

# Determination of rotational constants from 4 DR matches

The method used to determine the rotational constants from DR matches is described here, and illustrated by its application to three molecules: *trans*-cinnamaldehyde,  $\alpha$ -ionone, and  $\beta$ -ionone. This script requires only 4 DR matches between 5 frequencies as input: those of four *a*-type transitions, two from each of two *a*-ladders, and one cross-ladder transition connecting these two *a*-ladders. The basic steps of this script are explained here.

Table 1: DR matches used in the rotational constants determination of the three molecules studied (all frequencies in MHz).

	<i>trans</i> -cinnamaldehyde	$\alpha$ -ionone	$\beta$ -ionone
<i>a</i> -ladder 1	7641.872–8720.871	7105.530–7908.603	6862.499–7565.226
<i>a</i> -ladder 2	8517.532–9578.434	7794.830–8596.666	7044.137–7719.040
Cross-ladder 1	7641.872–12041.918	7908.603–11391.354	7565.226–10565.288
Cross-ladder 2	8517.532–12041.918	8596.666–11391.354	7044.137–10565.288

Table S1 summarizes the subset of DR matches (4 DR matches linking 5 frequencies) used in the test-case procedure. From these matches, a initial energy level diagram can be drawn, even if the relative energy ordering of the two ladders is unknown, as evidenced on Fig. S1. As a DR match indicates that two transitions share an energy level but its identity (upper or lower) is unknown, there are four possibilities of connectivity for the cross-ladder transitions, as illustrated in Fig. S2. Finally, for each case, the upper energy level of the cross-ladder transition can be either from the first or second *a*-ladder (Fig. S3).

In consequence, from an initial  $|J, K_a, K_c\rangle$  energy level (taken as the lowest one of the first *a*-ladder), it is possible to express the quantum numbers of all the other levels in each of these cases, and for every *b*- and *c*-type selection rules (cross-ladder). Our script determines all these possibilities following basic spectroscopic rules ( $K_a + K_c = J$  or  $J + 1$ ,  $K_a \leq J$ ,  $K_c \leq J$ ) and creates an assignment file for each of them and for every possible value of  $J$  and  $K_a$  in a given

