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ANALYTICAL CHALLENGE

Solution to trifluoroacetic acid NMR challenge

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The winner of the trifluoroacetic acid NMR challenge (published in volume 413 issue 1) is:

Irina Ihnatenko, Technische Universität Braunschweig, Germany.

The award entitles the winner to select a Springer book of their choice up to a value of €100,-.

Our Congratulations!

In a previous Analytical Challenge about phosphine [1, 2], we saw that isotopic labeling brings a new level of complexity to NMR spectra of simple substances. The trifluoroacetic acid NMR challenge [3] invites readers to further explore this aspect of analytical chemistry. To understand the ^{19}F-NMR spectrum of carbon-13 labeled trifluoroacetic acid (TFA), one has to consider all the interactions that fluorine-19 atoms can have with carbon-13 atoms, both of which have a non-zero nuclear spin, $I = ½$.

In TFA having only carbon-12 atoms, $F_3[^{12}C][^{12}C]OOH$, the three equivalent fluorine atoms have no neighboring atoms of non-zero nuclear spin. Thus, such a molecule will display a single resonance with chemical shift in the vicinity of −76 ppm (relative to $CFCl_3$). In the singly labeled TFA, $F_3[^{13}C][^{12}C]OOH$, however, fluorine atoms will interact with the single adjacent carbon-13 giving rise to a doublet with a wide coupling constant ($^1J_{FC} = 285$ Hz) as shown in Fig. 1. Similarly for the other singly labeled TFA, $F_3[^{12}C][^{13}C]OOH$, fluorine atoms will interact with carbon-13 two bonds away, leading to a doublet albeit with much smaller coupling constant ($^2J_{FC} = 45$ Hz) [4]. These two NMR spectra are depicted in Fig. 2.

Finally, in the doubly labeled TFA, $F_3[^{13}C][^{13}C]OOH$, fluorine atoms will interact with both cabon-13 atoms. First, the three equivalent fluorine atoms are coupling with the adjacent carbon-13 atom giving rise to a wide doublet ($^1J_{FC}$). But, in addition, this doublet is further split into doublets because the same fluorine atoms also interact with the distant carbon-13 atom ($^2J_{FC}$) [5]. The result of this double splitting leads to a doublet of doublets with a wide first split and a much narrower second split as shown in Fig. 2 (corresponding to Fig. 1A of the trifluoroacetic acid NMR challenge [3]).

This article is the solution to the Analytical Challenge to be found athttps://doi.org/10.1007/s00216-020-02867-3

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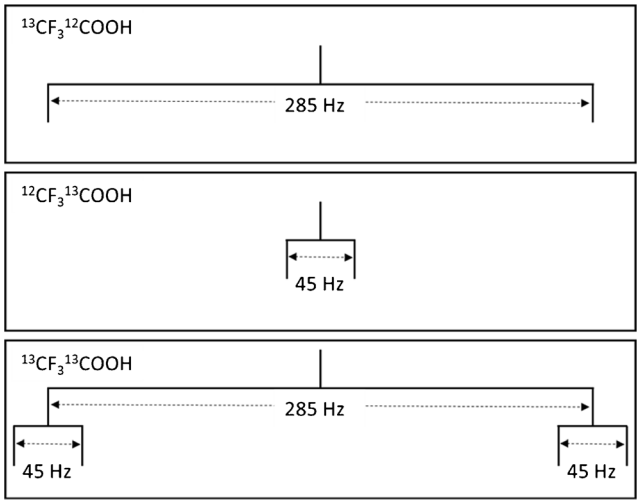

Fig. 1 Signal splitting patterns illustrating the ^{19}F-NMR spectra of carbon-13 labeled trifluoroacetic acids

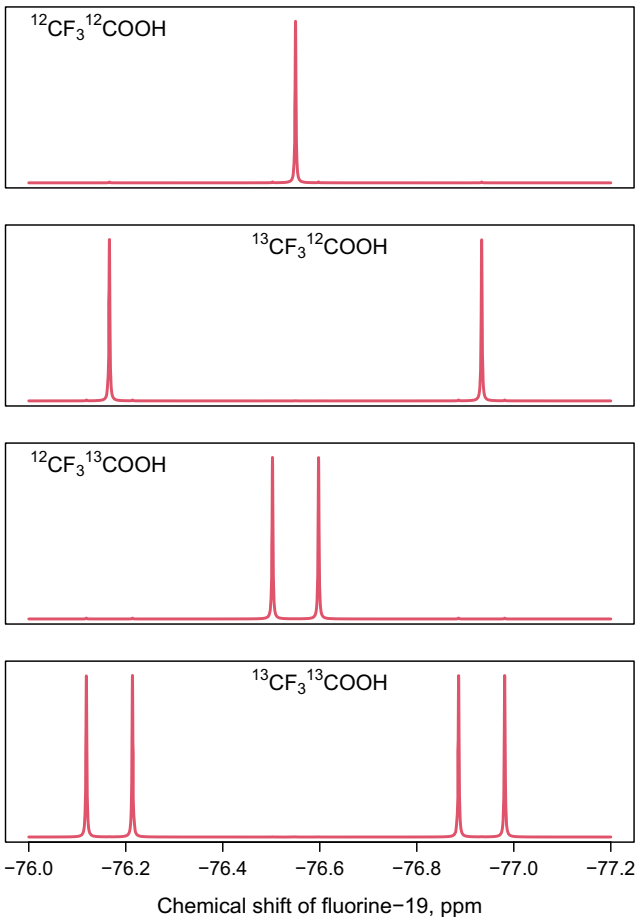

Fig. 2 ^{19}F-NMR spectra of carbon-13 labeled trifluoroacetic acids

Declarations

Conflict of interest The authors declare no competing interests.

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