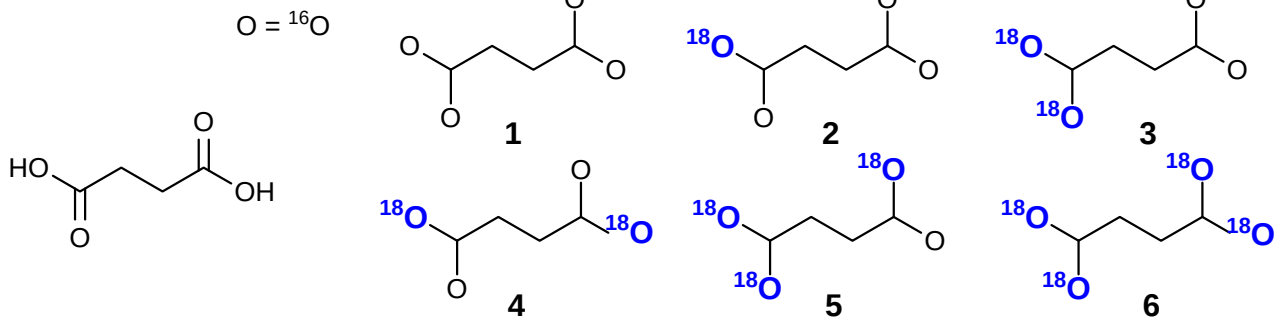
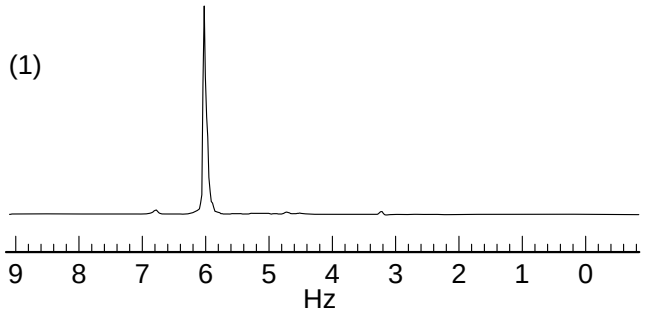
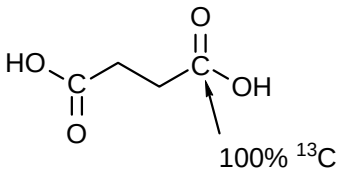
Problem R-09R. Interpret the proton noise decoupled 50.3 MHz ^{13}C NMR spectra of ^{13}C and ^{18}O labelled succinic acid. Only the carbonyl region is shown - the signals appear at δ 176. (Source: Roberts *J. Am. Chem. Soc*. **1993**, *115*, 12056)

There are 6 possible different ^{18}O labelled succinic acids (isotopomers), drawn as compounds 1-6 below. Under the conditions of the NMR experiment, proton/deuterium transfers are fast, so the protons/deuterons are not shown.

