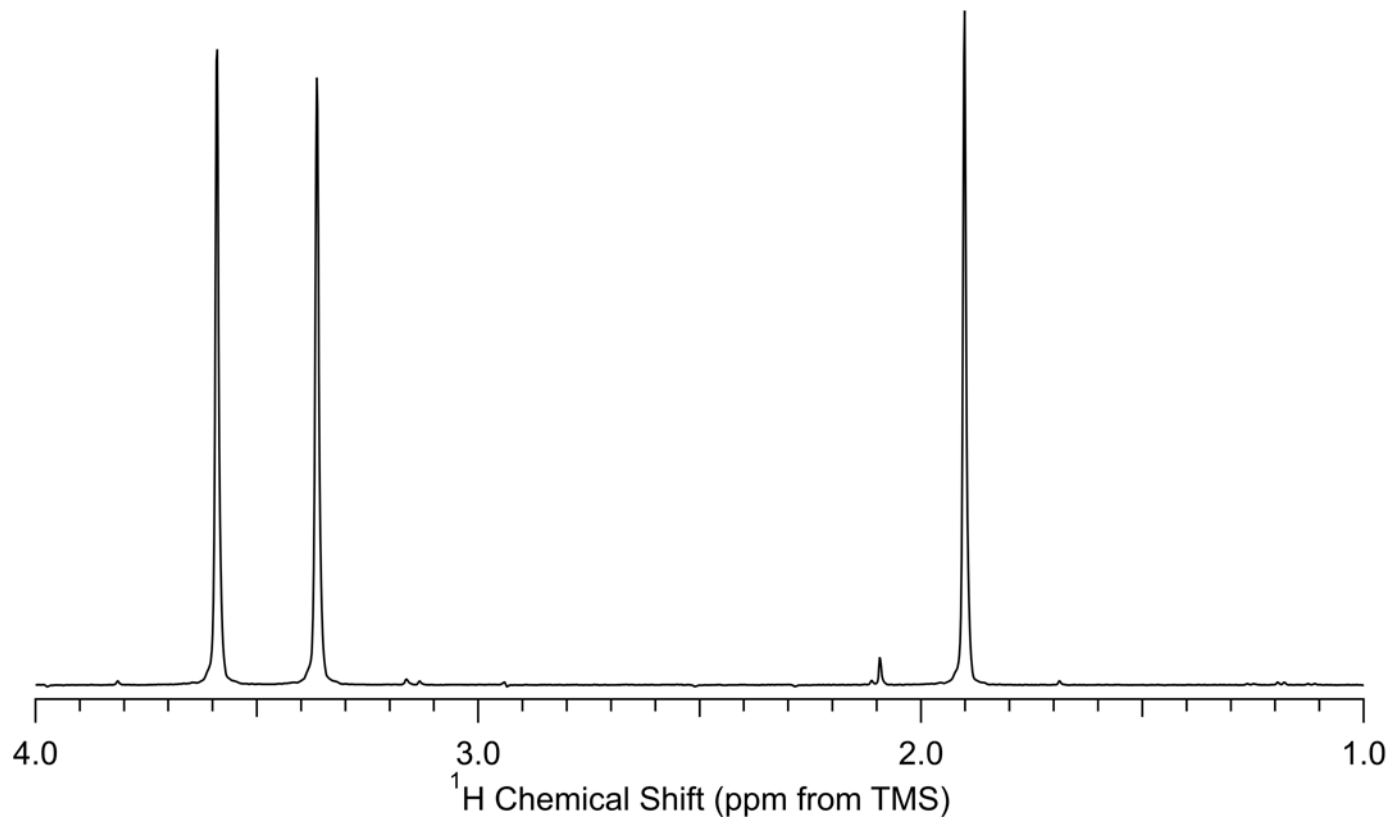
where:  $\tau = \frac{\tau_A \tau_B}{\tau_A + \tau_B}$

