Detecting Organic Nitrogen with ^{1}H-^{15}N HMBC Spectra

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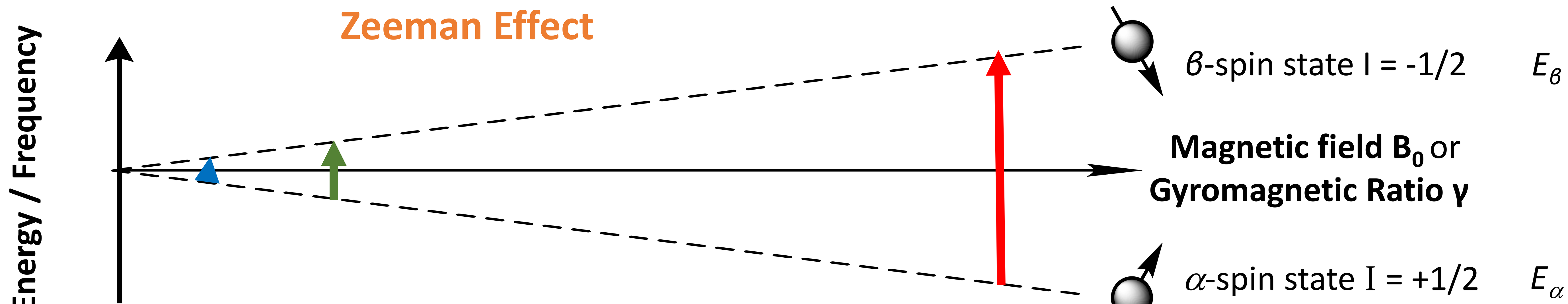
Abstract

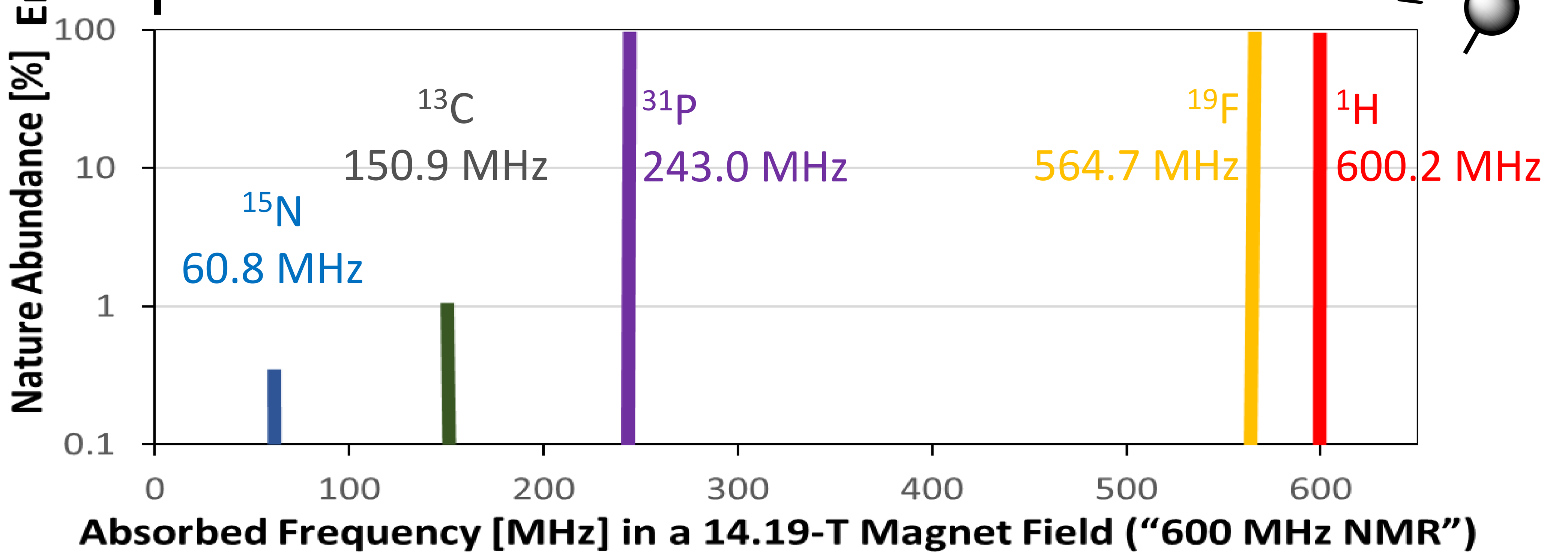
NMR spectroscopy has been the most important tool for the researches in organic/organometallic/polymeric chemistry, providing abundant information for the structure identifications, sample purities, and chemical dynamics. Because of its powerful functions, NMR spectroscopy has also been benefiting the studies of biomedical, pharmaceutical, agricultural, environmental, materials, and even forensic science.