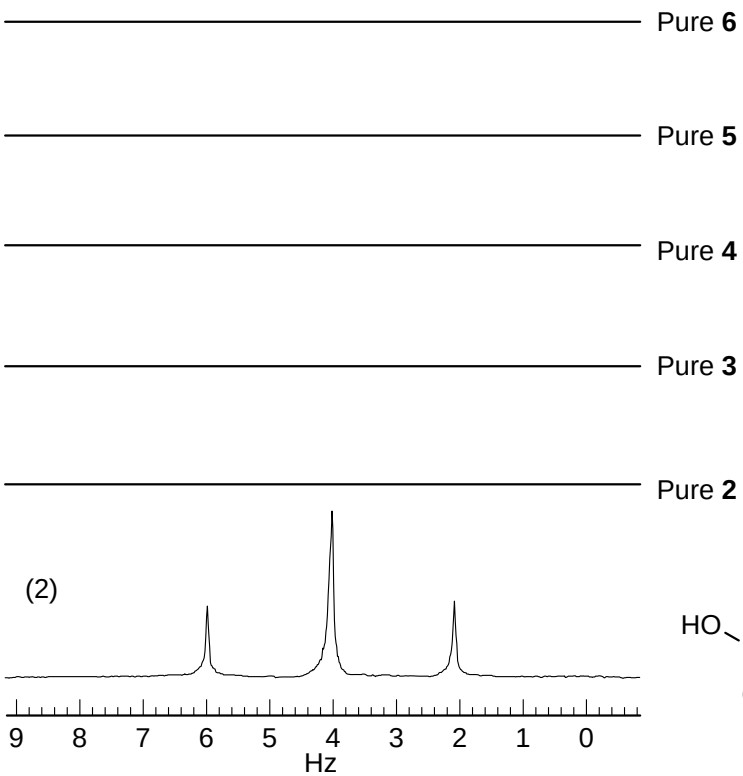


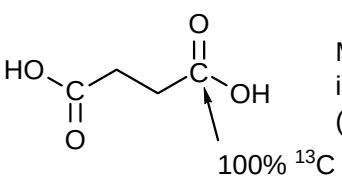
Spectrum (1) shows mono-^{13}C labelled succinic acid with ^{18}O at natural abundance (0.2%) (compound **1**).





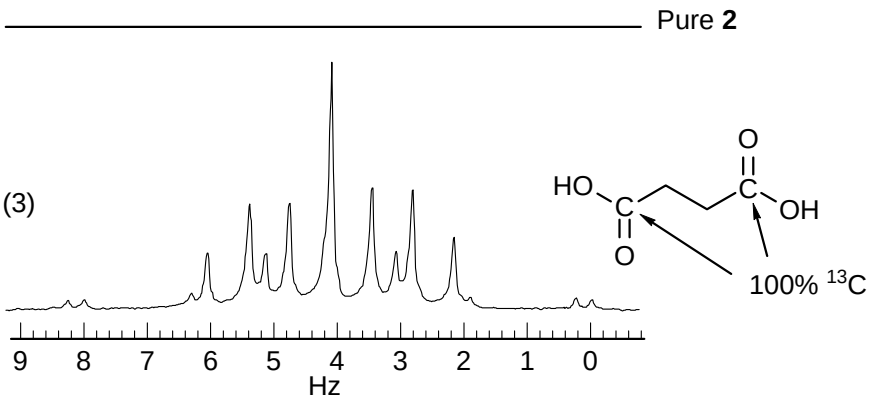
(a) Interpret spectrum (2) reproduced below. This sample was produced by heating a sample of succinic acid in $H_2{}^{18}O$ (ca 52% ^{18}O incorporation) and contains all 6 isotopomers (**1**-**6**). Show you understand the origin of the three peaks by sketching the signals you would expect to see for a sample of each pure isotopomer **2** to **6**.





Mono-^{13}C labelled, after heating in $H_2{}^{18}O$ for some time (mixture of isotopomers **1** to **6**)

(b) The sample for spectrum (3) was prepared similarly to spectrum (2), except that succinic acid was used in which both carboxyl groups are labelled 100% with ^{13}C. To help you get started in your analysis, sketch the spectrum you would expect for a pure sample of isotopomer **2**.



Double ^{13}C labelled,
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(mixture of isotopomers **1** to **6**)

(c) On spectrum (3), mark the peaks which correspond to isotopomers **1**, **2**, **3**, **4**, **5** and **6** by placing numbers on the appropriate peaks (amazingly, there are no superimposed peaks!). Make sure you account for the small peaks (i.e., those at 0.0, 0.3, 2.0, 6.3, 8.0 and 8.3 Hz). Report and identify any coupling constants you can measure.

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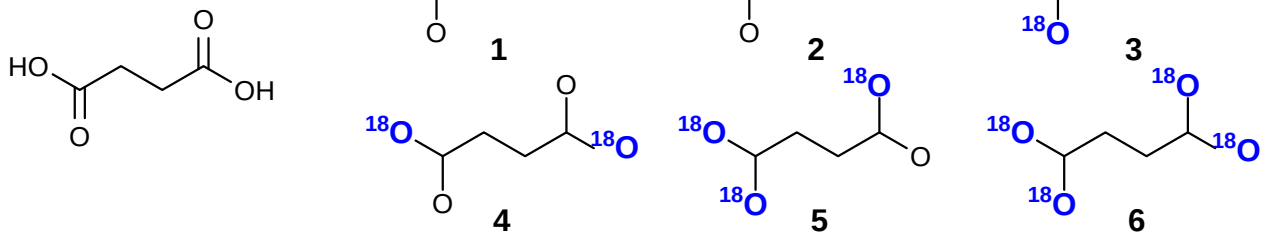

