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Two-dimensional NMR correlation experiments in the gas phase

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ABSTRACT

The application of common two-dimensional NMR correlation experiments to gaseous analytes for structural elucidation is reported. Standard sequences such as COSY, HSQC, and HMBC are readily applied to volatile hydrocarbons and fluorocarbons. In experiments using ^{19}F or ^{13}C as the observed nucleus, it is possible to take advantage of efficient spin-rotation relaxation to perform common experiments swiftly (a ^{19}F COSY acquired in 6 s is shown) or to render insensitive experiments possible on a practical timescale (e.g. a gas phase INADEQUATE at natural isotopic abundance in 14 h). NOE-based experiments were not successful on the gaseous systems studied.

1. Introduction

Two-dimensional (2D) NMR correlation experiments for solution-phase analyses have become ubiquitous since their introduction in the 1970s [1,2]. However, most common solution-phase correlation experiments have not been reported with gas-phase systems. The lone exception, to the author's knowledge, comes in the use of a modified HSQC pulse sequence in the determination of spin–spin coupling constants [3,4]. Reports of other multidimensional experiments in the gas phase are comprised of imaging work [5–7], various EXSY experiments [8–10], and the gas-phase DOSY work recently reported by our laboratories [11]. Recent years have seen the scope of gas-phase NMR expand, particularly in the study of chemical reaction kinetics directly inside an NMR probe [12]. In many cases, the reaction systems of interest generate a mixture of products, the spectral interpretation of which is not trivial. For that reason, it is of interest to develop and apply NMR techniques to facilitate the identification of these gaseous species. This study explores the applicability of common correlation experiments, such as would be useful for structural elucidation, to gaseous analytes.

2. Results and discussion

Preparation of gaseous samples suitable for 2D NMR analysis is straightforward. The most general preparatory method is the transfer of volatile species by vacuum line techniques into a standard 5 mm or 10 mm o.d. borosilicate glass NMR tube. Standard tubes can be flame-sealed; as an alternative, tubes fitted with a J. Young-type valve are commercially available. Analytes in a condensed phase can be added *via* pipette or microspatula. Tubes constructed of heavy-walled glass, quartz, or sapphire [13] can be employed when it is necessary to study systems at elevated pressure. However, this is not necessary for most analyses. The concentration of an ideal gas at 1.0×10^5 Pa (1 atm) and 298 K is 41 mM, which is more than sufficient for common ^1H and ^{19}F-detected 2D NMR experiments with modern spectrometers. Unless the analysis is limited by the quantity of sample, no advantage has been observed in restricting the sample to the sensitive volume of the NMR probe. The experiments were generally run without a deuterium field-frequency lock; however, for experiments requiring >1 h, a sealed capillary containing benzene-d_6 was sometimes added to the tube for that purpose.

In ^1H gas-phase NMR spectroscopy of most organic compounds near ambient temperature and pressure, the longitudinal (T_1) and transverse (T_2) relaxation times are similar to those in standard solution-phase spectroscopy. Therefore, many ^1H-detected correlation experiments can be successfully run using acquisition parameters also suited for solution-phase work. Fig. 1 shows COSY, TOCSY, and *J*-resolved spectra acquired on a gaseous mixture of 1-pentene and tetramethylsilane (b.p. 303 K and 301 K, respectively; trace 3-methyl-1-butyne is also visible). The experiments were performed at 303 K in a 16.4 T (700 MHz) system on the headspace of a sealed tube to which small droplets of each analyte had been added. The T_1 relaxation times under these conditions for the resonances associated with 1-pentene ranged from 3.1 s (methyl) to 7.9 s (vinyl H_a); for the tetramethylsilane resonance it was 3.2 s. Heteronuclear correlation experiments were also

