Problem R-06L (C_{10}H_8O_3)
200 MHz $^1$H NMR spectrum in CDCl$_3$

A Normal spectrum

B - A Difference spectrum

B Decouple at $\delta$ 6.97 before spectrum taken
Problem R-06L. On the next page are reproduced three spectra of 7-methoxychromanone. Spectrum A is a normal spectrum. Spectrum B was obtained by preirradiating signal c with the decoupler before taking the spectrum. The decoupler was off during the acquisition. The middle spectrum is the difference between the two (B minus A) (MRC 1985, 23, 90).

(a) What kind of experiment is this?

(b) Assign the signals to the appropriate proton (m, J given). Use the numbering given on the figure.

\[
\begin{align*}
  a & \text{ d, 9.3} \\
  b & \text{ d, 5.9} \\
  c & \text{ dd, 9.3, 2.7} \\
  d & \text{ d, 2.7} \\
  e & \text{ d, 5.9} \\
  f & \text{ s}
\end{align*}
\]

(c) Explain why signal c disappears in Spectrum B and is negative in Spectrum B-A.

(d) Explain why Spectrum B-A has positive signals for a and f, but not for any of the others (these signals are 30% and 2.3%, respectively, of the corresponding signals in Spectrum A).

(e) Why is the increase in signal f so small compared to the increase in signal a?

(f) Irradiation of signal d causes a 3.1% increase in signal f. What does this tell you about the conformation of the methoxy group?
Problem R-06L. On the next page are reproduced three spectra of 7-methoxychromone. Spectrum A is a normal spectrum. Spectrum B was obtained by preirradiating signal $c$ with the decoupler before taking the spectrum. The decoupler was off during the acquisition. The middle spectrum is the difference between the two (B minus A) (MRC 1985, 23, 90).

(a) What kind of experiment is this? Homonuclear NOE (1D NOESY)

(b) Assign the signals to the appropriate proton (m, J given). Use the numbering given on the figure.

\[
\begin{align*}
a & \quad d, 9.3 \quad \text{H}^5 \\
b & \quad d, 5.9 \quad \text{H}^2 \\
c & \quad d, 9.3, 2.7 \quad \text{H}^6 \\
d & \quad d, 2.7 \quad \text{H}^8 \\
e & \quad d, 5.9 \quad \text{H}^3 \\
f & \quad s \quad \text{OCH}_3
\end{align*}
\]

(c) Explain why signal $c$ disappears in Spectrum B and is negative in Spectrum B-A.

The signal $c$ has been saturated by the decoupler ($\alpha$ and $\beta$ states equal population), hence no signal. Subtracting A (normal intensity) from B gives a negative peak for B-A.

(d) Explain why Spectrum B-A has positive signals for $a$ and $f$, but not for any of the others (these signals are 30% and 2.3%, respectively, of the corresponding signals in Spectrum A).

The $a$ and $f$ signals are enhanced in intensity in spectrum B by the NOE effect from signal $c$. NOE effects are observed only for protons close in space to the irradiated proton ($c$). Thus $c$ must be close in space to $a$ and $f$.

(e) Why is the increase in signal $f$ so small compared to the increase in signal $a$?

Three reasons:

1. The protons in the methyl group principally relax each other, H$_6$ is thus a minor contributor to the total relaxation of the CH$_3$ protons.

2. The methyl group is partially relaxed by both protons H$_6$ and H$_8$ so either one of them can only contribute a smaller part.

3. Methyl groups often show substantial contributions from SR (Spin-Rotation) relaxation ($\tau_c$ is too short for effective DD relaxation). Only the fraction of relaxation caused by the DD mechanism contributes to the NOE.

(f) Irradiation of signal $d$ causes a 3.1% increase in signal $f$. What does this tell you about the conformation of the methoxy group?

2.3% NOE (H$_6$ -> Me)  3.1% NOE (H$_8$ -> Me)

Probably a little more of this conformation