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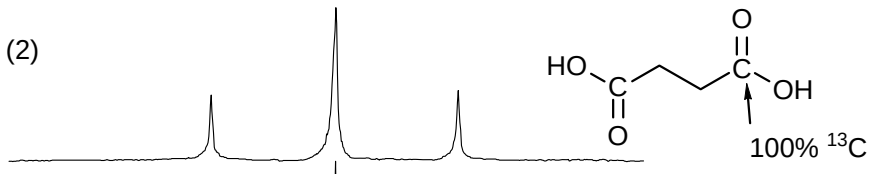

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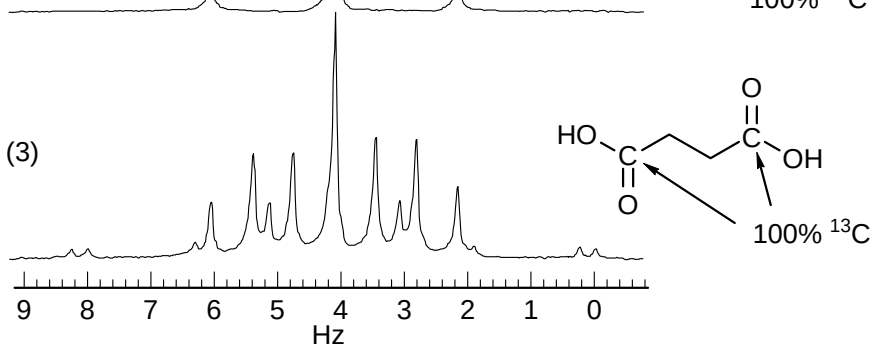

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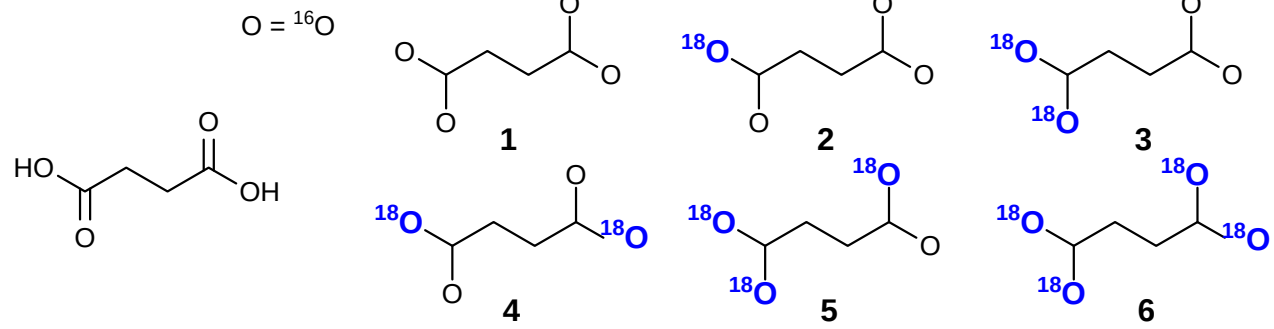

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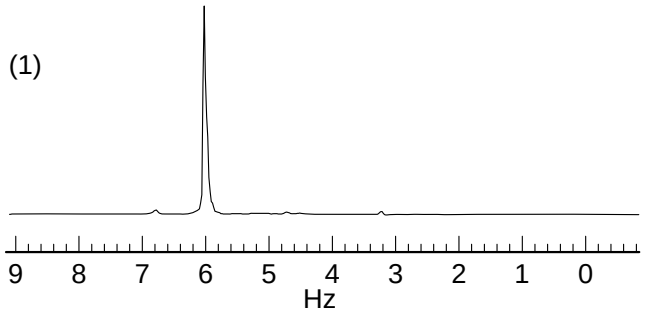
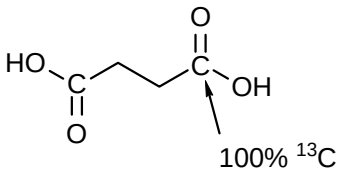
a





