The two additional transient absorptions at 320 and 380 nm are derived from 4-$CH_3OC_6H_4CO_2^\bullet$ since they "grow-in" after the laser pulse at the same rate at which the 720-nm absorption decays. They can therefore be used as "probes"[10] to measure the rate constants for reactions of 4-$CH_3OC_6H_4CO_2^\bullet$, though it is generally simpler to monitor the decay of the 720-nm band. The nature of the radicals responsible for these two transients will be discussed in the full paper.

Measurements of the rate of decay of 4-$CH_3OC_6H_4CO_2^\bullet$ at different (4-$CH_3OC_6H_4CO_2)_2$ concentrations yields both k[PO] and k_0. Any contributions to k_0 from pseudo-first-order reactions is, of course, due to reactions with impurities in the solvent. We obtained values for k_0 of $3.4 \pm 0.1 \times 10^5$ s^{-1} in Aldrich gold-label CCl_4 and ca. 4.4×10^5 s^{-1} in $CF_2ClCFCl_2$. (The latter value is less reliable because of the lower solubility of the peroxide in Freon.) We identify these k_0 values with the decarboxylation process

$$4\text{-}CH_3OC_6H_4CO_2^\bullet \rightarrow 4\text{-}CH_3OC_6H_4^\bullet + CO_2 \qquad (1)$$

Our "best" value for k_1 of 3.4×10^5 s^{-1} at 24 °C is in excellent agreement with a value of 2.7×10^5 s^{-1} at the same temperature which can be calculated from our absolute rate constant for reaction with styrene (Table I) and data given by Bevington et al.[11] for the competition between reaction 1 and the addition of 4-$CH_3OC_6H_4CO_2^\bullet$ to styrene. This agreement provides further confirmation that we have correctly identifed the 4-methoxybenzoyloxyl radical.

We are currently attempting to measure absolute rate constants for reactions of $C_6H_5CO_2^\bullet$ and other aroyloxyl radicals.

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Registry No. H_2, 1333-74-0; 4-methoxybenzoyloxyl, 33574-06-0; cyclohexane, 110-82-7; cyclohexene, 110-83-8; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; triethylsilane, 617-86-7; benzene, 71-43-2; styrene, 100-42-5.

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First Direct Observation of the Simultaneous Presence and of the Interconversion of Chain-Propagating Metal–Carbene and Metallacyclobutane Complexes in a Catalytic Olefin Metathesis Reaction: The Ring-Opening Polymerization of Norbornene

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The central step of the catalytic olefin metathesis reaction is known to consist of the reversible [2 + 2] addition of an olefin to a metal–carbene complex to form a metallacyclobutane compound.[1] Examples of both structural types have been synthesized which effectively catalyze such reactions,[2-7] but, although the propagating metal–carbene[2-6] or metallacyclobutane[7] intermediates derived from these two types of initiators have been observed and even isolated and well characterized in a few cases, their *simultaneous* presence and thus their *interconversion* in the course of a metathesis reaction has never been directly established.