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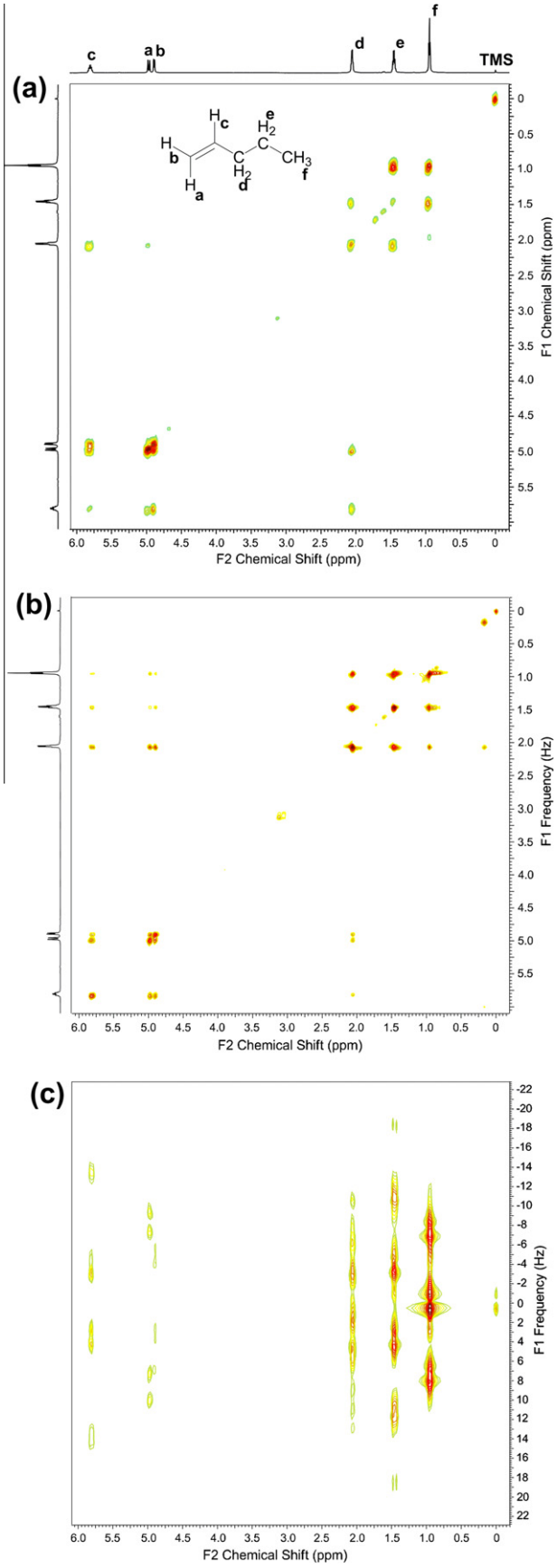

Fig. 1. ^{1}H homonuclear 2D experiments at 700 MHz on gaseous 1-pentene and TMS at their own vapor pressures at 303 K (each ca. 10^5 Pa). (a) COSY, (b) TOCSY, (c) *J*-resolved. 1D spectrum shown along axes. Each spectrum acquired in ca. 1 h.

successful on this sample; Fig. 2 shows its HSQC and HMBC spectra. The acquisition time for each spectrum was ca. 1 h.

The spectra shown in Figs. 1 and 2 were acquired in experiments without gradient coherence selection. Experiments with pulsed-field gradients (PFG) are possible with gaseous analytes, but their rapid translational diffusion renders diffusive signal loss potentially significant. (The diffusion constant for 1-pentene in this sample was determined to 3.4×10^{-6} m^2 s^{-1} at 303 K by a separate DOSY experiment.) This is particularly problematic in heteronuclear correlation experiments like HSQC, HMQC, or HMBC, in which diffusive signal loss occurs during the t_1 evolution period, part or all of which occurs between the gradient pulses that effect the coherence selection. By contrast, in the standard gradient COSY sequence, the t_1 evolution period occurs prior to the application of the PFG, and diffusive loss occurs only over the course of the gradient stabilization time and the width of the second pulse, together typically <1 ms. The signal intensity loss in applying a gradient COSY sequence on the 1-pentene sample using rectangular gradient pulses of 0.10 T/m strength and 1.0 ms duration was ca. 25%. This PFG strength and duration is adequate for coherence selection in most samples. Therefore, if signal intensity is ample (such that diffusive loss is not problematic, and the additional signal from the phase cycle is not needed), one may prefer the intrinsically faster gradient experiment. It is also true that convective flow, rather than translational molecular diffusion, may attenuate the signal in PFG experiments under some experimental circumstances. In our previous work on gas-phase DOSY systems near ambient temperature and pressure [11], it was found that the application of convection-correcting segments to DOSY pulse sequences had only a small effect on the obtained diffusion rates. We therefore concluded that convection has a much smaller effect than diffusion on signal intensity loss in PFG experiments. This conclusion may well be invalid under different conditions of sample pressure and average sample temperature, or with more significant thermal gradients across the sample tube.

^{19}F nuclei in the gas phase experience very efficient spin-rotation relaxation, rendering both the T_1 and T_2 relaxation times very short, typically 10–100 ms for organofluorine compounds at ambient temperature and pressure. This effect allows for very rapid spectral acquisition. Fig. 3a shows the ^{19}F COSY spectrum at 658 MHz of a mixture of 1-chlorononafluorobutane and 1,1,2-trifluoro-2-(trifluoromethoxy) ethene (a.k.a. perfluoromethyl vinyl ether, PMVE), with trace fluorotrichloromethane for referencing (off scale). This 64 increment gradient COSY spectrum was acquired in 6 s. The T_1 relaxation times under these conditions ranged from 48 ms to 149 ms for all resonances. The rapid relaxation to magnetic equilibrium can be advantageously employed in less sensitive experiments to permit rapid signal averaging. A phase-sensitive ^{19}F–^{13}C HSQC spectrum of the same mixture (Fig. 3b) was acquired in 50 min (128 increments, 64 averaged transients per increment), as a 0.15 s recycle delay was sufficient for the system.

