Reactive localized π-radical aromatic soot precursors: properties and concentration in flames - Supplemental Material

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1. Comparison of quantum chemical methods

The rate coefficients and hence kinetic simulations presented are expected to be sensitive to the energetics computed using quantum chemistry. In this work, the energies were computed using the composite method CBS-QB3, which is meant to give reasonable energies compared to other higher level methods, but at much less computational cost [1]. To verify how reasonable the CBS-QB3 method is, the barrier heights presented in Figure 4 were also computed using another higher level composite method, G4MP2, and a hybrid density functional known for improving the energetics of PAH systems, M06-2X [2]. The comparison of barrier heights predicted by these three methods is displayed in Table S1:

Table S1: Comparison of barrier heights predicted by CBS-QB3, G4MP2, and M06-2X methods.. The units are kcal/mol.

Reaction	CBS-QB3	G4MP2	M06-2X
R5+H→R5-+H_2	17.7	19.1	20.5
R5-+H_2→R5+H	6.6	10.3	6.8
R5+H→ R5H	1.4	2.2	1.7
R5H→R5+H	44.4	45.0	48.0
R5→R5M	72.2	71.6	73.9
R5M→R5	7.4	6.8	8.1
R5H+H→ R5M+H_2	13.2	11.8	14.5
R5M+H_2→ R5H+H	9.8	8.9	6.4
R5H+H→R5+H_2	10.9	9.0	11.9
R5+H_2→R5H+H	72.3	70.8	69.6
R52H+H→ R5H+H_2	5.8	6.4	7.5
R5H+H_2→ R52H+H	26.3	26.2	23.1

The values above suggest a mean deviation of 1.2 kcal/mol between the barriers predicted by CBS-QB3 and G4MP2, suggesting good agreement. Previous bench-marking between CBS-QB3 and G2 energies suggested a difference in 1.1 kcal/mol [1], so this is not entirely unexpected. There is a larger mean deviation of 2.3 kcal/mol between the barriers predicted by CBS-QB3 and M06-2X. This is significant, but not unreasonable. Given the uncertainty in M06-2X and CBS-QB3 methods are expected to be ±1-2 kcal/mol, the difference in barrier heights is still at the point where the two methods are suggesting very similar behaviour. It is worth noting that the largest differences

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in predicted barrier heights between CBS-QB3 and G4MP2 and CBS-QB3 and M06-2X are similar at 3.5 and 3.7 kcal/mol, but the average deviations still suggest that the choice of CBS-QB3 for energetics is reasonable and gives barrier heights in line with other quantum chemistry methods.

2. Rate calculations

2.1. Reactions with Barriers

For the reactions with barriers, the rates were computed using the standard transition state expression:

$$k = \frac{k_B T}{h} \frac{q^\dagger}{\prod_i^{n_{\text{reactants}}} q_i} \exp(\frac{-\Delta E_0}{RT}) \tag{1}$$

Where k is the rate constant, k_B is the Boltzmann constant, T is temperature, h is Planck's constant, q is the total partition function, and ΔE_0 is the classical barrier height.The partition functions for all species were computed using the Rigid-Rotor, Harmonic-Oscillator (RRHO) model, with frequencies and rotations determined at the B3LYP/6-311G(d,p) level of theory. To account for quantum tunneling effects, the simple Wigner correction was employed [3], giving the tunnelling correction factor, C_W as follows:

$$C_W = 1 - \frac{1}{24}\left(\frac{h\nu^\dagger}{k_B T}\right)^2 \tag{2}$$

With $\nu^\dagger$ being the magnitude of the imaginary frequency of the transition state. The Eckart tunneling correction is also commonly used [4], but the difference between the Eckart and Wigner correction in this case was negligible, with both predicting tunneling corrections of around 1.2 at 300 K and negligible tunneling correction at the higher temperatures.

In the subsequent kinetic simulations and kinetic Monte Carlo, the rates computed for acenaphthylene(A2R5) were assumed to be the same for a larger aromatic, acecoronene (A7R5), which is a coronene with a rim-based pentagonal ring. In order to show that this assumption is reasonable, some rates were recalculated for A7R5 and compared to those computed for A2R5. Since the CBS-QB3 calculations have too large a memory requirement for a molecule such as acecoronene, the rates were computed using energies, geometries, and vibrational frequencies all taken at the B3LYP/6-311G(d,p) level of theory. In this case, we chose hydrogen abstraction from, addition to, and migration on A7R5, representing the three main categories of hydrogen–PAH reactions studied in this work. Figure S1 presents the Arrhenius plots of these three processes for A2R5 and A7R5. Little difference is seen between the smaller and larger aromatic rates. The hydrogen addition to the R5 site is seen to decrease slightly for the larger species at low temperatures where soot does not form. Hence, it is expected that the rates calculated for A2R5 in this work should scale for larger PAHs with rim-based pentagonal rings as well.

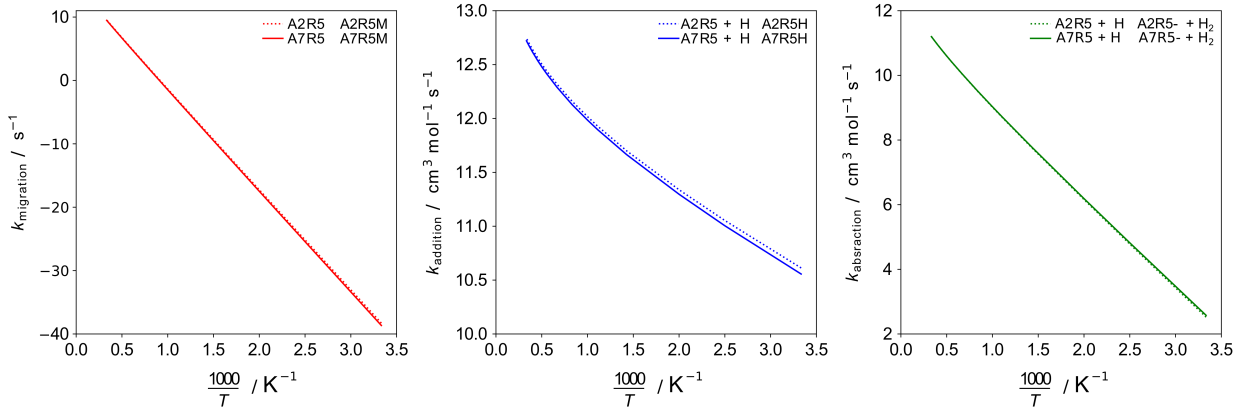


Figure S1: Temperature dependent rate constant for acenapthelene A2R5 and coronene A7R5 for some critical reactions in the reaction mechanism.

2.2. *Barrierless reactions*

In the case of the three barrierless reactions, there is no tight transition state, and application of transition state theory is not possible. To estimate the rate constants for these reactions, two methods were tried. The first was the application of RRKM theory with a simple Gorin Model, as implemented in Unimol [5]. The second was the use of momentum-resolved variational transition state theory (VTST) as implemented in ktools [6]. The unimolecular decomposition rates were determined using these methods, and the radical recombination rate was determined from the equilibrium constant for the overall reaction.