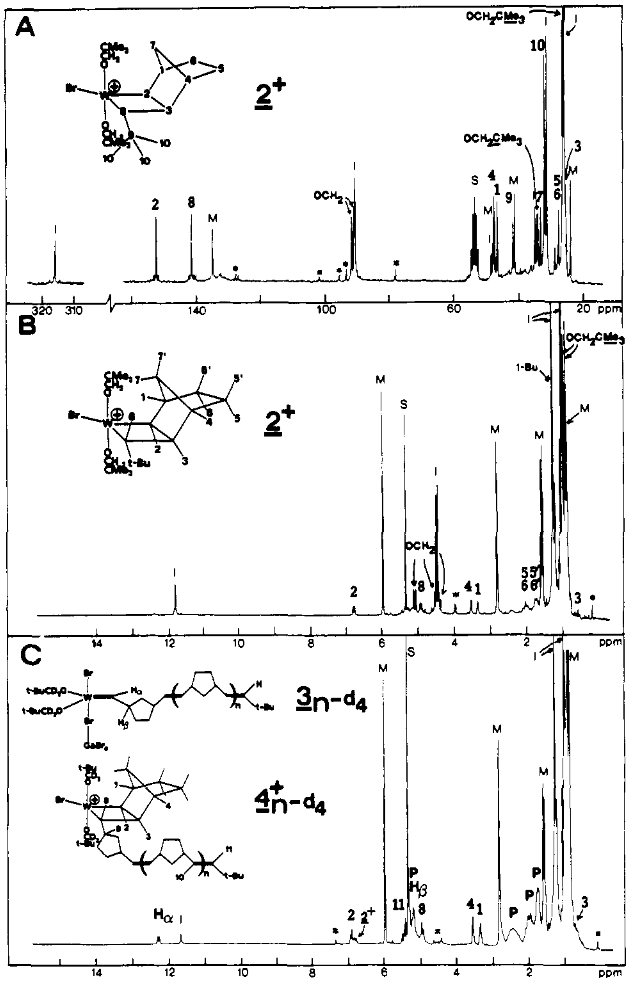

Figure 1. (A) $^{13}C[^1H]$ NMR spectrum, 50 MHz, at 205 K of the reaction mixture obtained after addition of ca. 1.5 equiv of NBE to a solution of 620 mg of W(CH-t-Bu)(OCH$_2$-t-Bu)$_2$Br$_2$·GaBr$_3$ (**1**·GaBr$_3$) at 190 K in 2.0 mL of CD_2Cl_2 and 20 min of average reaction time at 205 K. (B) ^1H NMR spectrum, 200 MHz, at 220 K of the reaction mixture obtained after addition of ca. 2 equiv of NBE to a solution of 10 mg of **1** and 0.7 equiv of $GaBr_3$ at 190 K in 0.4 mL of CD_2Cl_2 and 1 h of reaction time at 220 K. (C) ^1H NMR spectrum, 200 MHz, at 235 K of the reaction mixture obtained after addition of ca. 4 equiv of NBE to a solution of 11 mg of W(CH-t-Bu)(OCD$_2$-t-Bu)$_2$Br$_2$ (**1**-d_4) and 0.9 equiv of $GaBr_3$ at 190 K in 0.4 mL of CD_2Cl_2, 1 h and 30 min of reaction time at 220 K and 30 min of reaction time at 235 K. Peaks arising from residual **1** and NBE monomer, from the solvent, the NBE polymer chain, and from impurities are marked respectively with I, M, S, P, and *.

In the course of our study of the tungsten–carbene compound W(CH-t-Bu)(OCH$_2$-t-Bu)$_2$Br$_2$ (**1**), an extremely active catalyst for the metathesis of olefins in the presence of $GaBr_3$, we reported the observation of the chain carrying tungsten–carbene species derived from **1** on addition of various olefins at room temperature.[2-5] Bicyclo[2.2.1]hept-2-ene (norbornene, NBE), in particular,

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undergoes fast ring-opening polymerization by such a metathesis mechanism (instantaneous solidification of 10^4 equiv of NBE per **1** at 25 °C) and leads to the living polymer $W[{=}CH(C_5H_8)CH{=}(CH(C_5H_8)CH{=})_nCH\text{-}t\text{-}Bu](OCH_2\text{-}t\text{-}Bu)_2Br_2$ by successive insertions of monomer into the metal–carbon double bond.[5]

We now report that the NMR study of the reaction at low temperature allows us for the first time to follow successively (i) the conversion of the initiating metal–carbene complex into the initial metallacyclobutane complex by addition of a first equivalent of olefin, (ii) the orthogonal cleavage of this initial metallacyclobutane to yield the first member of the propagating tungsten carbene complex mentioned above ($n = 0$), and (iii) the formation and interconversion during the metathesis polymerization of the actual propagating metal–carbene and metallacyclobutane species derived from subsequent addition of monomer to this carbene complex.

Following the experimental procedure described in the caption for Figure 1B, an ^1H NMR spectrum of the mixture of **1**, $GaBr_3$, and NBE could be recorded at 200 K before the occurrence of any significant reaction. At 220 K, however, we observe the slow conversion of **1** into mainly one new species identified as the cationic tungstenacyclobutane compound $\mathbf{2}^+GaBr_4^-$ (Figure 1B).[8] It thus appears that the equilibria previously shown to occur for these tungsten–carbene complexes in the presence of $GaBr_3$ ($Ga/W \leq 1$)[3], i.e., $[W] + GaBr_3 \rightleftharpoons [W]\cdot GaBr_3 \rightleftharpoons [W]^+GaBr_4^-$, and arising from the interaction of the Lewis acid with one of the bromo ligands also prevails for the metallacyclobutane analogues. In this latter case, however, the equilibrium is not fully established since only the ionic form is detected, whereas in the carbene series[3] the central adduct is the dominant species. Hence metallacycle formation by addition of olefin to the metal–carbon double bond is accompanied by the loss of Br^- from the coordination sphere, whereas subsequent ring opening of the metallacycle to the carbene and the olefin (vide infra) involves recoordination of Br^-.