Carbon, hydrogen, oxygen, and nitrogen are the most common elements in organic molecule. However, while ^{1}H and ^{13}C NMR spectra are frequently measured, ^{15}N NMR spectra were relatively rare. This is due to the low gyromagnetic ratio and nature abundance of ^{15}N isotope. Usually ^{15}N NMR spectra were obtained when the sample is in very high concentration or the nitrogen is enriched with ^{15}N isotope, called isotope labelling.

Here we report a very useful method, using HMBC (Heteronuclear Multiple Bond Coherence) experiment to detect ^{15}N NMR signals. HMBC is one of the 2D NMR techniques, measuring the through-bond correlations inside a molecule. ^{1}H-^{15}N HMBC actually collects a series of measurements of ^{1}H NMR spectra. With a series of pulse sequence on ^{15}N channel, the ^{1}H NMR spectra would contain ^{15}N NMR information, called coherence. Therefore, HMBC could take the advantage of ^{1}H NMR signals with stronger intensities than ^{15}N signals, providing the opportunity for the indirect measurement of ^{15}N signals.

Introduction (NMR Principles and the Difficulty of ^{15}N NMR Spectra Measurement)





Energy difference between *α- and β*-spin states ~ radio frequency level

$$E_\beta - E_\alpha = \Delta E = h\nu = \gamma h \mathbf{B_0}/2\pi$$

Nucleus	$\gamma/2\pi$ (MHz.T^{-1})	Nature abundance
^{1}H	42.576	99.98%
^{19}F	40.053	100%
^{31}P	17.235	100%
^{13}C	10.705	1.1%
^{15}N	-4.316	0.4%

Boltzman Distribution: $P_\alpha = \dfrac{e^{-\beta E_\alpha}}{e^{-\beta E_\alpha} + e^{-\beta E_\beta}}$ $1/\beta$ = kT ~ 2.5kJ/mol at 300K >> ΔE ~ 0.24 J/mol at 600 MHz => $\beta\Delta E << 1$

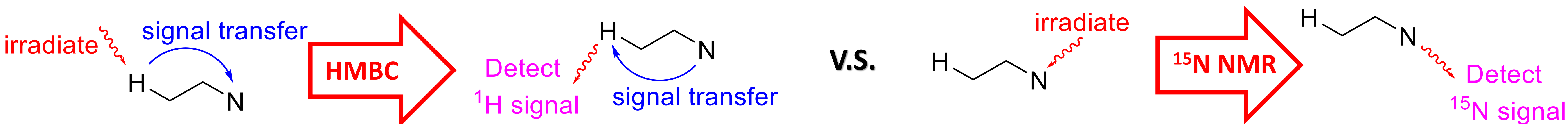
Population difference $P_\alpha - P_\beta = \dfrac{e^{-\beta E_\alpha} - e^{-\beta E_\beta}}{e^{-\beta E_\alpha} + e^{-\beta E_\beta}} \sim \dfrac{\beta \Delta E}{e^{-\beta E_\alpha} + e^{-\beta E_\beta}}$

NMR signal intensity ∝ Population difference ∝ γ
NMR signal intensity ∝ nature abundance