^{13}C relaxation times in the gas phase are also much shorter for a given molecule than in ordinary solutions [14]. Therefore, rapid signal averaging enables ^{13}C-detected experiments at natural isotopic abundance at lower molar concentrations than is possible in the solution phase. A striking example of this advantage is given in Fig. 4, which shows the ^{13}C INADEQUATE spectrum of gaseous propene (natural isotopic abundance, present at 0.51 M, which is dictated by its vapor pressure (1.5×10^6 Pa) at 30 °C) acquired in 14 h at 125 MHz. The T_1 relaxation times for propene under these conditions were 0.53 s, 0.43 s, and 2.4 s for the resonances associated with the carbon nuclei labeled a, b, and c, respectively. A 2 s recycle delay was therefore sufficient in the INADEQUATE experiment. While the INADEQUATE experiment is unlikely to be required in the analysis of ordinary gaseous mixtures, the more

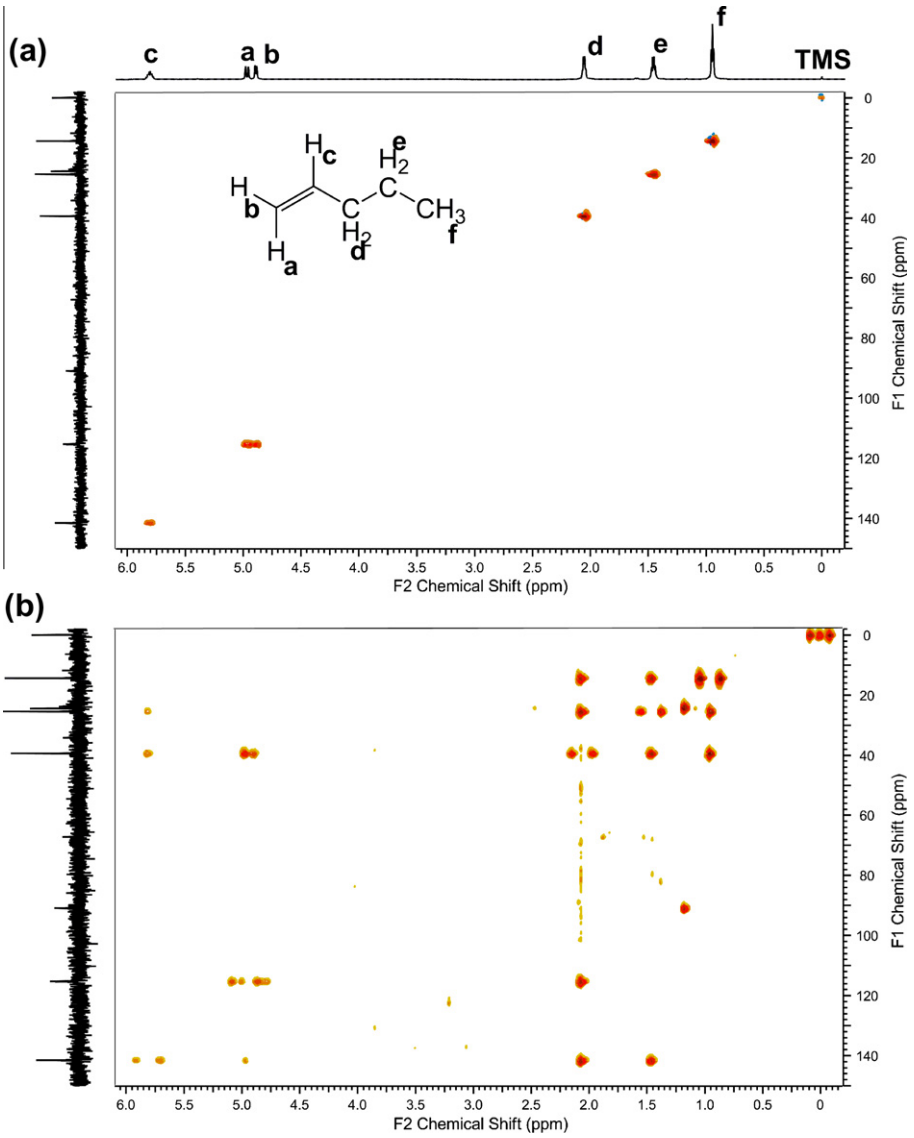

Fig. 2. ^{1}H–^{13}C 2D correlation experiments at 700 MHz on gaseous 1-pentene and TMS at their own vapor pressures at 303 K (each ca. 10^5 Pa). (a) HSQC, (b) HMBC. 1D spectra shown along axes. Each spectrum acquired in ca. 1 h.

sensitive HETCOR experiment may be more important. Fig. 5 shows a ^{13}C–^{1}H HETCOR spectrum of a mixture of ethyl acetate, methylcyclopentane, and TMS, acquired at 373 K in 16 h at 100 MHz. Each analyte was present at 26 mM, yielding an approximate (by the ideal gas law) total internal pressure of 2.3×10^5 Pa (2.3 atm) at the acquisition temperature.