A single isomer is observed for $\mathbf{2}^+$ for which the expected trans stereochemistry (see Figure 1B) of the metallacycle was checked by difference NOE.[9] The particularly low field chemical shifts of the two α protons of the metallacycle (6.77 and 4.91 ppm), much lower than those reported for the analogous bis(cyclopentadienyl)titanium compounds,[7] arise probably from the strong Lewis acidity of the tungsten center.

These observations are confirmed by the ^{13}C NMR spectrum of $\mathbf{2}^+$ which could be obtained similarly at 205 K (Figure 1A).[10] The similar low-field displacement (152.4 and 141.6 ppm) of the two C_α signals of the metallacycle is particularly notable as well as the low $^1J_{^{183}WC_\alpha}$ and the high $^1J_{C_\alpha H_\alpha}$ values, the latter confirming clearly the strong electron-withdrawing character of the tungsten in this cationic (10 e) complex. The most probable exo configuration[7,11] depicted in Figure 1A,B could not be confirmed by difference NOE, and we do not know whether the cycle is planar[7] or not.[6]

Upon warming of the reaction mixtures at 235 K (^1H NMR) or 220 K (^{13}C NMR) the concentration of initial tungstenacyclobutane $\mathbf{2}^+\cdot GaBr_4^-$ decreases and two further sets of resonances already slightly apparent at lower temperature develop (Figure 1C obtained from the deuterated derivative $W(CH\text{-}t\text{-}Bu)(OCD_2\text{-}t\text{-}Bu)_2Br_2$ (**1**-d_4)). One set corresponds to the propagating tungsten carbene complexes $\mathbf{3}_n$[12,13] (see Figure 1C) ($^1H_\alpha$ at 12.85 ppm, $^{13}C_\alpha$ at 316.2 ppm for $\mathbf{3}_n\cdot GaBr_3$[9]) already observed at room temperature[5] and resulting from the concomitant cleavage of the metallacycle of mainly $\mathbf{2}^+$ ($\rightarrow \mathbf{3}_0$), but also of the higher homologues $\mathbf{4}_{n-1}^+$ described below (leading to $\mathbf{3}_n$), and reconstitution of the second tungsten–bromine bond. The second set consists of two overlapping spectra, both similar to that of $\mathbf{2}^+$. These correspond to two isomers of the chain-propagating cationic tungstenacyclobutane complexes $\mathbf{4}_n^+GaBr_4^-$ (mainly $\mathbf{4}_0^+$)[13,14] (Figure 1C) resulting from the further addition of 1 equiv of NBE to $\mathbf{3}n\cdot GaBr_3$. We suggest that these two isomers differ in the trans or cis configuration of the metallacyclobutane ring,[14] the *trans* isomer then being preponderant (trans/cis varying from 1.5 to 4 depending on the reaction conditions).

At longer reaction times or higher temperatures, the metallacyclobutane compounds $\mathbf{4}_n^+GaBr_4^-$ slowly disappear in turn and are converted into $\mathbf{3}_{n+1}\cdot GaBr_3$[9], the only final products observed. The overall reaction occurs without loss of either tungsten–carbenes or gallium bromide, in agreement with the living nature of the system.[5]

In some cases, complete polymerization of NBE was achieved before the disappearance of the tungstenacyclobutanes $\mathbf{2}^+GaBr_4^-$ (or $\mathbf{4}_n^+GaBr_4^-$), and we were able to observe their isomerization into $\mathbf{3}_0\cdot GaBr_3$ (or $\mathbf{3}_{n+1}\cdot GaBr_3$) in the absence of norbornene. We cannot say, however, whether cleavage of the metallacycle occurs before coordination of $GaBr_4^-$ or vice versa. Regeneration of compounds $\mathbf{4}_n^+GaBr_4^-$ does not occur on cooling $\mathbf{3}_{n+1}\cdot GaBr_3$ to lower temperature, but homologous $\mathbf{4}_{n+1}^+$ is obtained by addition of further NBE to $\mathbf{3}_{n+1}\cdot GaBr_3$ at 220 K.[15]