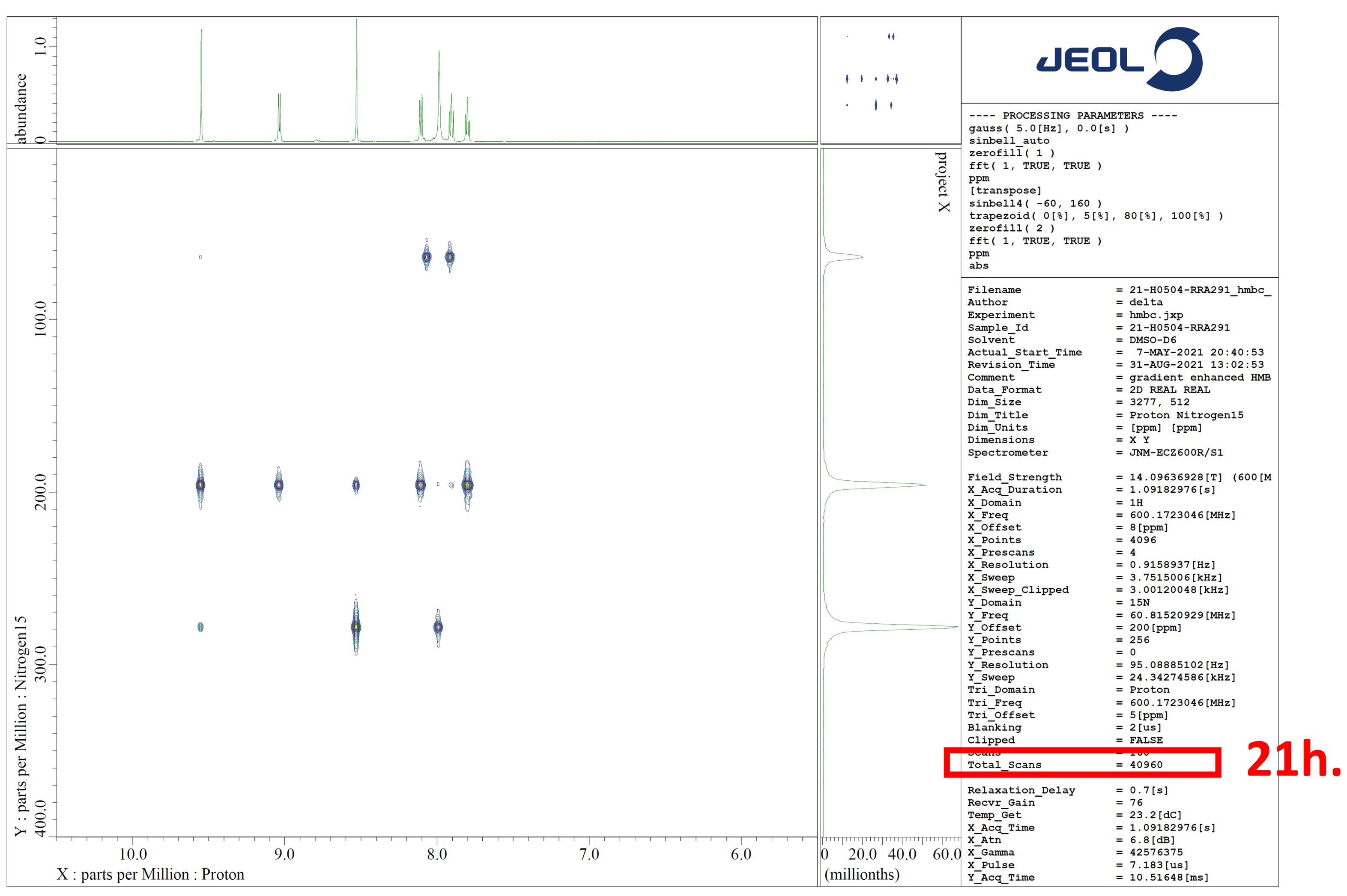
Intensity: ^{15}N NMR signal ~ 1/7 of ^{13}C signal ~1/2466 of ^{1}H signal

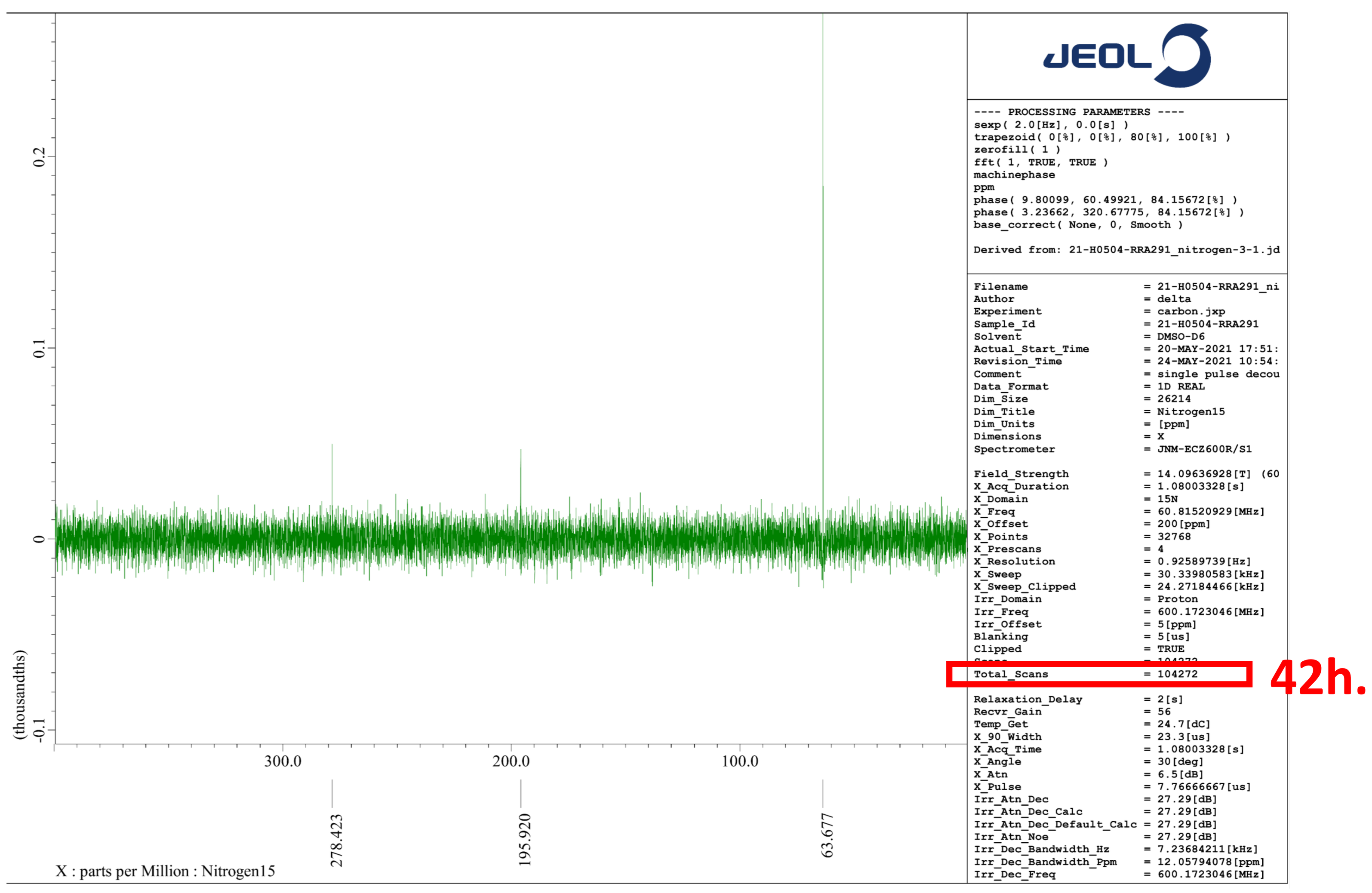
usually requires ^{15}N isotopic labelling