For the collisional parameters, the Lennard-Jones parameters of the PAHs were estimated from their molecular weight,M_w , based on the correlations of Wang et al. [7]:

$$\sigma = 1.234(M_w^{0.33}) \tag{3}$$

$$\frac{\epsilon}{k_B} = 37.15(M_w^{0.58}) \tag{4}$$

For the energy transfer parameters, a standard exponential-down form was adopted:

$$\alpha = \alpha_0 \left(\frac{T}{298}\right)^n \tag{5}$$

With α_0 taken as 300 cm^{-1} and n taken as 0.85.

2.2.1. *Gorin Model calculations*

In the Gorin model, the internal motion of the transition state is given by the vibrations and rotations of the separated fragments of the product, and the potential energy between the separated fragments needs to be provided. In this case, the free-rotor approximation was used for the rotations of the loose transition states. The potential energy surfaces for the barrierless reactions were determined using a relaxed scan at B3LYP/6-311G(d,p) level of theory. This was then used to fit a Morse potential for the interaction between the separated fragments to use in the Gorin/RRKM computations.:

$$E(r) = D_e[1 - \exp[-\beta(r - r_{\text{eq}})]^2, \tag{6}$$

with D_e being the bond dissociation energy, r the reaction coordinate, r_{eq} the equilibrium distance, and β the steepness of the potential energy function. The fitted Morse potentials are presented in Figure S2.

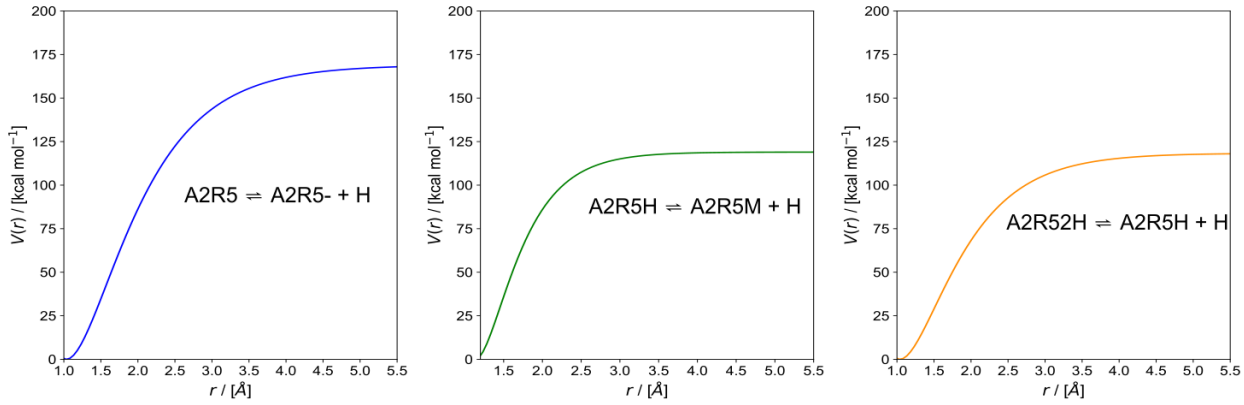


Figure S2: Fitted Morse potentials for barrierless reactions. The interaction potential energy surfaces were fitted to the B3LYP/6-311G(d,p) level of theory.

The geometries, frequencies, and rotations of the reactants and products were taken from the optimized structures at the B3LYP/6-311G(d,p) level of theory, consistent with the methodology for the reactions with barriers.

2.2.2. VTST calculations

The VTST calculations performed in this work follow the angular-momentum resolved microcanonical variational transition state theory (J-resolved VTST) implemented in ktools . The canonical rate constants are then computed by a 2D averaging over both the angular momentum and energy microcanonical rate constants [6].For these calculations, nine trial transition states were taken from a relaxed potential energy surface scan at the B3LYP/6-311G(d,p) level of theory, with the coordinate being the carbon-hydrogen bond distance. This is the same scan used to derive the potential energy surface for the Morse potential fits in Figure S2. Frequencies and rotations were calculated for each trial transition state by extracting each trial geometry and running a frequency calculation again using B3LYP/6-311G(d,p). Energies of each trial transition state relative to the reactant PAH were also taken at this level of theory, as well the energies of the separated H radical and PAH fragments. The numerical parameters for the energy and angular momentum density of states integration were taken from [8]. Namely, this involves an energy grain of 10 cm^{-1} and maximum energy of 20000 cm^{-1}, as well as an angular momentum grain of 1 cm^{-1} and maximum angular momentum of 1000 cm^{-1}. These are essentially the standard recommended parameters. Little variance was seen in the rate constants based on these parameters.

The rate constants will be most sensitive to the computed potential energy surface, determined at the B3LYP/6-311G(d,p) level of theory in this work. DFT methods can struggle with radical-radical reactions, which may require multi-configurational and multi-reference methods. To check that the B3LYP potential energy surface is reliable enough, a complete-active-space SCF (CASSCF) calculation was also used to generate the potential energy surface and compute the rate constant for the radical recombination reaction between A2R5- and H. The active space chosen consisted of two electrons and two orbitals, centered on the carbon-hydrogen bond in question in A2R5, essentially amounting to a CASSCF(2e,2o)/6-311G(d,p) calculation. A natural orbital calculation with mixing of the HOMO and LUMO orbitals in A2R5 was performed to provide the guess orbitals for the CASSCF calculation. The computed rate constant using this potential energy could then be compared, which is found in Figure S3.

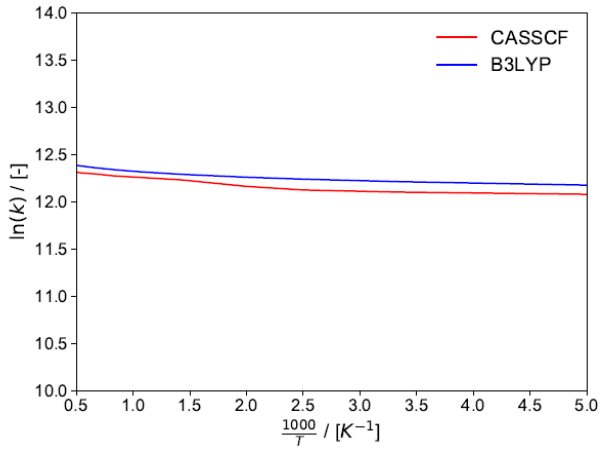


Figure S3: Comparison between rate constant computed for the A2R5- + H radical recombination reaction using B3LYP and CASSCF(2e,2o).

The comparison suggests that B3LYP overestimates the rate constant for the radical recombination by 6-11% when compared CASSCF and high and low temperatures respectively, due to B3LYP predicting a more attractive potential. Previous work on barrierless oxidation of PAH radicals by oxygen radicals also compared rate constants computed using B3LYP to those using the perturbation-corrected CASSCF, or CASPT2 [9]. The authors found B3LYP overestimated the rate constant by about 8%, which agrees with the results here. This suggests that whilst B3LYP does overestimate the rate constant compared to multi-configuration and multi-reference methods, it is not by a very large amount, suggesting that the B3LYP method is a reasonable choice for providing potential energy surfaces for a first estimate of these rate constants.