The only common class of 2D NMR experiments which were not successfully applied to gaseous analytes were NOE-based experiments. Given the great efficiency of the spin-rotation relaxation mechanism in ^{19}F and ^{13}C gas-phase NMR, it was not surprising that NOE experiments involving those nuclei were unsuccessful. The T_1 relaxation rates in ^{1}H gas-phase NMR, however, are in general much slower than in ^{19}F or ^{13}C. It was not clear whether spin-rotation relaxation is nevertheless the dominant relaxation mechanism (though less efficient than in ^{19}F or ^{13}C), or whether dipolar relaxation processes might contribute significantly to T_1 relaxation, and thus permit successful ^{1}H NOESY experiments. The latter possibility was not found to be the case. A gaseous mixture of ethylcyclopropane and ethylcyclobutane showed no cross-peaks in a simple ^{1}H NOESY spectrum, save only two miniscule resonances between the methyl and methylene resonances of the respective ethyl groups. NOESY experiments on 1-pentene and other hydrocarbons were likewise unsuccessful, performed with or without a zero-quantum filter, as were the selective 1D variants. Restricting the sample to the sensitive volume of the NMR probe did not yield better results. The failure of NMR techniques that require dipolar relaxation in the gas phase has been reported previously [15]. This may well be to the advantage of gas phase EXSY experiments, which therefore avoid the complications of concomitant NOE correlations.

3. Conclusions

This study demonstrates that common 2D NMR correlation experiments (though not NOESY or its congeners) can be applied with good effect to gaseous analytes. Experiments that directly detect nuclei subject to rapid spin-rotation relaxation, such as ^{19}F or ^{13}C, require less time or offer greater effective sensitivity than what is afforded by solution-phase analyses. Spectra have been obtained with samples at or near ambient pressure, rendering these experiments practical with standard glassware and without the need for extraordinary safety precautions. The detailed structural information obtained on gaseous analytes by these techniques may