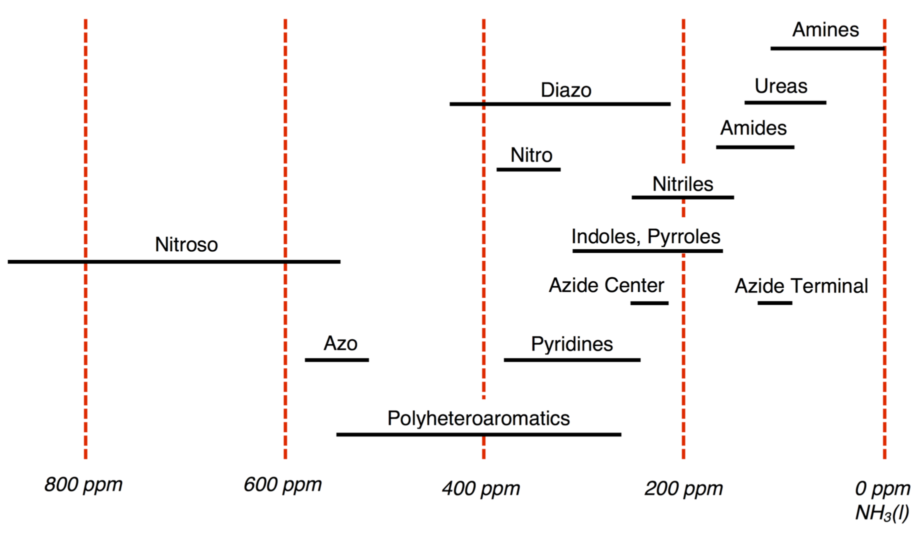
Materials and Methods: ^{1}H-^{15}N HMBC Spectrascopy



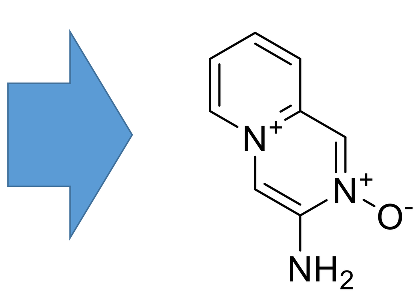
Results







HMBC also tells the information of bond connections.



https://en.wikipedia.org/wiki/Nitrogen-15_nuclear_magnetic_resonance_spectroscopy

Conclusions

- ✓ Direct measurements of ^{15}N NMR spectra are difficult because of low gyromagnetic ratio and nature abundance..
- ✓ HMBC takes the advantage of strong ^{1}H NMR signal, providing opportunities to observe weak signals of heteronuclei.
- ✓ HMBC also provides bond connecting information for structure identification..

Acknowledgements

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