Figure S4 compares the three barrierless reaction rate constants computed using the RRKM theory framework and the

simple Gorin model with those computed using the variational transition state theory (VTST) framework.

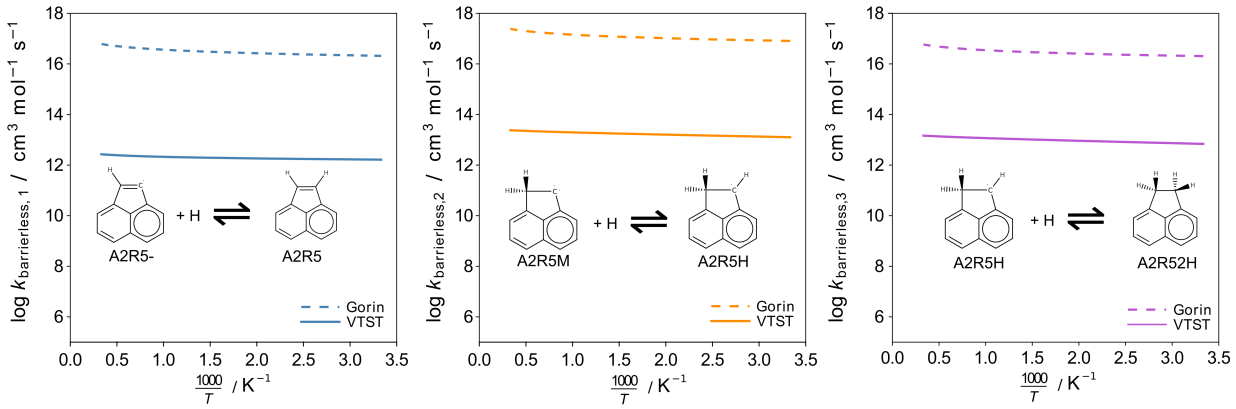


Figure S4: Temperature dependent rate constant for the three barrierless reactions computed using the Gorin model and variational TST (VTST).

In general, we find the Gorin model overpredicts the rate constants compared with the more accurate VTST method, possibly because one of the fragments of the product (the PAH radical) is very large and similar to the reactant PAH. We expect the VTST method to give a reasonable first estimate for these rates, especially given the difficulties of the Gorin model for this particular case and the reasonable performance of the B3LYP functional compared to CASSCF. However, it is known that the relative energies of the trial transition states can be improved upon, and other potential reaction coordinates may also play a role that have not been looked at here. Multi-configurational or multireference methods with larger active spaces than the one used for comparison here may be necessary for more accurate interaction energies. More advanced frameworks [such as variable reaction coordinate-transition state theory (VRC-TST)] are likely necessary to give a more accurate estimate of the rate constants of these barrierless reactions as well.

3. Spin-density calculations and Clar analysis

The electron spin density, $\rho^s(\mathbf{r})$, is defined as the difference between the spin density of the α and β electron spin densities:

$$\rho^s(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}). \tag{7}$$

It is a widely used as a metric to locate reactive sites in open-shell DFT calculations with a recent study of diradicals demonstrating this on aromatic species similar to those explored in this study [10].

The Clar analysis is a qualitative method to determine the reactivity of fused polycyclic aromatics. It centres around aromatic π-sextets that are defined as 'six π-electrons localized in a single benzene-like ring separated from adjacent rings by formal CC single bonds' [11]. Configurations are sought with the maximum number of sextets with double bonds or a radicals placed in the remaining positions. For a recent review we recommend the paper 'Forty years of Clar's aromatic π-sextet rule' [11]. For an algorithm for automatically computing the Clar structure we recommend the recent publication in the Proceedings by Liu and Green [12].

4. Kinetic simulations

The kinetic simulations presented in the main text have fixed mole fractions of reactants, including that of hydrogen radicals, and also make use of the computed rate constants. To see the impact on the presented results to the atomic hydrogen mole fraction and the rate constants, the kinetic simulations were performed using multiple starting hydrogen radical mole fractions, namely one order of magnitude smaller and larger than the 0.001 used as a default. The results for two of the main temperatures, 1400 K and 1500 K are presented in Figure S5:

