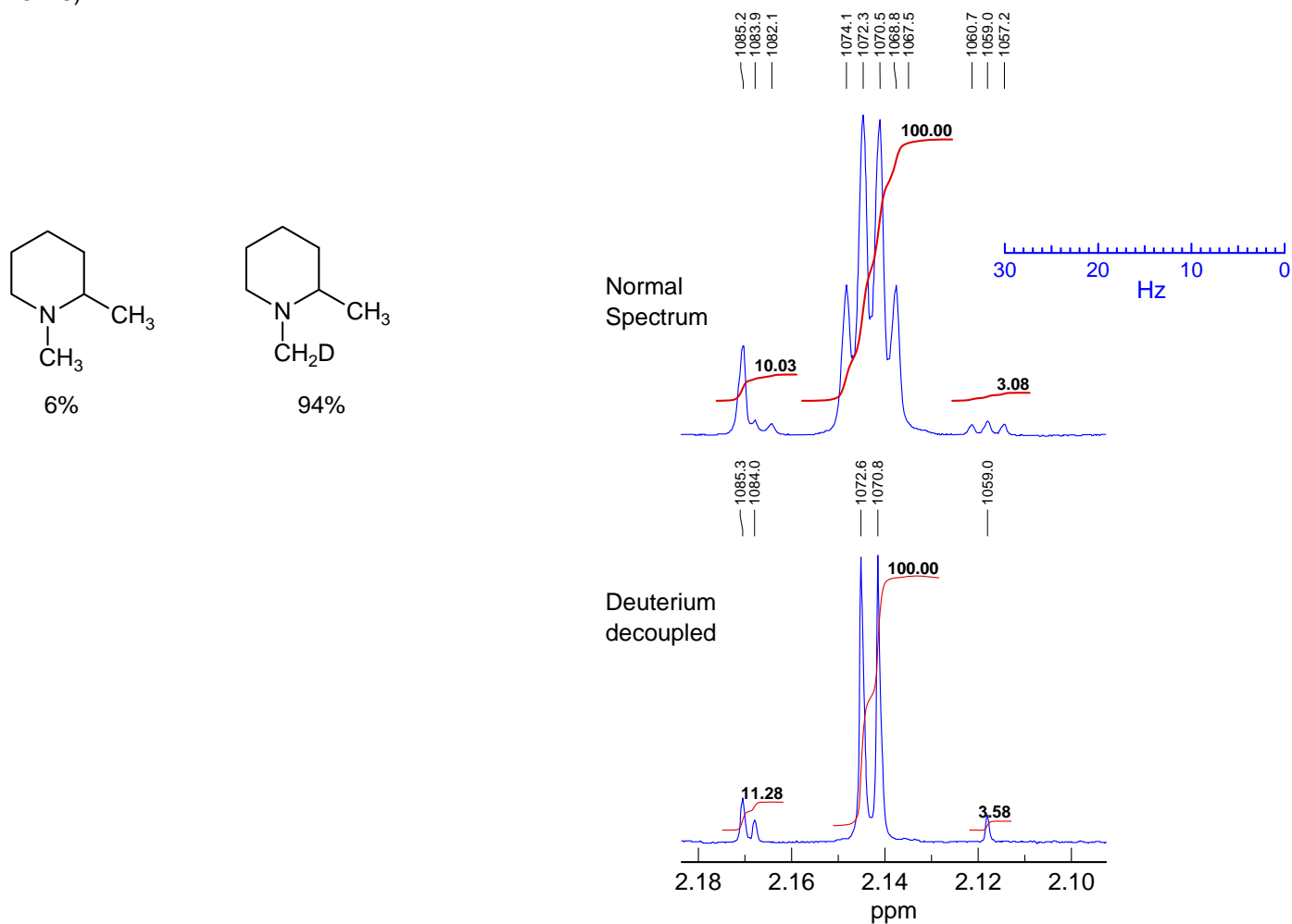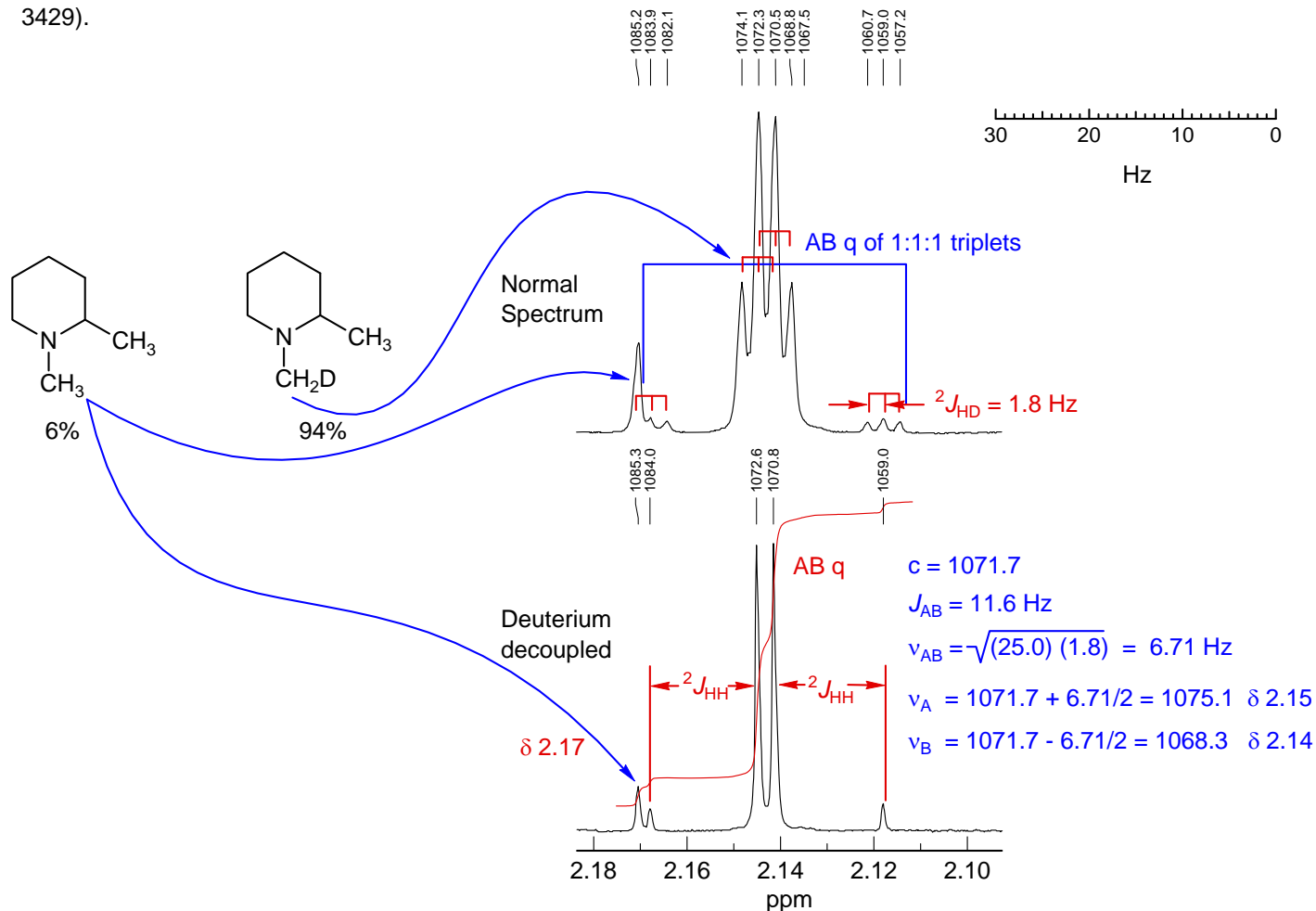**Problem R-13D**. ($C_7H_{15}N$) This problem requires you to interpret the partial 500 MHz ^{1}H NMR spectrum of a 1,2-dimethylpiperidine deuterated 94% on the N-methyl group (source: F. A. L. Anet *J. Am. Chem. Soc.* **1989**, *111*, 3429).