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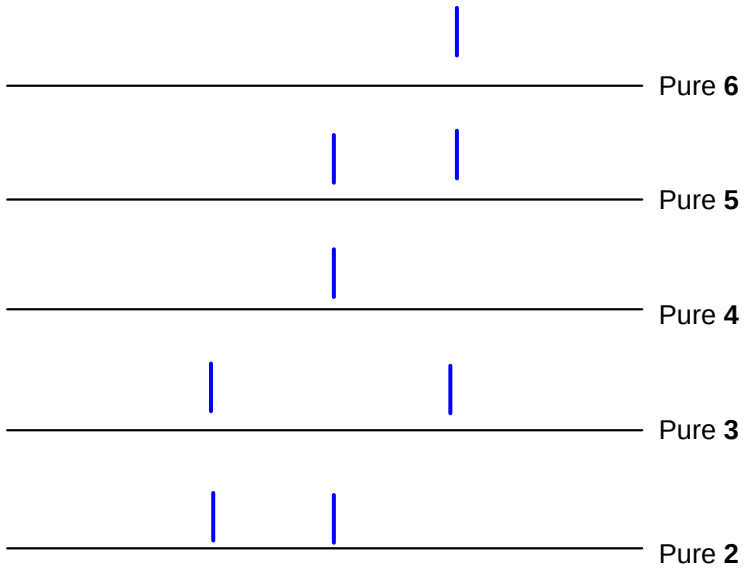

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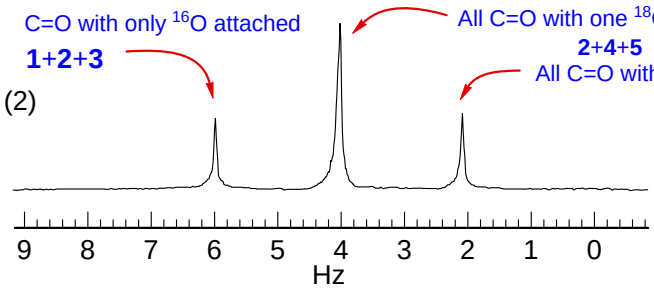
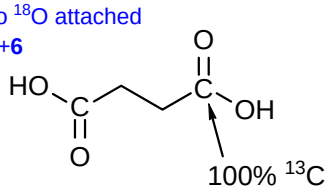
The ^{18}O will be randomly incorporated into both the ^{13}C enriched as well as ^{12}C carboxyl group

There is a one-bond carbon NMR isotope shift of 2 Hz upfield for ^{18}O vs ^{16}O on the observed carbon. The shift is double (4 Hz) if both ^{16}O are replaced by ^{18}O (as in **3**). Substitution on the O of the remote carboxyl group (4-bond isotope shift) has no detectable effect (i.e. the remote caboxyl carbon of **1**, **2** and **3** are superimposed at 6 Hz).





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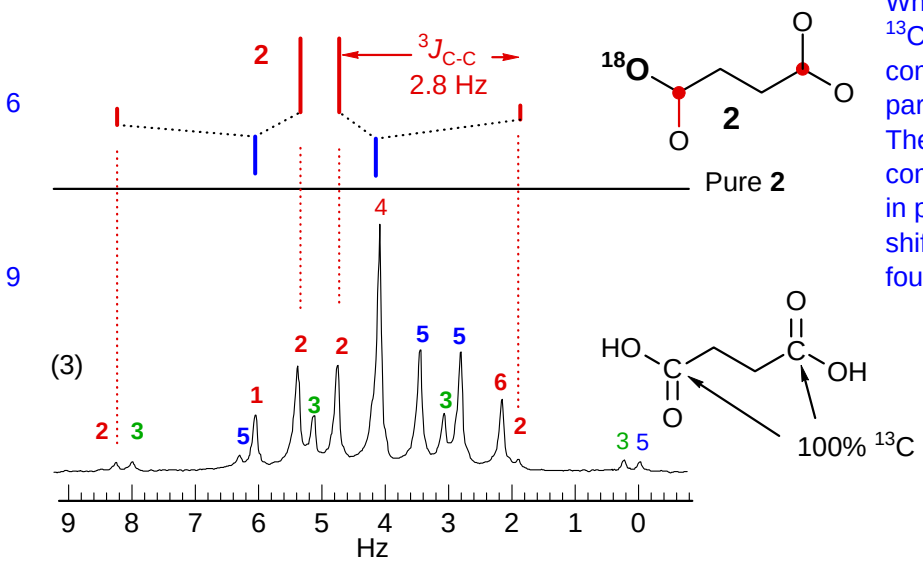

When both carbons are 100% enriched by ^{13}C, then each of the unsymmerically labelled compounds (those that have two peaks in part (a) **2**, **3** and **5**) will form an AB quartet. The $^3J_{CC}$ is 2.8 Hz. The symmetrical compounds (**1**, **4**, **6**) will show a singlet, just as in part (a). The three-bond $^{12}C/^{13}C$ isotope shift is too small to detect, as is the $^{18}O/^{16}O$ four-bond isotope shift on ^{13}C.