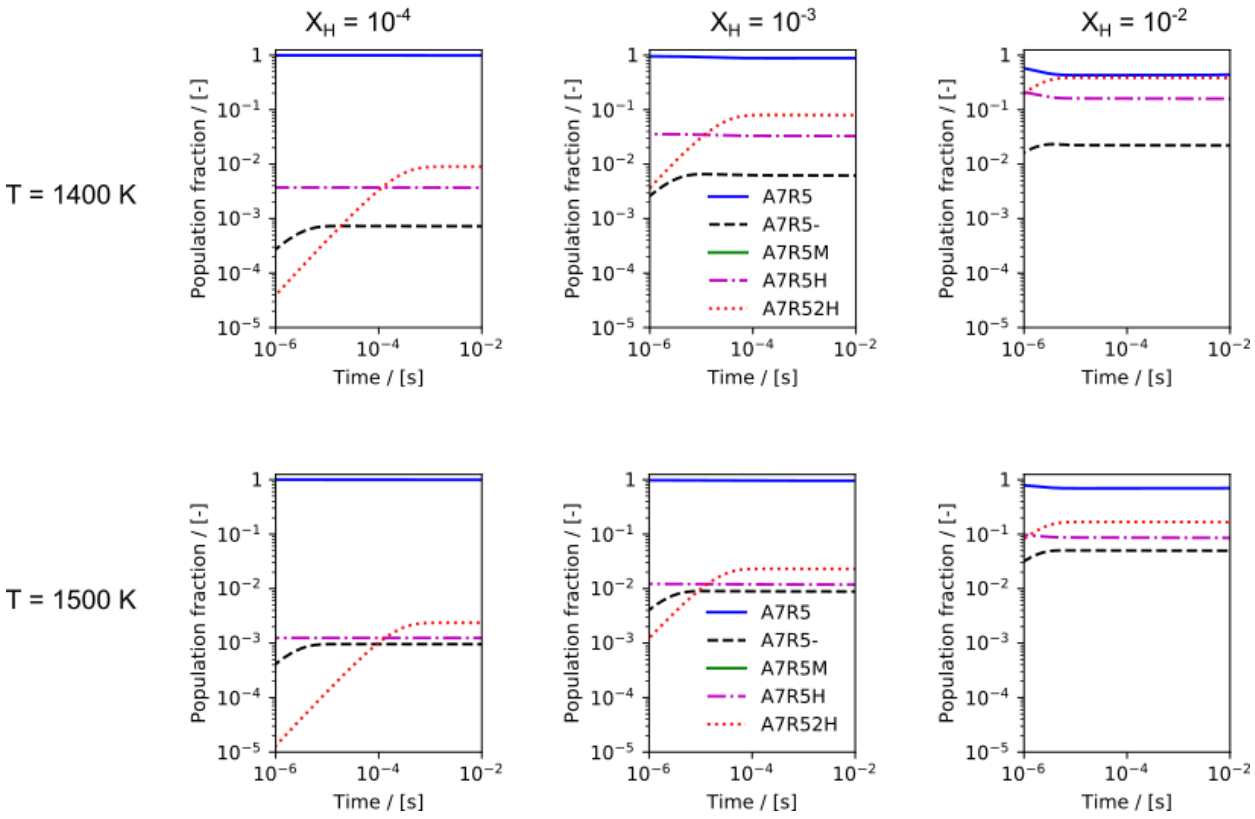


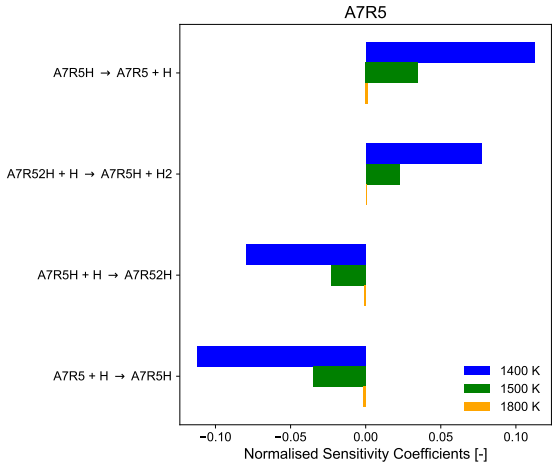
Figure S5: Kinetic simulations of a 0D homogeneous reactor with varying initial mole fractions of atomic hydrogen at temperatures of 1400 K and 1500 K.

The results in Figure S5 suggest that the mole fraction of atomic hydrogen does impact the fraction of reactant A7R5 that is converted to the σ radical A7R5-, localized π-radical A7R5H, and fully hydrogenated A7R52H. However, the relative amount of the three products is consistent regardless of initial atomic hydrogen concentration. The other main influence of the initial atomic hydrogen mole fraction is the speed at which the products form, which is also expected. The above findings are true for all the temperatures used in the kinetic simulations, so only two are shown as an example.

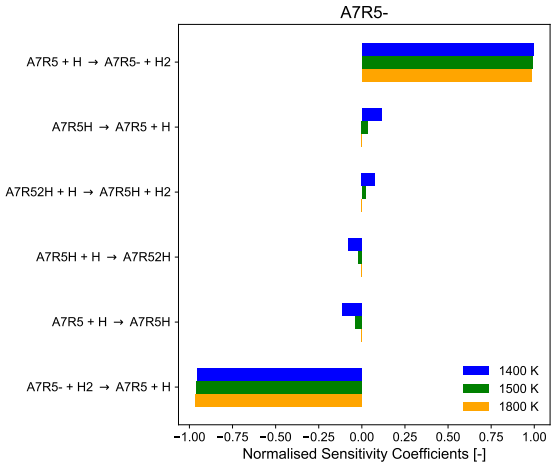
A sensitivity analysis was also performed on the mole fractions of the main species (A7R5, A7R5-, A7R5M, A7R5H, and A7R52H) to the 18 reactions in the mechanism developed. The normalized sensitivity coefficients were computed using the definition:

$$S_{ki} = \frac{x_i}{y_k} \frac{\partial y_k}{\partial x_i}, \tag{8}$$

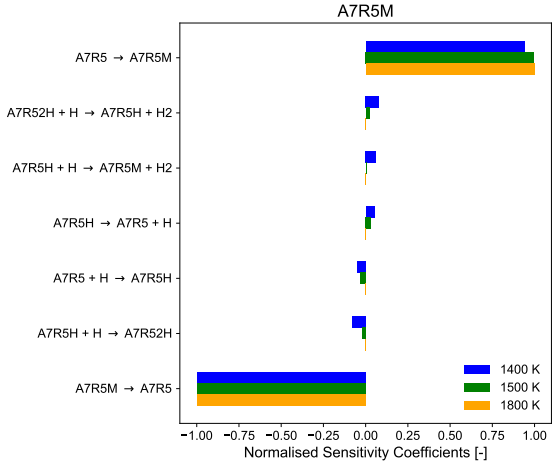
Where S_{ki} is the sensitivity of response y_k to a change in variable x_i. These sensitivity coefficients were computed at three temperatures: 1400, 1500, and 1800 K, representing the temperatures most of interest to flames and soot formation, and at a time of 1 ms, by which the mole fractions of species and the sensitivity coefficients are at steady state.



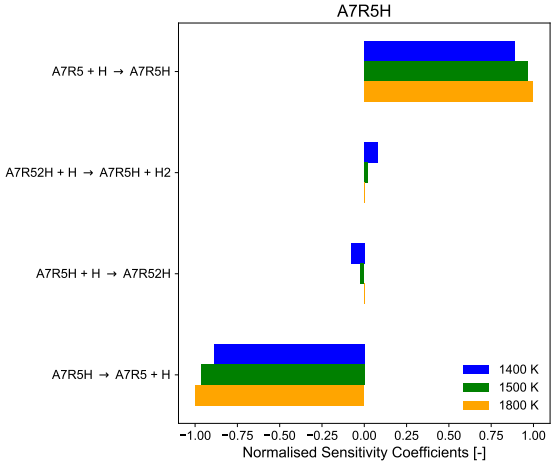
(a) A7R5



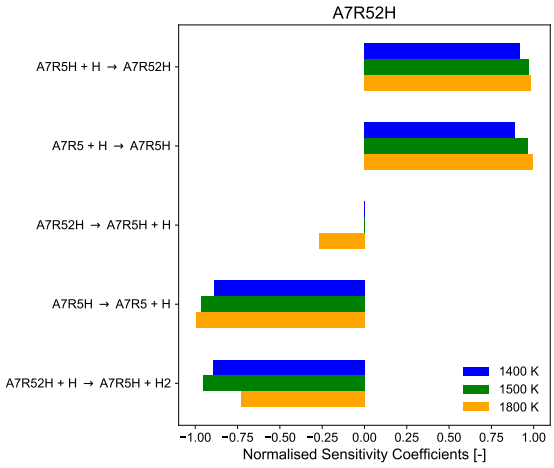
(b) A7R5-



(c) A7R5M



(d) A7R5H



(e) A7R52H

Figure S6: Normalised sensitivity coefficients for the main PAHs to the rate constants in the kinetic mechanism. Data is shown for three temperatures, 1400 K,1500 K,and 1800 K. Only non-zero sensitivity coefficients are displayed.