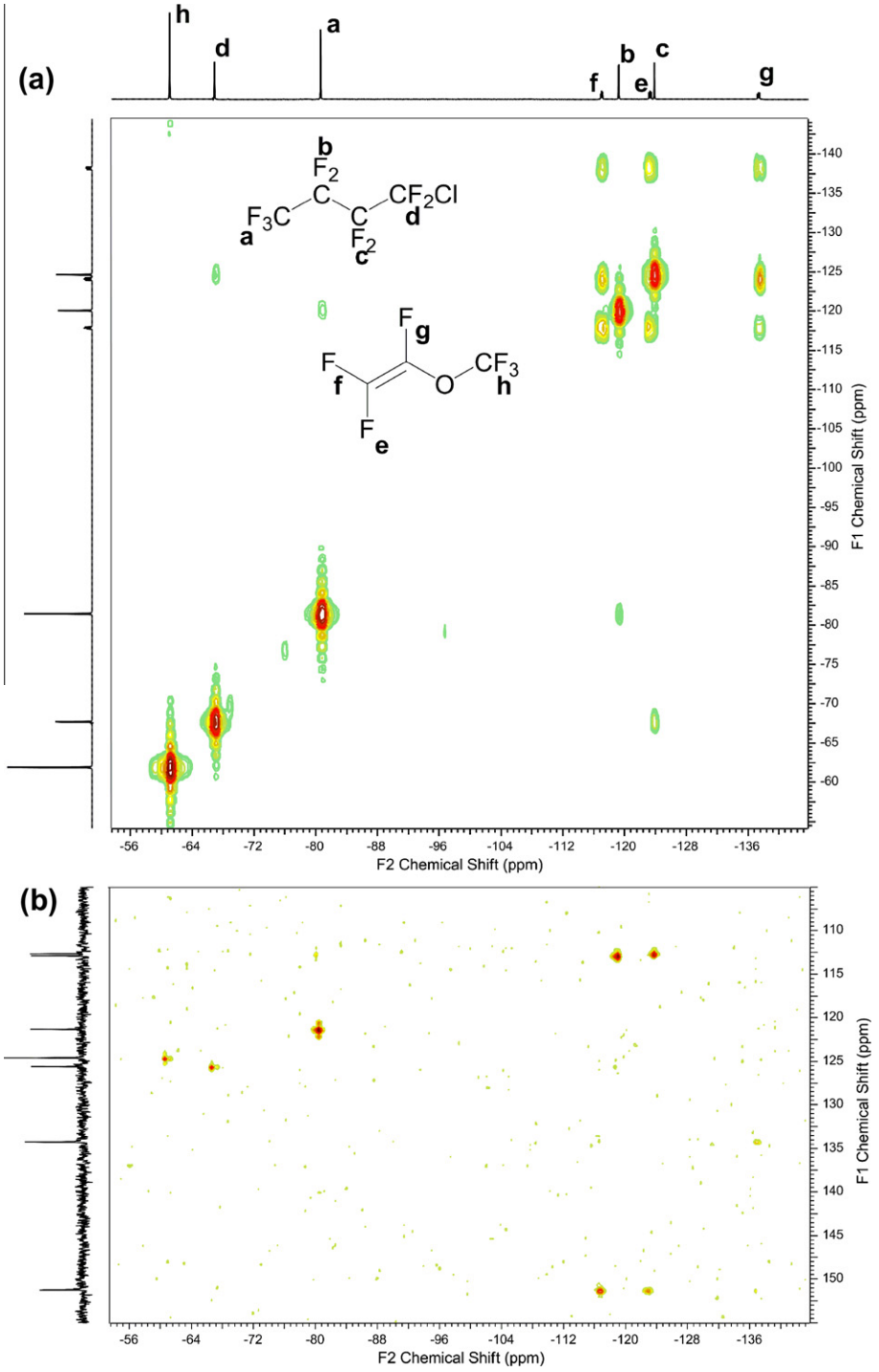

Fig. 3. ^{19}F-detected 2D correlation experiments at 658 MHz on a mixture of gaseous 1-chlorononafluorobutane and 1,1,2-trifluoro-2-(trifluoromethoxy) ethene, each at 1.4×10^5 Pa (1.4 atm) partial pressure at 303 K. (a) ^{19}F gCOSY, acquired in 6 s, (b) ^{19}F–^{13}C HSQC, acquired in 50 min. 1D spectra shown along axes.

serve as a useful complement to GC analyses, or may offer an alternative to gas chromatography for reactive materials not compatible with it. These NMR experiments can also generally be performed over a broad temperature range, advantageous to the study of equilibrium processes or thermally unstable analytes.

4. Experimental

1-Pentene (99% purity), 1-chlorononafluorobutane (99.9% purity), tetramethylsilane (TMS), and fluorotrichloromethane were obtained from Aldrich Chemical Co. Ethyl acetate (99.5+% purity) was obtained from EMD Co. Propene was obtained from the Phillips Co. 1,1,2-Trifluoro-2-(trifluoromethoxy) ethene (purity 99.9+%) was synthesized in-house. Methylcyclopentane was obtained from the former Chemical Samples Co. (Columbus, OH, USA).

The sample of 1-pentene with TMS was prepared by addition of liquid components to a 5 mm medium-walled NMR tube (Wilmad-Labglass Co.) via micropipette. The tube was then immersed in liquid nitrogen, evacuated, and flame-sealed. Sufficient quantities of analyte were added to retain a condensed phase in a small droplet on the bottom of the tube; NMR experiments were performed

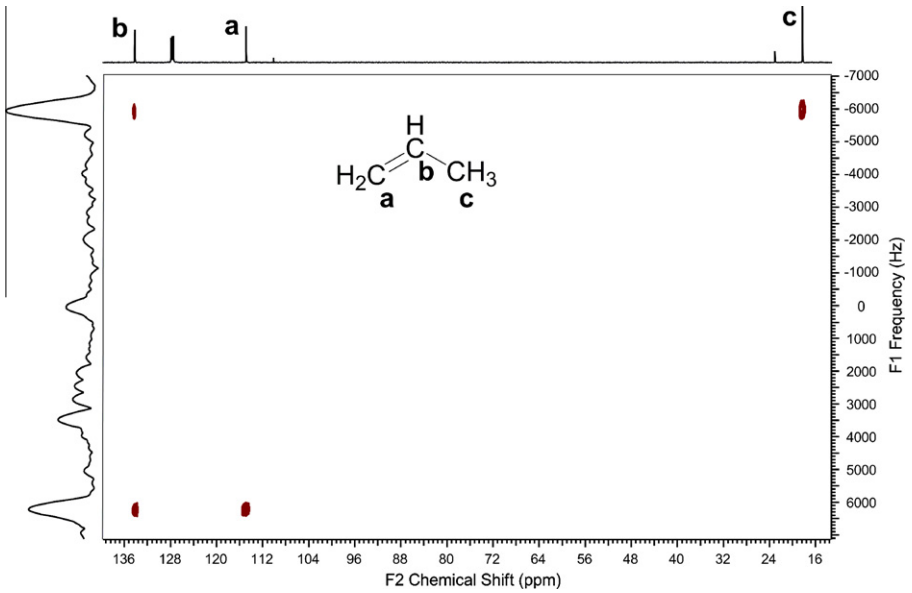

Fig. 4. ^{13}C INADEQUATE spectrum at 125 MHz of gaseous propene at its own vapor pressure (1.5×10^6 Pa) at 303 K. 1D spectrum shown along horizontal axis, projection shown along vertical. Acquisition time was 14 h in a ^{13}C-observe cryoprobe.