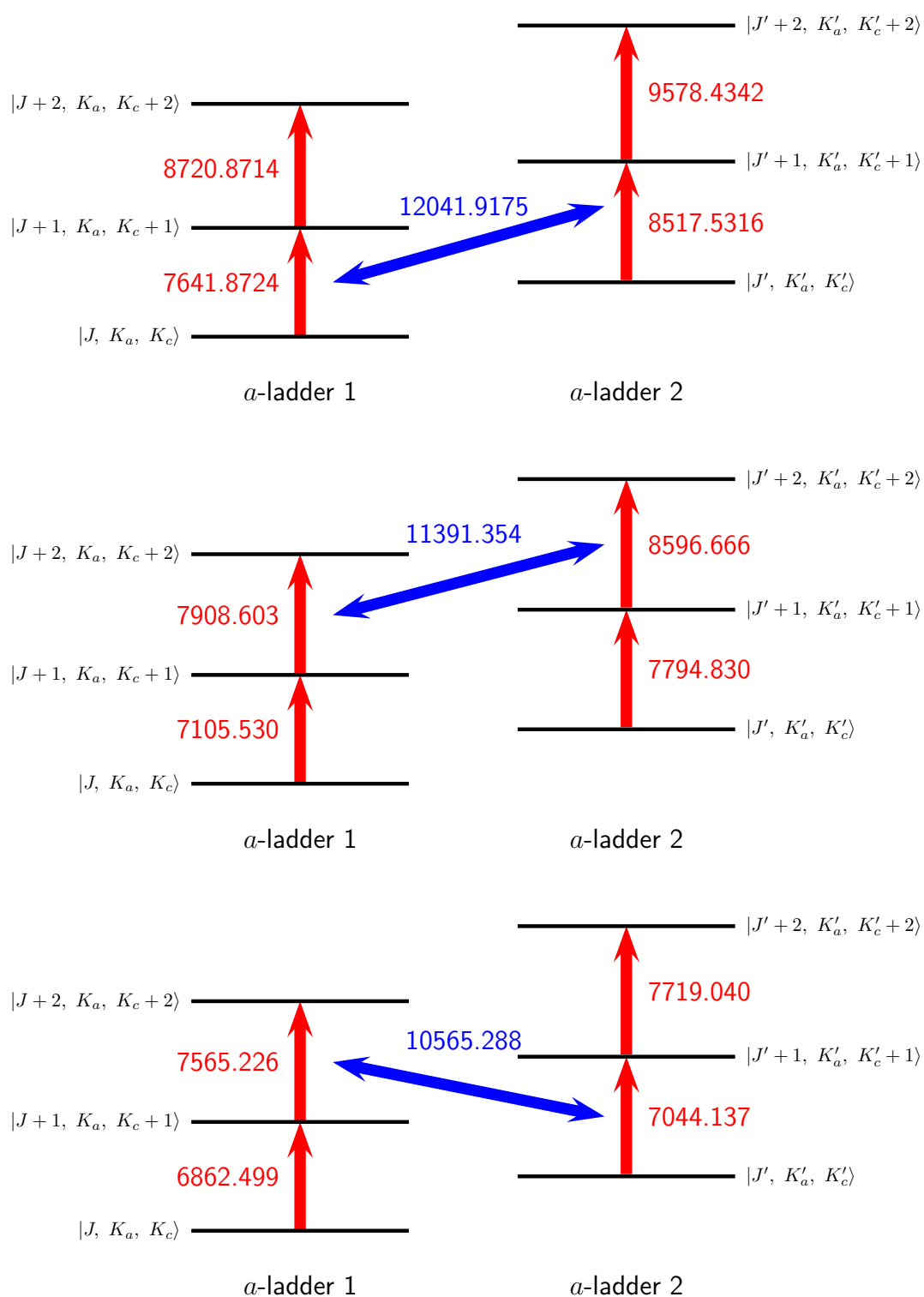


Figure 1: Initial energy level diagram for *trans*-cinnamaldehyde,  $\alpha$ - and  $\beta$ -ionone (from top to bottom, all frequencies in MHz). The relative energy position of the second ladder is set arbitrarily and the orientation of the cross-ladder (blue) transition is unknown.

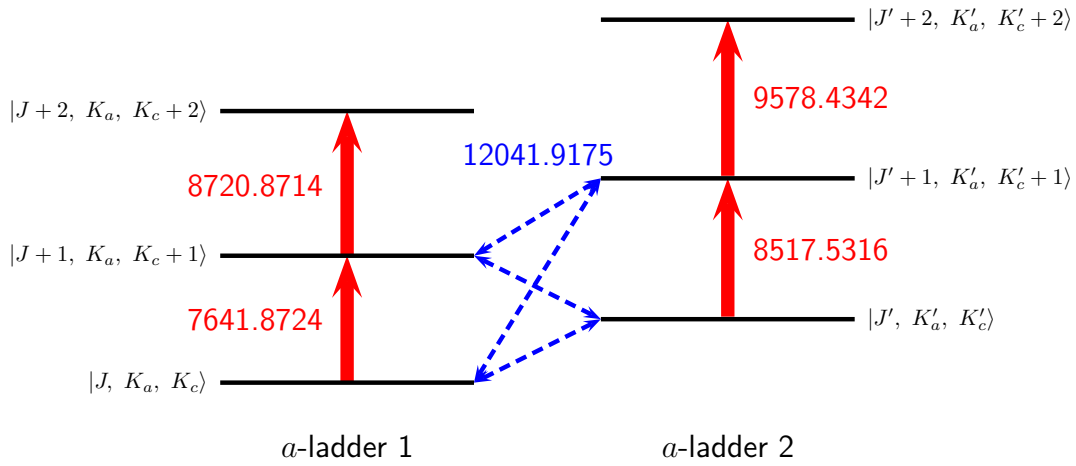


Figure 2: Possible connectivity of the two  $\alpha$ -ladder energy level involved in the cross-ladder transition for *trans*-cinnamaldehyde (all frequencies in MHz).