The possibility that tungstenacyclobutane compounds $\mathbf{4}_n^+GaBr_4^-$ react with NBE before cleavage to tungsten–carbenes $\mathbf{3}_{n+1}\cdot GaBr_3$ and thus behave as *kinetically distinct propagating species* is under investigation. This would be an alternative to the previous proposition that a metal-carbene species in which the previously formed cis double bond remains coordinated to the metal center may play such a role under some conditions.[11,16]

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[8] ^1H NMR of $\mathbf{2}^+$ (200 MHz, CD_2Cl_2, 220 K) δ 6.77 (d, 1 H, $^3J_{H_2H_3}$ = 9 Hz, H_2), 5.08 (d, 2 H, $^2J_{HH}$ = 12 Hz, $OCH_AH_X + OCH'_AH'_X$), 4.91 (d, 1 H, $^3J_{H_8H_3}$ = 10, $^2J_{WH_8}$ = 10.5 Hz, H_8), 4.51 (d, 1 H, $^2J_{H_AH_X}$ = 12 Hz, OCH_AH_X), 4.39 (d, 1 H, $^2J_{H'_AH'_X}$ = 12 Hz, $OCH'_AH'_X$), 3.51 (s, 1 H, H_4), 3.33 (s, 1 H, H_1), 2.02 (m, 2 H, $H_{5,6}$), 1.76 (m, 2 H, $H_{5',6'}$), 1.27 (s, 9 H, *t*-Bu), 0.95 and 0.89 (s, 9 H, OCH_2*t*-Bu), 0.56 (t, 1 H, $^3J_{H_3H_2} \simeq {}^3J_{H_3H_8}$ = 9.5 Hz, H_3). Difference NOE[9] confirmed these assignments. The identification of $\mathbf{2}^+GaBr_4^-$ is based on following observations: (i) Its formation from **1** occurs with the consumption of 1 equiv of NBE and 1 equiv of $GaBr_3$, but $GaBr_3$ is released during its subsequent conversion into $\mathbf{3}_0\cdot GaBr_3$ (vide infra). These latter observations are deduced from the changes in $GaBr_3/(\mathbf{1} + \mathbf{3}_n)$ ratios shown by the chemical shift variations of **1** or $\mathbf{3}_n$ in the course of the reactions.[3,12] (ii) In contrast to compounds **1** and $\mathbf{3}_n$, the ^1H NMR chemical shifts of this compound do not depend on the Ga/W ratio nor on the nature of the Lewis acid present (cf. v). We thus conclude it not to be an acid–base adduct similar to $\mathbf{1}\cdot GaBr_3$,[3] but a cationic species resulting from the cleavage of a bromide ion to form $GaBr_4^-$. (iii) The metallacyclobutane nature of $\mathbf{2}^+$ is shown by the two doublets at 6.77 and 4.91 ppm and the triplet at 0.56 ppm assigned to the H_2, H_8, and H_3 protons, respectively. Irradiation at 0.56 ppm causes the two doublets to collapse to singlets, whereas irradiation at 6.77 or 4.91 ppm causes the triplet to become a doublet. Satellites due to coupling of the H_α protons with ^{183}W could moreover be seen for H_8, but not for H_2 (but both corresponding ^{183}W–C_α couplings were observed[10]). The signals at 6.77 and 0.56 ppm do not appear when NBE-*2,3*-d_2 is used instead of NBE and the doublet at 4.91 ppm becomes a singlet. (iv) The presence of two unequivalent neopentoxo ligands containing diastereotopic methylenic protons is shown by the two AX quartets observed between 5.1 and 4.3 ppm. These are absent in $\mathbf{2}^+$-d_4 obtained from $W(CH\text{-}t\text{-}Bu)(OCD_2\text{-}t\text{-}Bu)_2Br_2$ (**1**-d_4) and are replaced by two septuplets in $\mathbf{2a}^{+}$[9] obtained from $W(CH\text{-}t\text{-}Bu)(O\text{-}i\text{-}Pr)_2Br_2$ (**1a**). Moreover, irradiation at 5.08 ppm causes both doublets at 4.51 and 4.39 ppm to collapse to a singlet. (v) The presence of at least one bromide ligand is shown by the chemical shift differences observed between $\mathbf{2}^+$ and $\mathbf{2b}^{+}$[9] obtained from $W(CH\text{-}t\text{-}Bu)(OCH_2\text{-}t\text{-}Bu)_2Cl_2$ (**1b**) and $GaCl_3$. The same spectrum is observed with $AlCl_3$ in place of $GaCl_3$.

