

Supplementary information for “Automatic assignment and fitting of spectra with PGOPHER”.

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The table below shows the results of a search using the techniques described in the main text on the broadband microwave spectra given by Seifert *et al*[1] for their conformer 2 of 1-hexanal. The same 3 fit and 6 check transitions were used, and the same starting rotational constants, as given in their Table S4. (Conformer 1 was not used, as there is a transition common to the fit and check transitions.) Using a search window of 300 MHz, an acceptance window of 0.3 MHz and a permissible range of A of ± 300 MHz and ± 20 MHz in B and C yields the candidate fits shown below in Table S1. The assignments from Seifert *et al* are shown in the final column. The rows labelled “alternate” result from assignments differing from the non-alternate assignments by 1-3 lines that are sufficiently close (a few MHz) to give a fit of similar quality. Note that all the ^{13}C species appear apart from β ; this appears to be a consequence of one of the check transitions not appearing in the experimental spectrum, and does not appear in the published line list for this species.

Table S1. Results of a search for Conformer 2 of 1-hexanal

n_{OK}	σ_{check}	l_{sum}	A	B	C	Δ^a	Assignment
6	0.036	0.0147	5391.998	1141.388	1027.596	0.030	$^{13}\text{C}\delta$
6	0.050	0.0146	5374.037	1116.876	1007.060	0.148	$^{13}\text{C}\zeta$
6	0.053	0.0159	5391.946	1141.536	1027.648	0.307	$^{13}\text{C}\delta$ alternate
6	0.056	0.0144	5390.032	1128.949	1017.391	0.152	$^{13}\text{C}\alpha$
6	0.062	0.9338	5399.851	1143.230	1028.978	0.053	^{12}C
6	0.062	0.0107	5335.683	1142.593	1026.924	0.157	$^{13}\text{C}\gamma$
6	0.084	0.6754	5399.715	1143.616	1029.113	0.471	^{12}C alternate
6	0.092	0.0199	5387.451	1131.119	1019.509	0.154	$^{13}\text{C}\epsilon$
6	0.102	0.0146	5374.023	1116.884	1007.074	0.144	$^{13}\text{C}\zeta$ alternate
6	0.103	0.0080	5427.971	1120.989	1014.808	-	?

^a Δ is the average root mean square difference between the rotational constants found in this search and those quoted by Seifert *et al*.

1. N. A. Seifert, I. A. Finneran, C. Perez, D. P. Zaleski, J. L. Neill, A. L. Steber, R. D. Suenram, A. Lesarri, S. T. Shipman and B. H. Pate, *J. Mol. Spectrosc.*, 2015, **312**, 13-21.