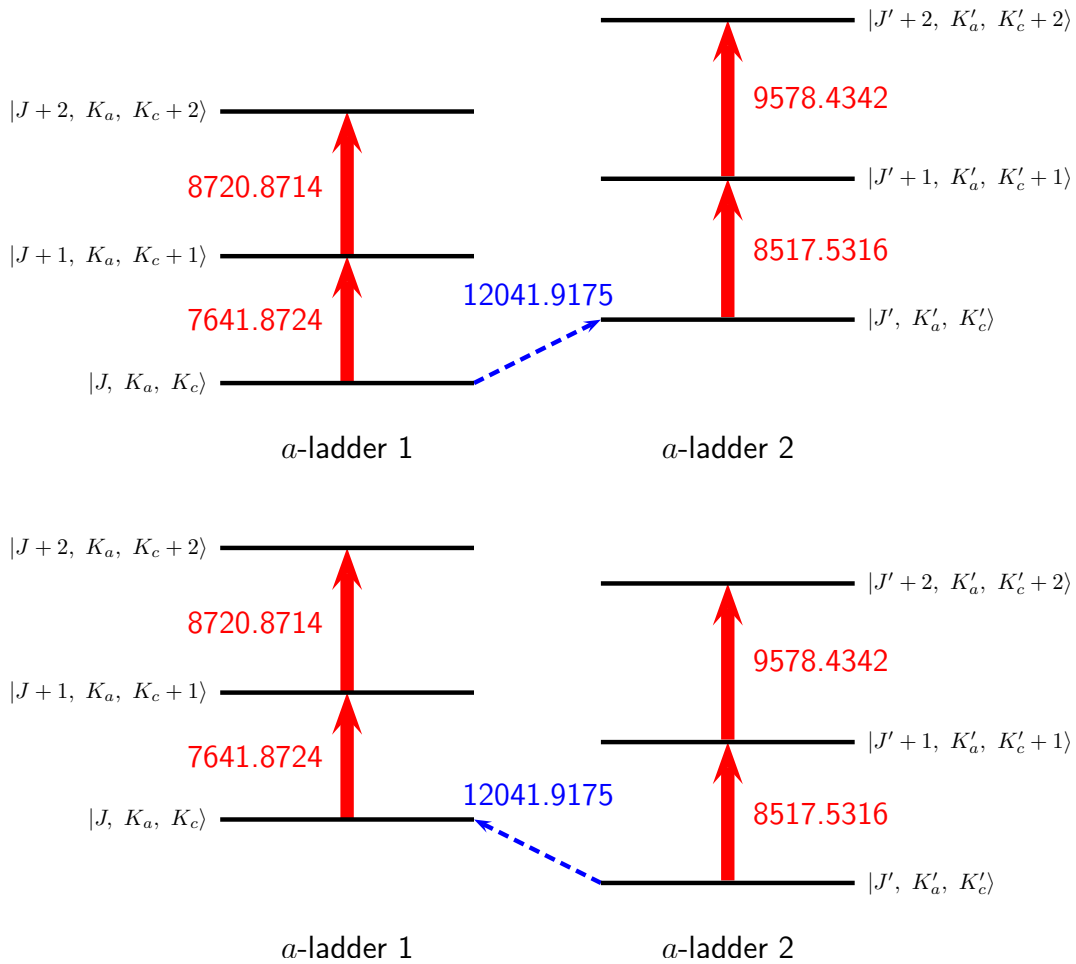


Figure 3: From one given cross-ladder connectivity, the  $\alpha$ -ladder 2 can be either higher or lower than the first one (here, one of the test-case of *trans*-cinnamaldehyde, all frequencies in MHz).

range. For instance, with  $0 \leq K_a \leq 5$  and  $5 \leq J \leq 15$ , 4032 assignments are possible.

Our script creates a `.lin` (Fig. S4) and a `.par` files (see main text for the initial estimation of the rotational constants) and run the `spfit` software for each of the cases. It then reads the final standard deviation of each fit that converges and for which  $A \leq B \leq C$ , and plot them. The best fit is identified by its smallest standard deviation, as visible in Figs. S5. This best-fit provides accurate rotational constants for the studied molecule (see main text) and an assignment for all transitions involved in the initial subset of DR matches. The results obtained for *trans*-cinnamaldehyde,  $\alpha$ - and  $\beta$ -ionone are presented in Fig. S6.