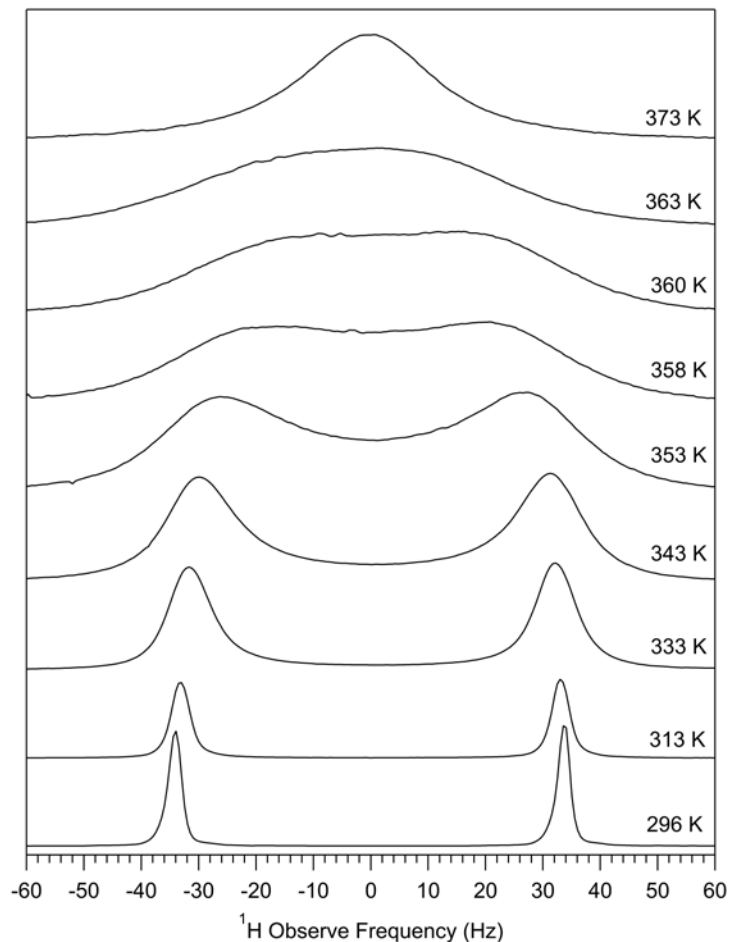
# Simulation of NMR Spectra

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





Expanded Region of  
N-methyl Signals  
With Re-centered Scale

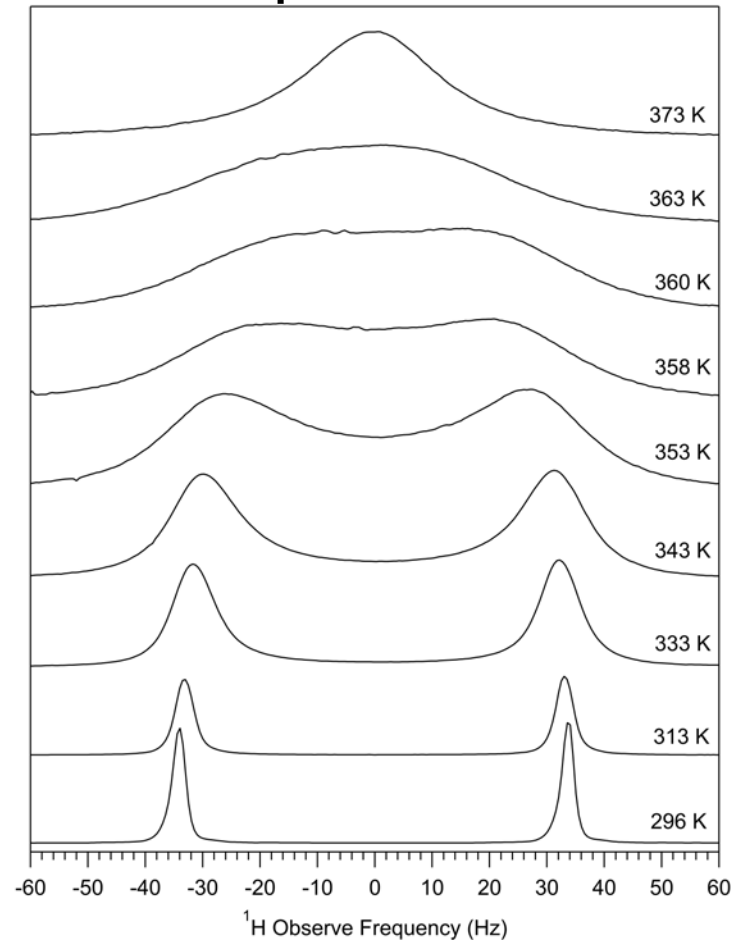
Measured at 7.0 T  
300 MHz for  $^1\text{H}$

Measured in Solution  
 $\text{C}_2\text{Cl}_4(l)$  - 393 K BP  
In Flame-Sealed  
Glass Tube