[9] NMR details are found in the supplementary material.

[10] ^{13}C NMR of $\mathbf{2}^+$ (50 MHz, CD_2Cl_2, gated decoupled, 205 K): δ 152.5 (d, $^1J_{CH}$ = 157, $^1J_{WC}$ = 80 Hz, C_2), 141.6 (d, $^1J_{CH}$ = 143, $^1J_{WC}$ = 70 Hz, C_8), 91.9 and 91.1 ppm (t, $^1J_{CH}$ = 147 Hz, OCH_2), 47.5 (d, $^1J_{CH}$ = 149 Hz, C_4), 46.6 (d, $^1J_{CH}$ = 145 Hz, C_1), 41.9 (s, C_9), 34.4 and 34.1 (s, OCH_2CMe_3), 33.3 (C_7 ?), 32.1 (q, $^1J_{CH}$ = 127 Hz, C_{10}), 27.8 (C_5 or C_6 ?), 26.4 (q, $^1J_{CH}$ = 127 Hz, OCH_2CMe_3), 25.6 (C_3).

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[12] Note that although a single spectrum is observed, this corresponds in fact to the mixture of $\mathbf{3}_n$, $\mathbf{3}_n\cdot GaBr_3$, and small quantities of $\mathbf{3}_n^+GaBr_4^-$ in fast dynamic exchange.[3]

[13] The various species $\mathbf{3}_0$, $\mathbf{3}_1$, $\mathbf{3}_2$, ... and $\mathbf{4}_0^+$, $\mathbf{4}_1^+$, $\mathbf{4}_2^+$, ..., corresponding to the successive steps of the polymerization, are not distinguished by NMR (see also ref 7) and are collectively represented as $\mathbf{3}_n$ and $\mathbf{4}_n^+$, respectively.

[14] ^1H NMR of $\mathbf{4}_n^+$ (200 MHz, CD_2Cl_2, 235 K):[9] major isomer, δ (ppm) 6.92 (d, 1 H, $^3J_{H_2H_3}$ = 10 Hz, H_2), 5.44 (d, 1 H, $^3J_{H_{11}H_{10}}$ = 13 Hz, H_{11}), 4.95 (t, 1 H, $^3J_{H_8H_3} = {}^3J_{H_8H_9}$ = 10 Hz, H_8), 0.74 (t, 1 H, H_3); minor isomer, δ of major isomer with H_2 at 6.87 ppm and H_{11} at 5.47 ppm. ^{13}C NMR of $\mathbf{4}_n^+$ (major isomer) (50 MHz, CD_2Cl_2, ^1H decoupled, 220 K): δ 154.2 (C_2), 134.5 (C_8).

[15] Different systems involving seven other carbene complexes[4] and several other olefins such as 1-MeNBE, 5,5′-Me_2NBE or cyclopentene were also studied and generally led to similar observations.

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Supplementary Material Available: Difference NOE results on $\mathbf{2}^+$; ^{1}H NMR spectra of $\mathbf{2a}^+$, $\mathbf{2b}^+$, $\mathbf{3}_n\cdot$GaBr$_3$, $\mathbf{4}_n{}^+$; and ^{13}C NMR spectra of $\mathbf{3}_n\cdot$GaBr$_3$ (2 pages). Ordering information is given on any current masthead page.

Two-Dimensional Pulse Techniques for Determination of Radio-Frequency Field Strengths and Proton Multiplicities in NMR Spectroscopy

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Heteronuclear multipulse methods range among the most important pulse techniques in modern NMR spectroscopy. These include, for example, two-dimensional (2D) pulse sequences for heteronuclear chemical shift correlation[1-6] or relayed correlation[7-13] spectroscopy and one-dimensional (1D) polarization transfer and editing techniques.[14-18] Common to all these techniques is that radio-frequency (rf) pulses are applied to two nuclear isotopes. Thus, such experiments must be preceded by determinations of the decoupler (usually ^{1}H) and observe rf field strengths.