6	1	5	5	1	4	7641.8724	0.050
7	1	6	6	1	5	8720.8714	0.050
6	2	5	5	2	4	8517.5316	0.050
7	2	6	6	2	5	9578.4342	0.050
5	1	4	6	2	5	12041.9175	0.050

Figure 4: Example of a `.lin` file created by our script for *trans*-cinnamaldehyde in Pickett’s format ( $[J' K'_a K'_c J'' K''_a K''_c$  frequency uncertainty], with frequencies and uncertainties in MHz). By default, an uncertainty of 50 kHz is used for all lines.

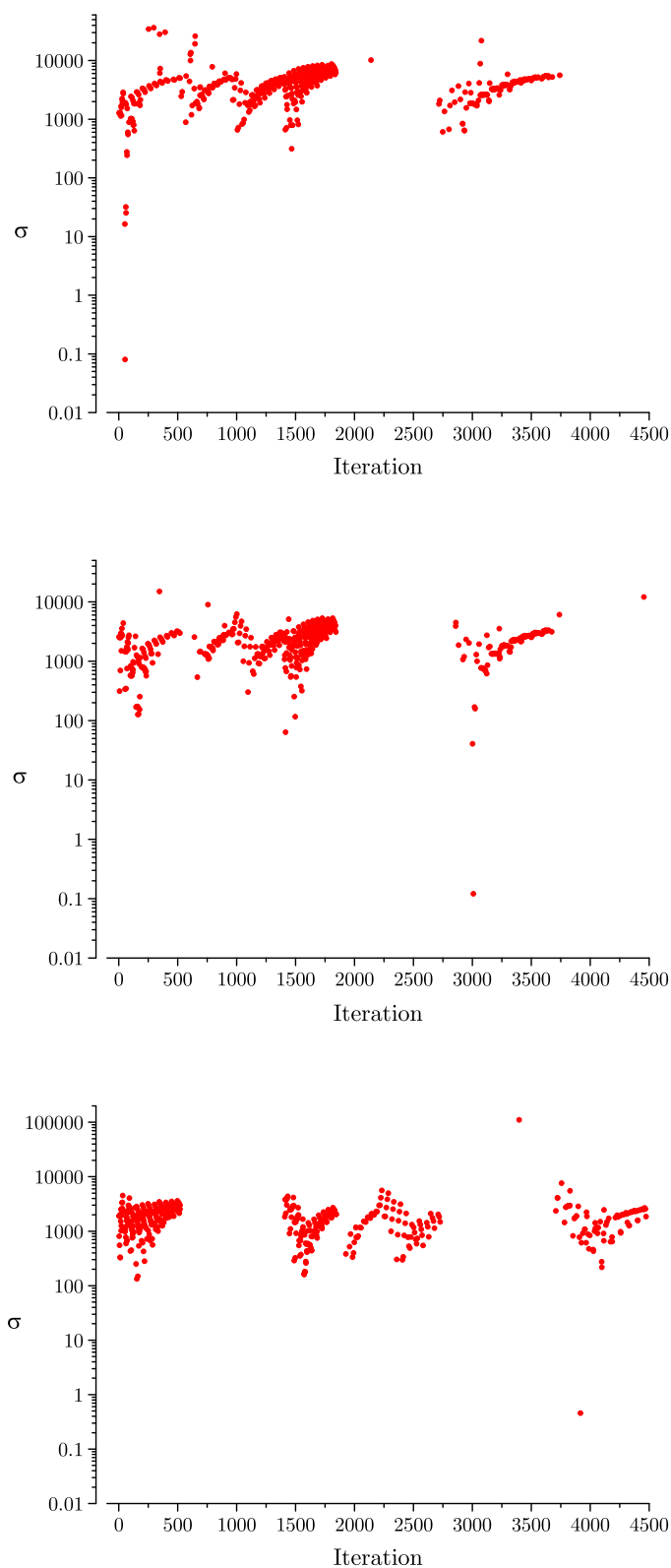


Figure 5: Plots displaying the reduced standard deviation ( $\sigma$ , unitless) derived from the least-square fits (obtained by assuming a 50 kHz uncertainty on the line frequencies in the fit) performed on five transitions of *trans*-cinnamaldehyde,  $\alpha$ -, and  $\beta$ -ionone linked by DR (from top to bottom). Among the 4470 fits performed, 570, 507 and 483, respectively, converged (as indicated by the red dots). The best fits, at iterations 54, 3008, and 3917, are readily apparent (see Fig. S6 for assignments).