Normal Spectrum

1085.2 1083.9 1082.1

1074.1 1072.3 1070.5 1068.8 1067.5

1060.7 1059.0 1057.2

100.00

10.03

3.08

30   20   10   0
Hz

Deuterium decoupled

1085.3 1084.0

1072.6 1070.8

1059.0

100.00

11.28

3.58

2.18   2.16   2.14   2.12   2.10
ppm

6%

94%

N—CH$_3$
CH$_3$

N—CH$_3$
CH$_2$D

Identify all of the peaks in both the top and bottom spectra. Briefly explain the pattern, extract all coupling constants and determine exact chemical shifts, and report them in the standard format (e .g., δ 3.44, t, $^nJ_{xy}$ = 3.5 Hz).

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1070.5
1068.8
1067.5

1060.7
1059.0
1057.2

30   20   10   0

Hz

AB q of 1:1:1 triplets

Normal
Spectrum

$^2J_{HD}$ = 1.8 Hz

6%   94%

1085.3
1084.0

1072.6
1070.8

1059.0

AB q

c = 1071.7

J_{AB} = 11.6 Hz

$\nu_{AB} = \sqrt{(25.0)\,(1.8)} = 6.71$ Hz

ν_A = 1071.7 + 6.71/2 = 1075.1   δ 2.15

ν_B = 1071.7 - 6.71/2 = 1068.3   δ 2.14

Deuterium
decoupled

$^2J_{HH}$ $^2J_{HH}$

δ 2.17

2.18   2.16   2.14   2.12   2.10

ppm

Identify all of the peaks in both the top and bottom spectra. Briefly explain the pattern, extract all coupling constants and determine exact chemical shifts, and report them in the standard format (e .g., δ 3.44, t, $^nJ_{xy}$ = 3.5 Hz).

3   · The signals we are looking at are the N-CH$_3$ protons (δ 2.17) and the N-CH$_2$-D protons (2.11-2.17). Note the upfield isotope shift for D.

3   · In the deuterium decoupled spectrum the singlet at δ 2.17 is N-<u>CH$_3$</u>

9   · In D-decoupled the AB quartet centered at δ 2.14 is the N-CH$_2$-D group. The CH$_2$ group is diastereotopic (there is an asymmetric center at C-2) and so forms an AB quartet.

$^2J_{AB}$ = 11.7 Hz, δ_A = 2.15, δ_B = 2.13

3

· Normal spectrum: each peak of the AB quartet is split into a 1:1:1 triplet by coupling to D. $^2J_{HD}$ = 1.8 Hz

View

one of these is disfavored slightly