Observe fields are traditionally calibrated by determining the 180° or 360° pulse widths. Determination of the decoupler rf field strength can be done by various indirect methods[19] which search for zero-crossings of the observed S spin (e.g., ^{13}C or ^{15}N) signal while incrementing the length of decoupler pulses. A very high accuracy can be achieved,[19] but the key experiments (the zero-crossing of S spin signals) are unfortunately associated with low sensitivity.

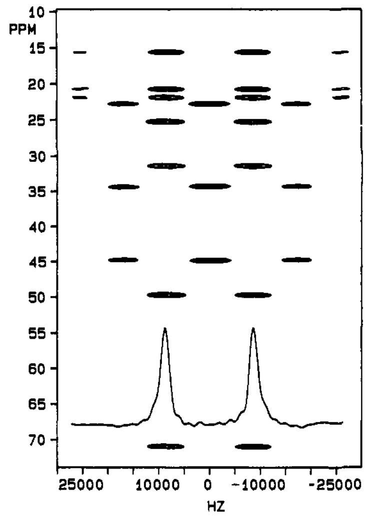

Figure 1. Contour plot (absolute value representation) of a ^{13}C 2D SEMUT spectrum of menthol recorded on a Varian XL-300 NMR spectrometer. A section at 70.8 ppm of a phase-sensitive 2D transformation (zero-filled to 32K points along t_1) is shown as an insert. The decoupler rf field strength determined from such sections of phase-sensitive spectra yields $t_{90}(^1\mathrm{H}) = 29.1 \pm 0.2\ \mu\mathrm{s}$ for all ten ^{13}C multiplets. This value compares favorably with $t_{90}(^1\mathrm{H}) = 28.8 \pm 0.3\ \mu\mathrm{s}$ obtained by the more time-consuming 1D SEMUT method.[19] Instrumental time is 3.2 min.

In this paper we introduce two new 2D pulse techniques for fast and accurate calibration of the decoupler rf field strength. In addition the second method can be extended to include calibration of the observe channel in a way which, compared to the 2D observe channel calibration technique suggested earlier,[20] does not exhibit the disturbing modulation effects observed when relaxation between the individual experiments is incomplete.[21]

The first technique, useful in ^{13}C NMR, is a 2D version of SEMUT:[17,18]

$$\begin{array}{lll} I\,(^1\mathrm{H}): & \text{decouple} & | \;-\tau-\;\; \theta \;\;-\tau'-\text{decouple} \\ S\,(^{13}\mathrm{C}): & & 90^\circ-\tau-180^\circ-\tau-\text{acquire} \end{array} \qquad (1)$$

where the $\theta°$ pulse incremented to constitute the evolution period t_1 of the 2D experiment. τ and τ' should be adjusted to $(2\,^1J_{\mathrm{CH}})^{-1}$; they can be chosen unequal ($\tau' < \tau$) to suppress J cross-talk.[18,19] The resulting 2D spectra have the attractive feature that they contain multiplicity information. C, CH, CH$_2$, and CH$_3$ resonances appear as singlets, 1:1 doublets, 1:2:1 triplets, and 1:3:3:1 quartets, respectively. The line separations in these multiplets are determined by twice the decoupler rf field strength. For a separation of ν Hz, the 90° decoupler pulse time is

$$t_{90}(^1\mathrm{H}) = (2\nu)^{-1} \qquad (2)$$

Figure 1 shows a contour plot of a 2D SEMUT spectrum of menthol along with the section through the high-frequency CH carbon resonance.

To avoid foldings, the ω_1 spectral width must be larger than 6 times the decoupler rf field strength, $\gamma_I B_2/2\pi$ (Hz); for our spectrometer we use increments $\Delta t_1 = 16.7\ \mu\mathrm{s}$, corresponding to about 60 kHz. After the standard t_2 Fourier transformation, the imaginary (dispersive) part is discarded and the t_1 data apodized by using a Lorentzian to Gaussian transformation followed by zero-filling to typically 1024 points. For the sake of generality, a complex Fourier transformation is then applied along t_1 where the real part represents the 2D SEMUT spectrum; for other 2D calibration techniques (vide infra) the 2D spectrum is found as the imaginary part. The number N of t_1 increments determines the accuracy of the calibration. We typically employ $N = 32$ (i.e., $t_1^{\max} = 534\ \mu\mathrm{s}$, which yields an accuracy of about 1% for the 90°

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