Figure S6 shows that the PAHs are generally sensitive to only a few key reactions, with the sensitivity coefficients being of opposite signs for corresponding forward and backward reactions. For all species other than A7R5, the sensitivity coefficients are similar for the three temperatures and tend to be either close to 0 or 1. A7R5 has sensitivity coefficients that are between 0 and 0.1, most likely due to it being in such excess mole fraction compared to the other PAHs. Figure 6(a) shows that A7R5 is most sensitive to the reaction with atomic hydrogen to produce A7R5H. This reaction has the lowest barrier of the reactions involving A7R5. Reactions that generate A7R5H from A7R52H also impact the fraction of A7R5 as a result. For A7R5-(Figure 6(b)), the key reaction is the hydrogen abstraction from A7R5, which is expected as this is the only reaction producing A7R5. Similarly, the key reaction for A7R5M is the hydrogen migration occurring on A7R5(Figure 6(c)). Even though this reaction has a very high barrier especially compared to those that generate A7R5M from A7R5H, A7R5 is present in a much higher fraction. A7R5H is entirely dependent on the hydrogenation of A7R5, with Figure 6(d) showing the opposite behavior of that for A7R5. Finally, for forming A7R52H, the key reactions are the barrierless hydrogen addition to A7R5H, and well as the preceding hydrogen addition to form A7R5H form A7R5. The reverse hydrogen loss from A7R5H as well as the hydrogen abstraction from A7R52H are crucial to reducing the fraction of A7R52H. Overall, the reaction with the most importance is seen to be the hydrogenation of A7R5 to form A7R5H.

5. Kinetic Monte Carlo simulations

A kinetic Monte Carlo model was used to study the formation of localized π-radicals on PAHs having multiple five-member rings. In the model a PAH is represented as a list of sites that can have different site types. In this model, there are five site types used to study the formation of localized π-radicals and other intermediate species formed in the activation process. These site types are analogous to the ones shown in the main text for acenaphthylene: R5, R5-, R5H, R5M and R52H. Reactions for these sites were assumed to be analogous to those of acenaphthylene and are shown in Table 1 in the main document. The site specific reaction rate is computed as:

$$r_i = k_i \times [A] \times N_{\text{site},i}, \tag{9}$$

where r_i is the site specific reaction rate for reaction i with rate constant k_i, $[A]$ is the concentration of the gas phase species involved in the reaction and $N_{\text{site},i}$ is the number of sites present in the PAH that can undergo reaction i.
Other important physics for PAHs have been neglected in the model to focus solely on the kinetics of localized π-radicals. Particle processes such as coagulation, sintering or condensation were not considered. This way the PAHs are not interacting with each other and only undergo gas-phase reactions. Other important surface reactions, such as HACA growth or acetylene desorption are not included. Although this is a large simplification, it allows the number of carbon atoms in all the simulated PAHs to be constant and only the radical behaviour due to hydrogen atoms be explored, which is the focus of this work. Table S2 summarizes the reactions included for all the available sites.
The kinetic Monte Carlo simulations tracked the evolution of 100,000 PAHs in a batch reactor at the same conditions used for the kinetic simulations, namely a pressure of 1 atmosphere and initial mole fractions of 10^{-7}, 0.001, and 0.1 for the starting PAH, H, and H_2 with the rest as N_2. A temperature of 1000 K was used to study the localized π-radicals as they are present in higher concentrations. Two simulations were performed with different starting PAHs. In the first case, coronene with two rim five-membered rings was used, while in the second case, coronene with three rim five-membered rings was used. The PAHs selected are shown in Figure 4 in the main text.

In both simulations, the population fraction of PAHs with one localized π-radical reaches a maximum at around 10^{-6} s with approximately half of the population present in this state. In the first simulation, this species stays at around this population fraction while producing a peak for the species with two localized π-radicals at around 4×10^{-6} s and a population fraction of 0.35. In the second case, the peaks for the species with two and three localized π-radicals are located at the same time with population fractions at around 0.4 and 0.2 respectively. The population fraction for the single localized π-radical shows a minimum at this location with a population fraction at around 0.35. In both simulations, the number of hydrogen saturated PAHs increases after the localized π-radical peaks by the consumption of these species. The number of fully saturated species reaches a plateau at around 4×10^{-5} s with a population fraction of around 0.8 and 0.7 in each simulation. These saturated species coexist with localized π-radicals but probably only the species with a single localized π-radical has a significant population fraction (around 0.2). The last part of both

Table S2: Reactions used in the kinetic Monte Carlo simulations and their rate parameters. The units are kcal/mol, K, $cm^3mol^{-1}s^{-1}$ and s^{-1}.

Reaction	A	n	E
R5+H→R5-+H_2	$1.99 \cdot 10^8$	1.88	16.76
R5-+H_2→R5+H	$7.08 \cdot 10^5$	2.11	4.89
R5+H→ R5H	$1.63 \cdot 10^9$	1.51	0.77
R5H→R5+H	$1.93 \cdot 10^{10}$	1.24	44.66
R5→R5M	$2.65 \cdot 10^{11}$	0.70	71.85
R5M→R5	$3.19 \cdot 10^{11}$	0.40	6.88
R5H+H→ R5M+H_2	$7.29 \cdot 10^7$	1.48	11.84
R5M+H_2→ R5H+H	$4.85 \cdot 10^5$	1.89	7.49
R5H+H→R5+H_2	$2.17 \cdot 10^7$	1.86	9.24
R5+H_2→R5H+H	$1.20 \cdot 10^5$	2.56	69.86
R52H+H→ R5H+H_2	$4.42 \cdot 10^7$	1.83	4.33
R5H+H_2→ R52H+H	$2.41 \cdot 10^6$	1.78	24.28
R5→R5-+H	$2.87 \cdot 10^{15}$	−0.32	117.47
R5-+H →R5	$4.90 \cdot 10^{11}$	0.21	0.00
R5H→R5M+H	$4.61 \cdot 10^{15}$	−0.35	109.87
R5M+H→R5H	$1.19 \cdot 10^{13}$	0.09	0.28
R52H→R5H+H	$1.89 \cdot 10^{16}$	−0.40	86.38
R5H+H→R52H	$6.95 \cdot 10^{12}$	0.10	0.35

simulations shows a decrease in the number of saturated species. This is due to the consumption of the hydrogen radical facilitating hydrogen loss reactions leading to a higher number of species with one localized π-radical. These simulations show that localized π-radicals are intermediate species that are quickly formed and can appear under different conditions.

6. Molecular parameters

The molecular parameters determined by the quantum chemical methods used in this work are provided in Table S3. The transition states are numbered to correspond to the order of reactions in Table 1 in the main text, with each transition state corresponding to a pair of forward and reverse reactions in the Table. For the three barrierless reactions, the trial transition states used in the rate calculations are provided.