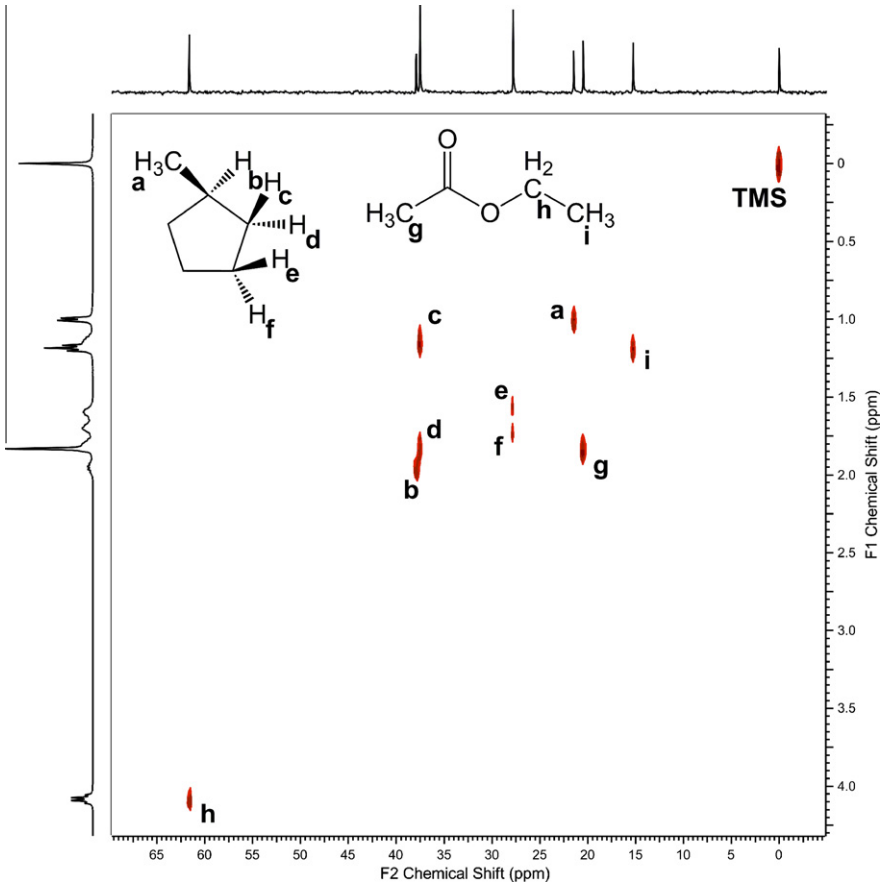

Fig. 5. ^{13}C–^{1}H HETCOR spectrum at 100 MHz of a gaseous mixture of ethyl acetate and methylcyclopentane with TMS, each at 7.9×10^4 Pa (0.78 atm) at 373 K. 1D spectra shown along axes. Acquisition time was 16 h.

on the headspace. The sample of ethyl acetate, methylcyclopentane, and TMS was prepared by addition of 1.00×10^{-4} mol of each liquid component into a short 10 mm o.d. ampule used for gas phase analyses at elevated temperature [7]. The ampule was attached to a vacuum manifold, immersed in liquid nitrogen, evacuated, and flame-sealed.

The sample of 1-chlorononafluorobutane, 1,1,2-trifluoro-2-(trifluoromethoxy) ethene, and fluorotrichloromethane was prepared by vacuum line transfer of the gaseous species into a medium-walled 5 mm NMR tube immersed in liquid nitrogen. The transfer was mediated by a manifold of known volume equipped with a high-precision barometer, such that 1.00×10^4 mol each of 1-chlorononafluorobutane and 1,1,2-trifluoro-2-(trifluoromethoxy) ethene were added. 5.0×10^{-6} mol gaseous fluorotrichloromethane were then added to the tube, which was flame-sealed.

The sample of propene was created by condensation of gaseous propene from a vacuum manifold into a 5 mm medium-walled NMR tube immersed in liquid nitrogen, containing a droplet (ca. 10 μL) of TMS and a droplet (ca. 10 μL) of 1-butene. A sufficient quantity of propene was transferred to result in liquefied propene being present at ambient temperature in the tube. The tube was flame-sealed. The vapor pressure of propene at 303 K is ca. 1.5×10^6 Pa, within the safe operating range of this type of NMR tube.

All spectra were acquired at 303 K except for the HETCOR shown in Fig. 5, which was acquired at 373 K. ^{1}H and ^{13}C spectra were referenced to internal tetramethylsilane (0 ppm). ^{19}F spectra were referenced to internal $CFCl_3$ (0 ppm).

The 1-pentene COSY spectrum (Fig. 1a) was acquired on a Varian VNMRS 700 MHz spectrometer equipped with a 5 mm H,F {C} probe. 256 t_1 increments were acquired, with 8 transients averaged per increment. The acquisition time was 0.15 s, and the recycle delay was 1.5 s. A steady-state gradient-90° pulse-gradient was applied prior to each pulse train to randomize the magnetization. The spectrum was acquired in magnitude mode. The spectral window was 4845 Hz in each dimension. 256 points of forward linear prediction were applied in the F_1 dimension (16 coefficients, 256 point basis set). Squared sine-bell apodization was applied in both dimensions with the Fourier transform. Both dimensions were transformed with 1024 points.

The 1-pentene TOCSY spectrum (Fig. 1b) was acquired on a Varian VNMRS 700 MHz spectrometer equipped with a 5 mm H,F {C} probe. 200 t_1 increments were acquired, with 4 transients averaged per increment. The acquisition time was 0.15 s, and the recycle delay was 1.5 s. A steady-state gradient-90° pulse-gradient was applied prior to each pulse train to randomize the magnetization. The spectrum was acquired in phase-sensitive mode. The spectral window was 4845 Hz in each dimension. The spin-lock was effected with the MLEV-17 sequence applied for 150 ms. Exponential apodization was applied in both dimensions with the Fourier transform (6 Hz in F_2, 10 Hz in F_1). Both dimensions were transformed with 1024 points.

