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Gas-phase NMR and computations on hydrocarbons in volatile fractions of crude oil

Gerard S. Harbison, University of Nebraska at Lincoln

1. Gas phase spectra and $^1\text{H}/^{13}\text{C}$ chemical shieldings of hydrocarbons

Gas phase proton NMR studies have been dominated by investigations of the chemical shielding, most of which targeted small molecules. Relatively little is known

about larger, still volatile hydrocarbons. Additionally, most gas phase NMR studies have not considered analytical applications, probably because of expectedly broad resonances and low signal-to-noise. In the present work high-resolution spectra were acquired under relatively low-pressure conditions. These results provide shielding measurements useful for direct comparison to computational studies performed in vacuo. More complex spectra involving magnetic inequivalence were better resolved upon the addition of sulfur hexafluoride, which provides significant collisional narrowing.

An example of the quality of the spectra obtained is shown in Fig. 1; a full set of chemical shifts and coupling constants were obtained for *cis*-2-butene, in the low pressure limit. These results are currently being compared to the results of high level quantum calculations.

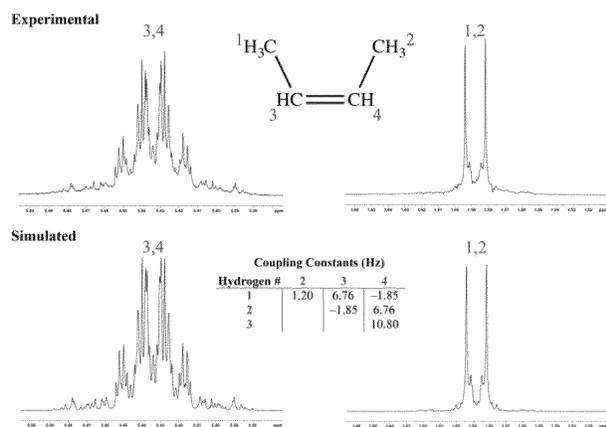


Fig 1: ^1H spectra of *cis*-2-butene

2. Gas Phase NMR of Natural Gas and Volatile Fractions of Crude Oil

Natural gas samples were prepared using a laboratory gas outlet connected to a gas manifold. Valved NMR tubes with an outer diameter of 5 mm were filled with ~ 0.98 bar of natural gas. These samples were analyzed on a 700 MHz spectrometer. Additionally a flow system was constructed to measure natural gas composition *in situ*. This system was installed on a 300 MHz spectrometer with the flow inlet connected directly to a laboratory gas outlet.

Crude oil samples were obtained from the following regions: South Central Texas, Central Texas, Pennsylvania, Colorado, and the Caspian Sea. Raw crude was transferred to a glass vessel, connected to the vacuum manifold, and pumped to remove air in the free spaces. Standard 5 mm NMR tubes were connected to the manifold and evacuated of air, and subsequently placed in a liquid nitrogen vessel. The glass vessel containing the crude sample was heated to 100°C using a water bath. The pressure gauge was monitored during the volatile collection and released gases were condensed in the NMR tube. A small portion of methane was added as an internal reference and the final sample was flame sealed. Among the various crudes, fractionation at 100°C resulted in varied pressures, which is simply a result of different distributions of light hydrocarbons in the crudes. Resulting NMR samples were examined with ^1H and ^{13}C spectroscopy using a 700 MHz spectrometer equipped with a cryo-probe.