Table S3: c

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
A2R5	1.51369, 1.22272, 0.67637	160.6312, 212.2204, 229.5168	C	-2.34218	-0.68054	0.00000
		375.5957, 423.159 , 461.6136	C	-2.34218	0.68054	0.00000
		470.8489, 518.8925, 561.3866	C	-0.94994	1.16015	0.00000
		583.1068, 615.7972, 668.6125	C	-0.94994	-1.16015	0.00000
		675.1756, 695.8043, 741.4581	C	-0.14036	0.00000	0.00000
		767.1492, 788.5525, 818.0417	C	-0.32068	-2.38670	0.00000
		848.5523, 879.4611, 917.722	C	1.10261	-2.42557	0.00000
		929.529, 935.6892, 975.9356	C	1.25391	0.00000	0.00000
		985.6868, 1027.4973, 1034.7901	C	1.87757	-1.28127	0.00000
		1056.5173, 1102.8013, 1113.0583	C	-0.32068	2.38670	0.00000
		1176.0211, 1203.3192, 1224.5083	C	1.10261	2.42557	0.00000
		1246.4027, 1273.1128, 1331.6423	C	1.87757	1.28127	0.00000
		1385.4273, 1419.4025, 1447.3473	H	-3.21855	-1.31448	0.00000
		1457.2574, 1489.6995, 1515.4895	H	-3.21855	1.31448	0.00000
		1540.6269, 1636.3861, 1652.1428	H	-0.87850	3.31737	0.00000
		1660.5381, 3159.3329, 3159.7332	H	1.59237	3.39317	0.00000
		3168.6979, 3169.4351, 3182.7225	H	2.95975	1.35899	0.00000
		3183.7073, 3200.9957, 3221.0518	H	2.95975	-1.35899	0.00000
			H	1.59237	-3.39317	0.00000
			H	-0.87850	-3.39317	0.00000

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
A2R5-	1.56870, 1.22312, 0.68726	158.1604, 211.7702, 234.8394	C	0.44222	2.40507	0.00000
		365.9805, 422.2192, 455.6347	C	-0.90358	2.32644	0.00000
		485.1009, 516.1269, 552.6865	C	-1.23620	0.88080	0.00000
		554.085, 618.3232, 642.6263	C	1.09132	1.09666	0.00000
		671.0141, 688.2074, 754.3557	C	0.00000	0.18614	0.00000
		770.447, 797.0971, 812.9752	C	2.37012	0.58659	0.00000
		840.1392, 872.6622, 920.9952	C	2.53806	-0.82598	0.00000
		928.9291 ,976.4076, 986.8351	C	0.13495	-1.20170	0.00000
		1012.08, 1031.7287, 1056.3304	C	1.46877	-1.70167	0.00000
		1090.2451, 1167.6643, 1194.6237	C	-2.39430	0.13507	0.00000
		1205.6838, 1235.7052, 1252.5362	C	-2.29360	-1.28656	0.00000
		1263.4701, 1373.4181, 1401.6	C	-1.08114	-1.94678	0.00000
		1447.5664, 1448.8846, 1471.606	H	-1.61549	3.13921	0.00000
		1512.7411, 1520.9119, 1629.8265	H	-3.37471	0.59924	0.00000
		1643.7139, 1654.851 , 3161.0084	H	-3.20970	-1.86691	0.00000
		3163.9455, 3171.8949, 3175.9922	H	-1.05267	-3.03121	0.00000
		3184.2171, 3188.0393, 3222.2358	H	1.64566	-2.77200	0.00000
			H	3.54614	-1.22510	0.00000
			H	3.24109	1.23226	0.00000
A2R5M	1.50145, 1.20956, 0.67260	144.843, 163.492, 202.7958	C	-0.79134	2.34769	0.00003
		254.4366, 419.2057, 428.5045	C	0.72980	2.42083	0.00010
		464.2313, 475.9896, 510.0364	C	1.11978	1.02275	0.00015
		558.3445, 558.4874, 634.9857	C	-1.20614	0.87926	0.00006
		655.286, 685.7899, 747.0245	C	-0.00556	0.15269	0.00010
		785.7457, 801.0669, 815.215	C	-2.38837	0.17642	0.00019
		843.7856, 857.9647, 924.4306	C	-2.34664	-1.24890	0.00003
		928.7468, 961.3645, 986.235	C	0.07446	-1.25156	0.00009
		1008.393, 1026.977, 1039.35	C	-1.16184	-1.95585	0.00002
		1061.125, 1121.906, 1127.757	C	2.39062	0.45049	0.00001
		1177.044, 1196.673, 1216.306	C	2.50517	-0.95427	0.00019
		1238.357, 1250.277, 1275.35	C	1.38842	-1.78490	0.00013
		1374.639, 1378.687, 1385.938	H	3.27201	1.08197	0.00023
		1447.716, 1456.847, 1483.576	H	3.49105	-1.40531	0.00045
		1523.099, 1612.737, 1626.462	H	1.52859	-2.86164	0.00006
		1652.207, 3012.862, 3031.815	H	-1.17235	-3.04053	0.00006
		3159.704, 3160.334, 3169.604	H	-3.28476	-1.79318	0.00010
		3176.928, 3183.237, 3190.451	H	-3.35109	0.67691	0.00028
			H	-1.16654	2.90716	0.86784
			H	-1.16700	2.90670	0.86791

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
A2R5H	1.47468, 1.19468, 0.66268	170.3032, 190.7333, 216.2963	C	0.82045	2.33346	0.00008
		287.5742, 420.0461, 454.1295	C	-0.69473	2.30166	0.00015
		469.2814, 481.7613, 509.3379	C	-1.14638	0.97945	0.00005
		545.1728, 577.9081, 617.9264	C	1.19755	0.86172	0.00006
		659.609, 662.844, 685.4863	C	0.00892	0.12198	0.00004
		740.6954, 778.6514, 808.7336	C	2.40200	0.18446	0.00003
		816.8664, 856.2646, 857.5635	C	2.38132	-1.23093	0.00010
		893.6522, 930.4582, 959.353	C	-0.04778	-1.28083	0.00001
		969.8473, 978.5591, 1028.561	C	1.19963	-1.95447	0.00009
		1053.638, 1067.824, 1125.534	C	-2.41499	0.36204	0.00010
		1138.669, 1175.141, 1177.134	C	-2.48199	-1.04077	0.00008
		1212.905, 1222.791, 1242.714	C	-1.35365	-1.85760	0.00001
		1289.258, 1335.113, 1364.605	H	-1.31245	3.18958	0.00030
		1405.079, 1422.666, 1443.701	H	-3.32541	0.95032	0.00015
		1462.199, 1467.719, 1514.214	H	-3.46005	-1.51061	0.00011
		1573.63, 1623.589, 1637.39	H	-1.46762	-2.93608	0.00005
		2999.679, 3016.457, 3157.369	H	1.22818	-3.03904	0.00009
		3158.408, 3167.87, 3174.315	H	3.32538	-1.76504	0.00000
		3181.327, 3184.091, 3208.089	H	3.35213	0.70798	0.00017
			H	1.21927	2.86140	0.87657
			H	1.21854	2.86054	0.87766
A2R52H	1.41036, 1.19512, 0.65211	85.6747, 164.0514, 219.5089	C	-0.78391	2.34018	0.00014
		235.3543, 423.7538, 447.3318	C	0.78390	2.34018	0.00012
		453.055, 474.2656, 511.0779	C	1.17382	0.87245	0.00001
		552.6746, 565.6852, 630.9546	C	-1.17383	0.87245	0.00004
		644.2181, 666.5684, 761.3488	C	0.00000	0.09142	0.00000
		766.0514, 799.6823, 815.9587	C	-2.39257	0.23654	0.00002
		838.3509, 856.8868, 888.925	C	-2.42328	-1.18457	0.00004
		913.2981, 945.9971, 975.3811	C	0.00000	-1.32057	0.00003
		984.5958, 1013.422, 1023.635	C	-1.27405	-1.94885	0.00002
		1038.13, 1065.049, 1106.537	C	2.39257	0.23655	0.00001
		1170.877, 1177.028, 1196.821	C	2.42328	-1.18456	0.00004
		1235.083, 1242.175, 1245.419	C	1.27405	-1.94884	0.00000
		1249.208, 1280.098, 1307.44	H	3.32468	0.79167	0.00006
		1386.556, 1393.677, 1449.184	H	3.38736	-1.68205	0.00011
		1463.871, 1470.6, 1496.875	H	1.34057	-3.03174	0.00008
		1502.527, 1532.966, 1636.878	H	-1.34056	-3.03175	0.00003
		1639.264, 1659.333, 3033.115	H	-3.38736	-1.68205	0.00003
		3043.176, 3055.386, 3075.498	H	-3.32469	0.79166	0.00005
		3155.721, 3155.966, 3166.161	H	-1.18309	2.85754	0.87711
		3167.009, 3179.388, 3180.612	H	-1.18290	2.85746	0.87753
			H	1.18323	2.85778	0.87692
			H	1.18274	2.85723	0.87772