The 1-pentene 2D *J*-resolved spectrum (Fig. 1c) was acquired on a Varian VNMRS 700 MHz spectrometer equipped with a 5 mm H,F {C} probe. 64 t_1 increments were acquired, with 8 transients averaged per increment. The acquisition time was 0.25 s, and the recycle delay was 2.0 s. The spectrum was acquired in phase-sensitive mode. The spectral window was 4845 Hz in the F_2 dimension and 50 Hz in the F_1 dimension. Exponential apodization was applied in the F_2 dimension with the Fourier transform, and sine-bell apodization in the F_1 dimension. The F_2 dimension was transformed with 2048 points, and the F_1 dimension was transformed with 128 points. The spectrum was tilted 45° in the figure.

The 1-pentene HSQC spectrum (Fig. 2a) was acquired on a Varian VNMRS 700 MHz spectrometer equipped with a 5 mm H,F {C} probe. 128 t_1 increments were acquired, with 8 transients averaged per increment. The acquisition time was 0.15 s, and the recycle delay was 1.5 s. A steady-state gradient-90° pulse-gradient was applied prior to each pulse train to randomize the magnetization. The delay time in the INEPT transfer was optimized for 146 Hz coupling. The spectrum was acquired in phase-sensitive mode. A WURST-40 adiabatic broadband ^{13}C decoupling sequence was applied during acquisition. The spectral window was 4845 Hz in F_2 and 29,918 Hz in F_1. 128 points of forward linear prediction were applied in the F_1 dimension (16 coefficients, 128 point basis set). Exponential apodization was applied in both dimensions (6 Hz in F_2, 100 Hz in F_1) with the Fourier transform. Both dimensions were transformed with 1024 points.

The 1-pentene HMBC spectrum (Fig. 2b) was acquired on a Varian VNMRS 700 MHz spectrometer equipped with a 5 mm H,F {C} probe. 128 t_1 increments were acquired, with 8 transients averaged per increment. The acquisition time was 0.15 s, and the recycle delay was 1.5 s. A steady-state gradient-90° pulse-gradient was applied prior to each pulse train to randomize the magnetization. The delay time was optimized for 8 Hz coupling. The spectrum was acquired in phase-sensitive mode. ^{13}C was not decoupled during acquisition. The spectral window was 4845 Hz in F_2 and 29,918 Hz in F_1. 128 points of forward linear prediction were applied in the F_1 dimension (16 coefficients, 128 point basis set). Exponential apodization was applied in both dimensions (6 Hz in F_2, 240 Hz in F_1) with the Fourier transform. Both dimensions were transformed with 1024 points.

The 1-chlorononafluorobutane and 1,1,2-trifluoro-2-(trifluoromethoxy) ethene ^{19}F COSY spectrum (Fig. 3a) was acquired on a Varian VNMRS 700 MHz spectrometer equipped with a 5 mm H,F {C} probe. 64 t_1 increments were acquired, with 1 transient per increment. The acquisition time was 0.010 s, and the recycle delay was 0.050 s. A steady-state gradient-90° pulse-gradient was applied prior to each pulse train to randomize the magnetization. The spectrum was acquired in magnitude mode. The spectral window was 59,524 Hz in each dimension. Rectangular gradient pulses were used for encoding and decoding – 0.10 T/m for 1.0 ms, 0.5 ms recovery time. 8 points of backward linear prediction were applied in the F_2 dimension (8 coefficients, 128 point basis set). Sine-bell apodization was applied in both dimensions with the Fourier transform. Both dimensions were transformed with 1024 points.

The 1-chlorononafluorobutane and 1,1,2-trifluoro-2-(trifluoromethoxy) ethene ^{19}F–^{13}C HSQC spectrum (Fig. 3b) was acquired on a Varian VNMRS 700 MHz spectrometer equipped with a 5 mm H,F {C} probe. 128 t_1 increments were acquired, with 64 transients averaged per increment. The acquisition time was 0.025 s, and the recycle delay was 0.150 s. A steady-state gradient-90° pulse-gradient was applied prior to each pulse train to randomize the magnetization. The delay time in the INEPT transfer was optimized for 270 Hz coupling. The spectrum was acquired in phase-sensitive mode. A WURST-40 adiabatic broadband ^{13}C decoupling sequence was applied during acquisition. The spectral window was 78,125 Hz in F_2 and 10,000 Hz in F_1. 384 points of forward linear prediction were applied in the F_1 dimension (4 coefficients, 128 point basis set). Exponential apodization was applied in both dimensions (20 Hz in F_2, 22 Hz in F_1) with the Fourier transform. The F_2 dimension was transformed with 2048 points, and the F_1 dimension was transformed with 1024 points.