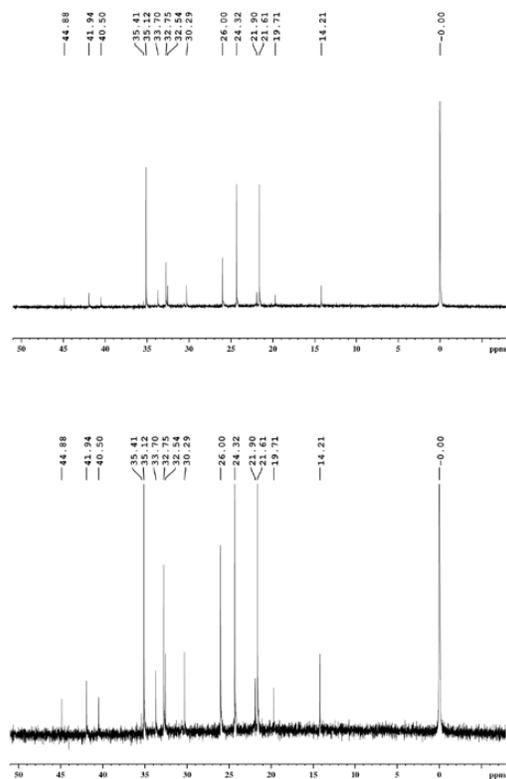


Fig 2: ^{13}C NMR spectra of volatiles from a Colorado crude

This is a representative table of the composition of volatiles from the same crude, compared with one from the Caspian Sea region.

Colorado sample			
Hydrocarbon	Peak	# of C	% v/v
Ethane	9.4044	2	6.39
Propane	30.3270	1	41.2
Iso-butane	6.9378	1	9.43
n-Butane	51.4873	2	34.97
2-Methylbutane	4.8180	1	6.55
n-Pentane	1.0000	1	1.36
Cyclopentane	0.3887	5	0.11

These methods demonstrate the usefulness of gas phase NMR as an analytical method to give insight into the composition of natural gases and various light fractions of crude oils, including minor components such as cyclopentane.

Caspian Sea sample			
Hydrocarbon	Peak Integral	# of C	% v/v
Ethane	1.0000	2	0.5000
Propane	0.7392	1	0.7392
Iso-butane	1.8393	3	0.6131
n-Butane	3.4427	2	1.7214
2-Methylbutane	0.9423	1	0.9423
n-Pentane	0.4413	1	0.4413
Cyclopentane	0.4044	5	0.0809
3-Methylpentane	0.1573	2	0.0787
Cyclohexane	0.2594	6	0.0432
2,2-Dimethylbutane	0.3438	3	0.1146

3. New Enhancements of Quantum Rotor Induced Polarization in γ -Picoline

The bane of gas-phase NMR measurements is sensitivity. Recently, there has been renewed interest in the Haupt effect, an enhancement of the nuclear spin polarization produced through quantum mechanical tunneling of protons in low-barrier methyl rotors, as a result of threefold proton spin states of A and E symmetry. Obviously since methyl groups are ubiquitous in hydrocarbons, such enhancements could be very useful.

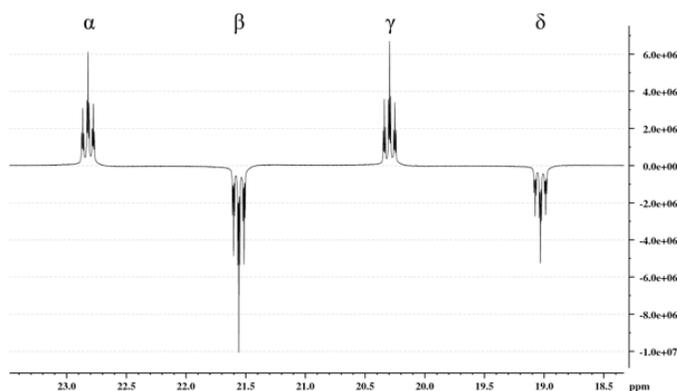


Fig 3: quantum-enhanced ¹³C NMR spectrum of γ -picoline

By working with neat liquids rather than solutions, we were able to obtain enhancements much larger than previously observed. For example, in Fig. 3, we show a single-scan ¹³C NMR spectrum of the methyl region of natural abundance γ -picoline. The enhancement was a factor of 1800 over Boltzmann. Work on achieving polarizations of this magnitude in the gas phase is ongoing.

This project has allowed me to begin experimental studies of gas-phase NMR, and several manuscripts are in preparation. My student, Seth Blackwell, has successfully defended his thesis and graduated, and is currently a postdoctoral at Los Alamos National Laboratory.