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS1	1.43116, 1.20327, 0.65368	-732.9177, 128.8627, 160.6037	C	0.04125	2.40732	0.00083
		180.3818, 213.3142, 244.1654	C	-1.24500	1.99142	0.00135
		367.9618, 422.289, 458.3417	C	-1.34775	0.53122	0.00064
		489.6633, 515.6901, 554.1845	C	0.88945	1.19425	0.00031
		562.8106, 619.0876, 650.487	C	0.00152	0.09015	0.00016
		665.2671, 684.147, 760.7001	C	2.24263	0.93404	0.00003
		772.4443, 799.573, 814.0807	C	2.67878	-0.42211	0.00046
		839.6454, 849.0038, 861.1132	C	0.39314	-1.24823	0.00024
		922.6599, 929.8134, 952.109	C	1.79873	-1.48654	0.00060
		977.2957, 987.5613, 1015.154	C	-2.34561	-0.41794	0.00064
		1032.398, 1057.29, 1092.857	C	-1.97699	-1.79228	0.00010
		1169.789, 1198.267, 1207.921	C	-0.65902	-2.20842	0.00030
		1239.708, 1257.731, 1266.471	H	0.39960	3.42709	0.00079
		1376.66, 1402.949, 1447.427	H	-2.45305	2.97252	0.00083
		1451.173, 1473.504, 1511.997	H	-3.39475	-0.14403	0.00105
		1517.85, 1630.734, 1645.007	H	-2.76487	-2.53710	0.00006
		1655.86, 2651.014, 3161.484	H	-0.42562	-3.26788	0.00066
		3163.372, 3171.867, 3174.815	H	2.17645	-2.50350	0.00099
		3184.717, 3187.355, 3218.189	H	3.74499	-0.61992	0.00073
			H	2.97913	1.73047	0.00015
			H	-3.08872	3.50497	0.01359
TS2	1.46000, 1.20441, 0.66827	-300.059, 157.6491, 177.687	C	-0.83637	2.25229	0.09254
		183.1713, 228.3167, 250.0121	C	0.52999	2.34695	0.09872
		380.9903, 422.7254, 462.4449	C	1.10283	0.99853	0.04448
		470.9302, 517.9014, 560.4033	C	-1.21220	0.82586	0.06239
		581.4629, 617.716, 668.5148	C	0.00354	0.10670	0.02762
		671.9354, 696.419, 754.0365	C	-2.38947	0.10952	0.05759
		768.4872, 788.4441, 817.1647	C	-2.32400	-1.31177	0.01762
		848.0358, 878.7151, 916.5276	C	0.10577	-1.28374	0.01541
		929.7666, 930.9945, 977.4929	C	-1.12583	-1.99961	0.01948
		987.1036, 1028.793, 1035.771	C	2.37341	0.46008	0.01402
		1057.246, 1096.852, 1113.252	C	2.51485	-0.95447	0.03109
		1176.233, 1204.016, 1222.994	C	1.42906	-1.81065	0.04525
		1246.274, 1272.805, 1330.808	H	1.09860	3.26602	0.13206
		1380.023, 1417.507, 1444.069	H	3.26046	1.08458	0.02434
		1455.777, 1486.482, 1509.888	H	3.51505	-1.37270	0.05418
		1516.542, 1633.627, 1649.02	H	1.58559	-2.88369	0.07774
		1659.332, 3160.886, 3161.461	H	-1.12363	-3.08404	0.05100
		3170.271, 3171.544, 3184.173	H	-3.25287	-1.87126	0.01403
		3185.116, 3209.285, 3228.236	H	-3.35775	0.59815	0.07894
			H	-1.22679	2.74859	2.08353
			H	-1.52800	3.07623	0.19448