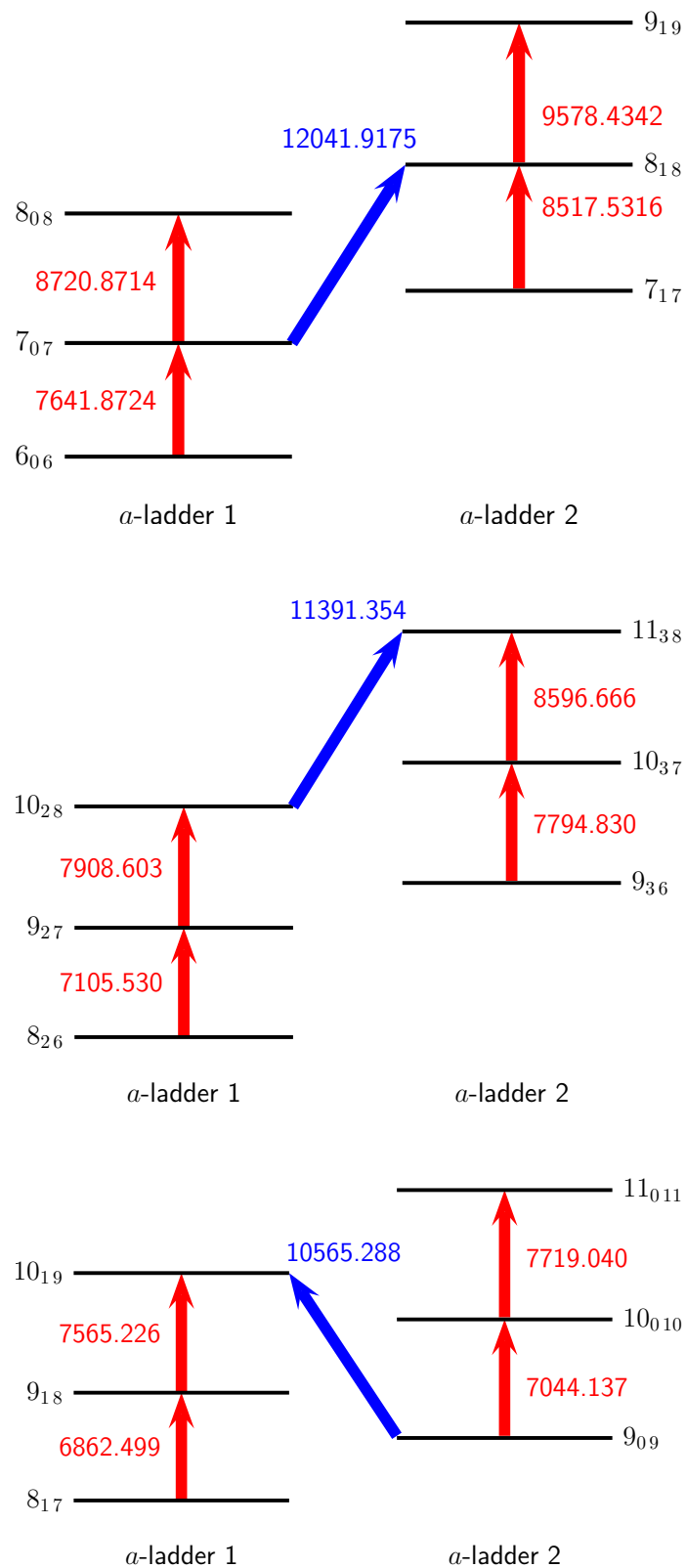


Figure 6: Energy level diagram for *trans*-cinnamaldehyde,  $\alpha$ - and  $\beta$ -ionone (from top to bottom) determined from the best-fit obtained using our script (all frequencies in MHz).