Double ^{13}C labelled,
after heating in $H_2{}^{18}O$ for some time
(mixture of isotopomers **1** to **6**)

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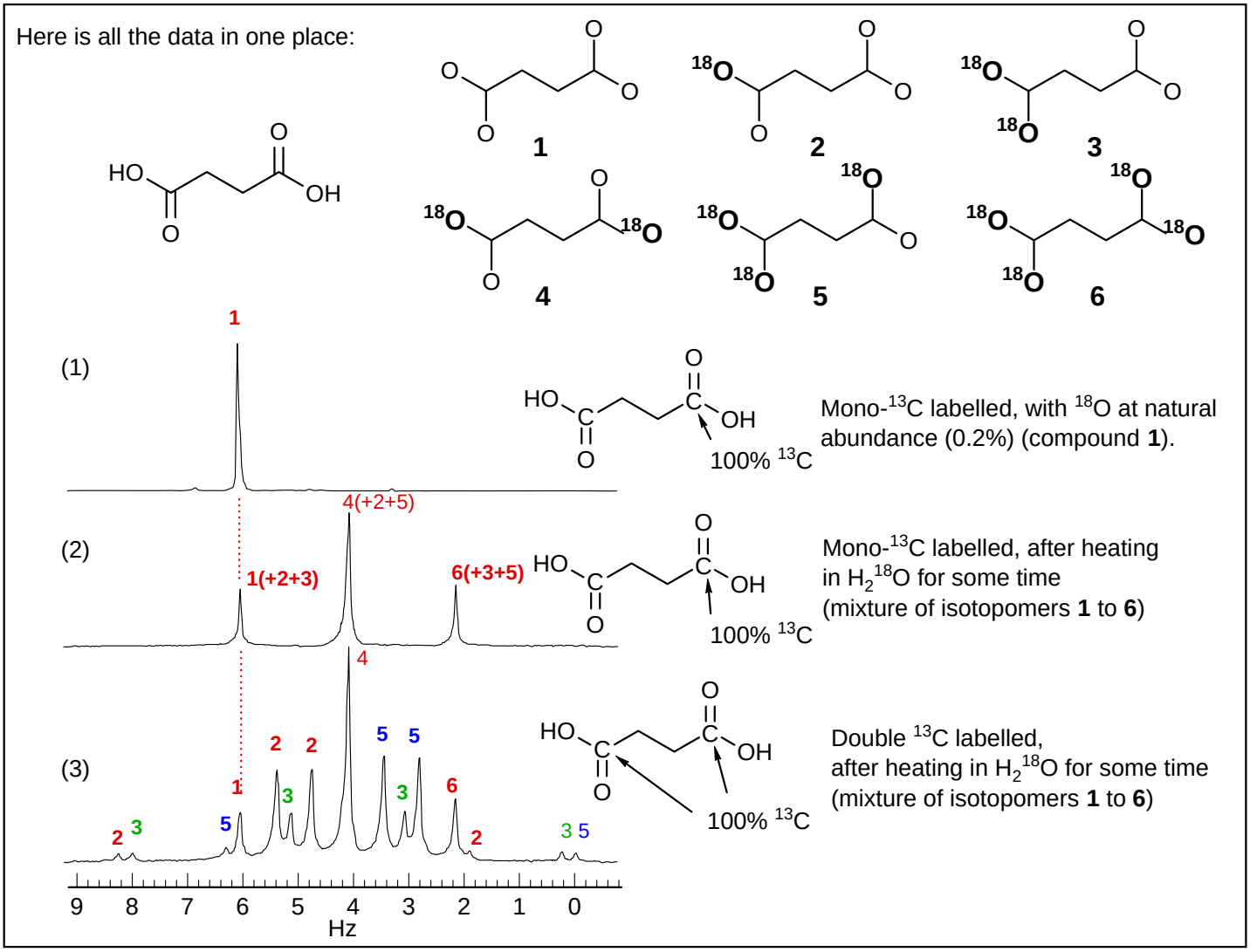

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