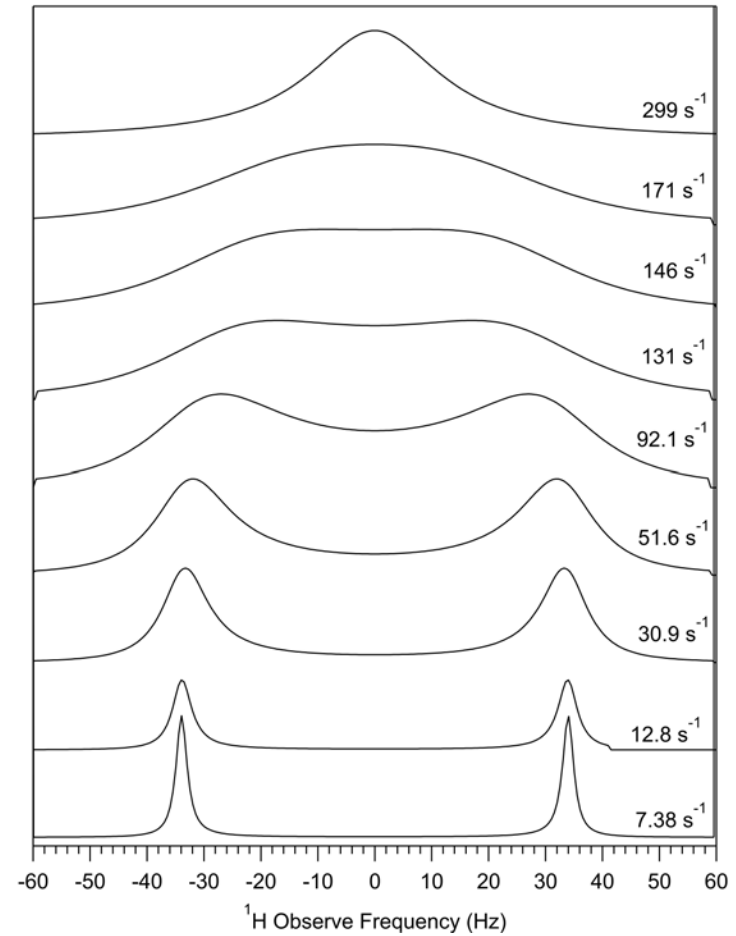
# Experimental & Simulated NMR Spectra

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## Experiment

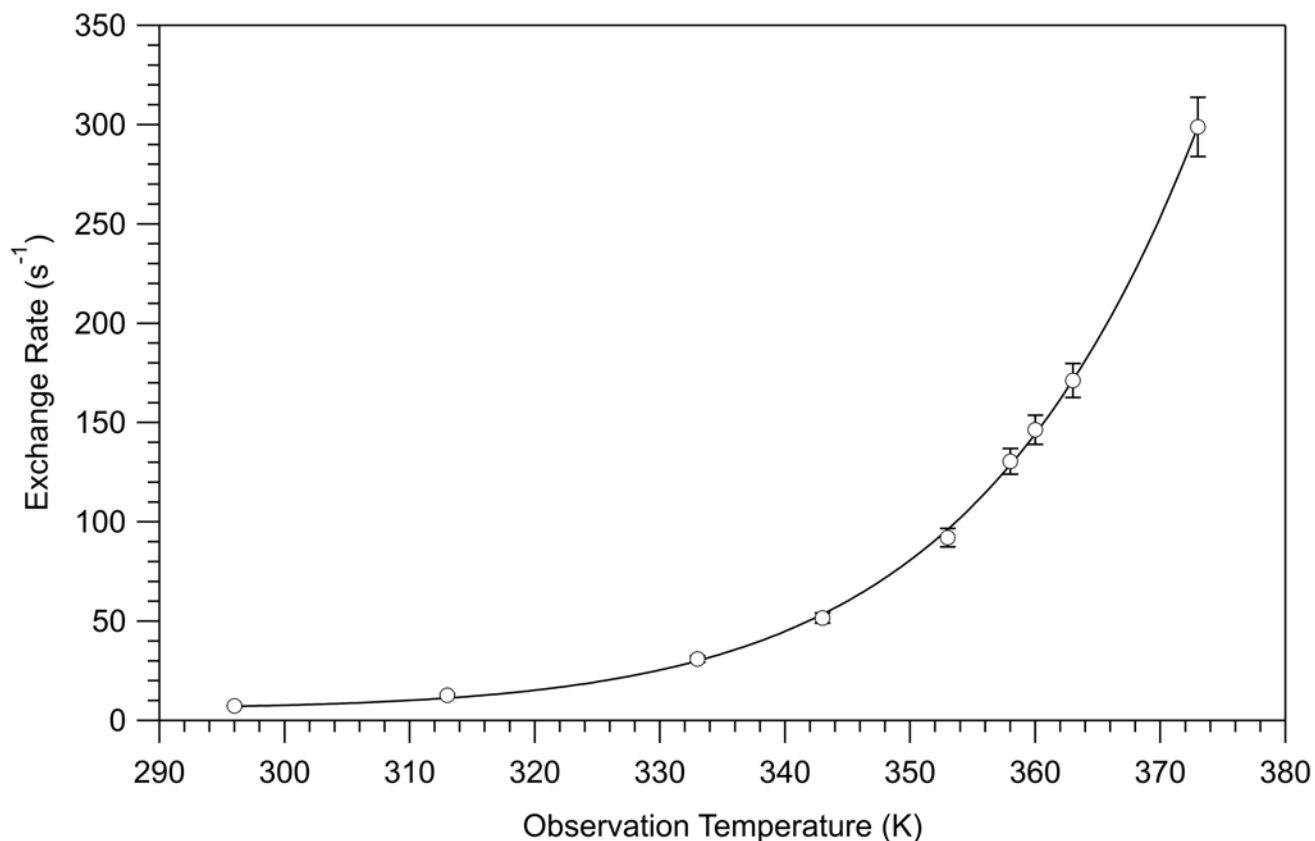


## Simulated



# Arrhenius Plot for Activation Energy

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Experimental:  
 $64370 \pm 3 \text{ kJ mol}^{-1}$

Literature:  
 $70290 \text{ kJ mol}^{-1}$

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

# Acknowledgements

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Professor Tenaya Newkirk for Spectrometer Access

Mr. Ross Gadde for Experimental Technique