The propene INADEQUATE spectrum (Fig. 4) was acquired on a Bruker Avance 500 MHz spectrometer equipped with a 5 mm ^{13}C {^{1}H} cryoprobe. 64 t_1 increments were acquired, with 384 transients per increment. The acquisition time was 0.10 s, and the recycle delay was 2.0 s. The spectrum was acquired in magnitude mode. Broadband ^{1}H decoupling was effected throughout the acquisition by the WALTZ-16 sequence. The spectral window was 31,447 Hz in the F_2 dimension and 27,669 Hz in the F_1 (double-quantum) dimension. The delay time was optimized for $^1J_{CC}$ = 50 Hz. Squared sine-bell apodization was applied in both dimensions with the Fourier transform. The F_2 dimension was transformed with 4096 points, and the F_1 dimension was transformed with 512 points.

The ethyl acetate and methylcyclopentane ^{13}C–^{1}H HETCOR spectrum (Fig. 5) was acquired on a Bruker Avance DRX 400 MHz

spectrometer equipped with a 10 mm ^{13}C {^{1}H} probe. The spectrum was acquired at 100 °C, at which temperature the analytes were fully vaporized. 64 t_1 increments were acquired, with 800 transients per increment. The acquisition time was 0.125 s, and the recycle delay was 1.00 s. The spectrum was acquired in magnitude mode. Broadband ^{1}H decoupling was effected during acquisition by the WALTZ-16 sequence. The spectral window was 16,340 Hz in the F_2 dimension and 2201 Hz in the F_1 dimension. The delay time was optimized for $^{1}J_{CH}$ = 145 Hz. Squared sine-bell apodization was applied in both dimensions with the Fourier transform. The F_2 dimension was transformed with 2048 points, and the F_1 dimension was transformed with 128 points.

T_1 relaxation times were determined by inversion-recovery experiments.

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References

[1] S. Berger, S. Braun, 200 and More NMR Experiments, third ed., Wiley-VCH, Weinheim, 2004.
[2] T.D.W. Claridge, High Resolution NMR Techniques in Organic Chemistry, second ed., Elsevier Ltd, Oxford, 2009.
[3] M. Wilczek, W. Kozminski, K. Jackowski, ^{15}N, ^{13}C and ^{1}H nuclear magnetic shielding and spin–spin coupling constants of 1-^{13}C, ^{15}N-enriched acetonitrile in gaseous mixtures with SF_6 and CO_2, Chem. Phys. Lett. 358 (2002) 263–270.
[4] E. Wielogorska, W. Makulski, W. Kozminski, K. Jackowski, ^{15}N ^{13}C and ^{1}H nuclear magnetic shielding and spin-spin coupling in gaseous ^{15}N-enriched methylamine, J. Mol. Struct. 704 (2004) 305–309.
[5] D.O. Kuethe, A. Caprihan, E. Fukushima, R.A. Waggoner, Imaging lungs using inert fluorinated gases, Magn. Reson. Med. 39 (1998) 85–88.
[6] R.W. Mair, M.S. Rosen, R. Wang, D.G. Cory, R.L. Walsworth, Diffusion NMR methods applied to xenon gas for materials study, Magn. Reson. Chem. 40 (2002) S29–S39.
[7] M.S. Conradi, B.T. Saam, D.A. Yablonskiy, J.C. Woods, Hyperpolarized ^{3}He and perfluorocarbon gas diffusion MRI of lungs, Prog. Nucl. Magn. Reson. Spect. 48 (2006) 63–83.
[8] M. Tomaselli, B.H. Meier, P. Robyr, U.W. Suter, R.R. Ernst, An rf-driven nuclear spin-diffusion experiment using zero-angle sample spinning, Chem. Phys. Lett. 214 (1993) 1–4.
[9] F. Engelke, S. Bhatia, T.S. King, M. Pruski, Dynamics of hydrogen at the surface of supported ruthenium, Phys. Rev. B 49 (1994) 2730–2738.
[10] C.Y. Cheng, J. Pfeilsticker, C.R. Bowers, Hyperpolarized xenon-129 2D-NMR exchange cross-peak signals in nanotubes by interruption of the gas flow, J. Am. Chem. Soc. 130 (2008) 2390–2391.
[11] A.A.. Marchione, E.F. McCord, Spectral separation of gaseous fluorocarbon mixtures and measurement of diffusion constants by^{19}F gas phase DOSY NMR, J. Magn. Reson. 201 (2009) 34–38.
[12] A.A. Marchione, D.C. Roe, P.J. Krusic, Gas phase NMR for chemical reaction kinetics, in: R.K. Harris, R.E. Wasylishen (Eds.), Encyclopedia of Magnetic Resonance, Wiley Interscience, 2010.
[13] D.C. Roe, Sapphire NMR tube for high-resolution studies at elevated pressure, J. Magn. Reson. 63 (1985) 388–391.
[14] M.M. Folkendt, B.E. Weiss-Lopez, N.S. True, Proton and carbon-13 spin-lattice relaxation in gaseous benzene, J. Phys. Chem. 92 (1988) 4859–4863.
[15] N.S. True, Gas phase studies of chemical exchange processes, in: R.K. Harris, R.E. Wasylishen (Eds.), Encyclopedia of Magnetic Resonance, Wiley Interscience, 2010.