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS3	1.50926, 1.21951, 0.67655	1017.592, 158.8464, 199.9855	C	-0.70996	2.32413	0.02175
		219.0254, 370.4618, 420.5196	C	0.72517	2.42513	0.09341
		465.7205, 469.7029, 515.7124	C	1.13429	0.99134	0.01274
		563.1697, 581.5858, 586.0134	C	-1.18235	0.90538	0.01550
		657.1252, 674.0994, 691.8641	C	0.00154	0.14592	0.01737
		771.9919, 779.8376, 811.343	C	-2.39257	0.24651	0.00262
		819.0084, 853.3095, 893.2031	C	-2.38836	-1.17570	0.00182
		931.8761, 950.3252, 985.9964	C	0.04192	-1.25482	0.00228
		999.2526, 1019.371, 1035.054	C	-1.21816	-1.91399	0.00492
		1056.926, 1090.752, 1142.709	C	2.38099	0.39746	0.00034
		1180.332, 1198.636, 1225.036	C	2.46581	-1.02091	0.00791
		1240.806, 1250.621, 1265.106	C	1.34282	-1.83069	0.00631
		1341.425, 1384.427, 1399.142	H	3.28310	0.99934	0.00359
		1450.283, 1458.358, 1484.983	H	3.44614	-1.48432	0.01257
		1519.51, 1627.099, 1637.992	H	1.45668	-2.90993	0.01003
		1656.949, 2151.579, 3160.05	H	-1.26429	-2.99802	0.01722
		3161.322, 3162.072, 3170.955	H	-3.33921	-1.69682	0.00747
		3175.326, 3184.978, 3187.287	H	-3.33792	0.77857	0.00373
			H	-0.08499	2.69672	0.99476
			H	-1.36634	3.17585	0.17603
TS4	1.40629, 1.18430, 0.65339	-663.4584, 113.2598, 166.5378	C	-0.44291	2.38518	0.15502
		195.5064, 240.2032, 387.3528	C	1.07880	2.18575	0.17303
		415.0508, 422.3491, 461.6543	C	1.25119	0.73648	0.06344
		479.9208, 509.0039, 512.5101	C	-1.07135	1.00517	0.02523
		554.5374, 586.2847, 643.4207	C	-0.00934	0.08462	0.01801
		653.1332, 685.1034, 764.0237	C	-2.35734	0.52091	0.01022
		790.4238, 813.8793, 825.0913	C	-2.56187	-0.88845	0.05376
		847.8424, 869.8592, 917.2111	C	-0.17619	-1.31355	0.01775
		922.2652, 942.7957, 983.9538	C	-1.51661	-1.78862	0.05529
		998.8308, 1024.112, 1028.555	C	2.39762	-0.04917	0.07065
		1044.509, 1064.004, 1128.033	C	2.26136	-1.45212	0.02587
		1146.913, 1178.889, 1200.691	C	1.01977	-2.07498	0.01639
		1215.651, 1234.763, 1249.17	H	1.69753	2.89517	0.93158
		1260.235, 1278.608, 1372.074	H	3.38155	0.40523	0.10186
		1381.317, 1414.637, 1449.29	H	3.15470	-2.06672	0.02705
		1458.783, 1484.678, 1524.807	H	0.96615	-3.15862	0.04703
		1617.24, 1626.455, 1653.144	H	-1.71402	-2.85492	0.08086
		2831.244, 3005.804, 3085.291	H	-3.57955	-1.26237	0.08399
		3159.487, 3160.822, 3169.446	H	-3.21720	1.18242	0.00351
		3175.053, 3182.959, 3188.018	H	-0.71377	2.84594	1.11526
			H	-0.75585	3.09711	0.61229
			H	1.54178	2.80936	1.75205

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS5	1.42509, 1.17583 0.64684	-1290.1429, 160.9668, 178.3319	C	-1.06411	2.14747	0.10254
		195.5291, 242.8594, 307.8906	C	0.44086	2.32226	0.12555
		381.1747, 419.9608, 480.7207	C	1.04621	1.07194	0.05971
		484.0802, 504.7729, 511.2934	C	-1.27406	0.67700	0.07407
		546.1306, 588.9151, 620.5483	C	-0.00198	0.08219	0.02737
		665.3861, 684.0768, 687.0399	C	-2.39433	-0.14222	0.06994
		744.8536, 773.2547, 806.255	C	-2.20230	-1.53968	0.01702
		820.5892, 852.4098, 857.1278	C	0.21966	-1.30293	0.02416
		891.7283, 953.5657, 961.5138	C	-0.94100	-2.11808	0.03073
		970.2687, 977.4101, 1041.186	C	2.38392	0.60875	0.01928
		1058.674, 1070.273, 1104.878	C	2.61226	-0.77031	0.04383
		1122.955, 1162.566, 1177.036	C	1.58422	-1.71700	0.06467
		1211.256, 1212.612, 1241.055	H	0.93463	3.28351	0.15205
		1290.921, 1309.917, 1333.041	H	3.21737	1.30115	0.03687
		1341.174, 1361.916, 1411.572	H	3.63755	-1.12368	0.07647
		1414.997, 1450.229, 1468.565	H	1.82627	-2.77288	0.11472
		1514.687, 1567.089, 1613.121	H	-0.84244	-3.19765	0.07060
		1623.137, 3083.499, 3159.317	H	-3.07449	-2.18442	0.01432
		3160.046, 3171.925, 3176.048	H	-3.39859	0.26504	0.10547
		3183.616, 3186.623, 3218.695	H	-1.44826	2.64730	0.99067
			H	-1.64343	2.72992	0.82207
			H	-1.66472	3.13531	1.87091
TS6	1.36048, 1.17601, 0.64414	-871.5455, 120.3469, 166.0348	C	1.14075	2.11020	0.03286
		197.0162, 238.9329, 290.1818	C	-0.37836	2.39367	0.18937
		349.3253, 423.9356, 463.2573	C	-1.02706	1.02698	0.05582
		466.152, 477.4358, 511.5174	C	1.28470	0.62339	0.06693
		553.026, 584.9715, 636.1963	C	-0.00852	0.05404	0.02668
		650.2546, 668.0886, 761.8176	C	2.37864	-0.21515	0.07689
		785.4119, 804.6561, 815.2845	C	2.16195	-1.61712	0.03974
		841.0303, 876.7976, 893.7061	C	-0.25118	-1.33425	0.02413
		916.3493, 958.8596, 977.908	C	0.89702	-2.17120	0.01567
		986.6564, 1019.608, 1030.617	C	-2.33762	0.61452	0.00345
		1039.842, 1065.044, 1110.711	C	-2.61336	-0.77830	0.06456
		1161.091, 1177.451, 1198.327	C	-1.61434	-1.73106	0.07274
		1213.956, 1231.797, 1244.777	H	-3.15942	1.32232	0.02125
		1249.13, 1281.984, 1308.012	H	-3.64857	-1.09986	0.10474
		1347.83, 1388.81, 1391.443	H	-1.86788	-2.78497	0.11594
		1448.37, 1458.743, 1472.077	H	0.77804	-3.24897	0.05045
		1484.414, 1511.935, 1534.022	H	3.02427	-2.27507	0.04937
		1633.974, 1637.746, 1656.608	H	3.39156	0.17139	0.10318
		3027.335, 3065.792, 3093.37	H	1.79093	2.67104	0.70586
		3157.57, 3158.75, 3168.569	H	1.47720	2.50193	1.05274
		3170.818, 3181.16, 3182.756	H	-0.74282	3.11094	0.55119
			H	-0.58825	2.82205	1.17569
			H	1.74915	2.95489	2.06805

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS7-trial-1	1.49336, 1.21140, 0.66884	-895.3748, 158.6706, 211.362	C	0.55900	2.39286	0.00000
		237.1969, 359.1814, 421.1159	C	-0.77537	2.23710	0.00000
		454.9893, 476.6342, 515.5637	C	-1.22298	0.85816	0.00000
		551.3945, 551.7173, 612.3648	C	1.11128	1.01452	0.00000
		643.0252, 654.7657, 664.8882	C	0.00000	0.13413	0.00000
		675.0342, 718.1834, 759.1463	C	2.37250	0.46093	0.00000
		770.1884, 810.9212, 812.3008	C	2.49509	-0.95876	0.00000
		841.1713, 861.5861, 923.6991	C	0.08274	-1.25776	0.00000
		932.3504, 978.8548, 989.0049	C	1.40093	-1.80129	0.00000
		1010.139, 1030.049, 1055.692	C	-2.40676	0.15892	0.00000
		1084.367, 1168.609, 1195.752	C	-2.35091	-1.26187	0.00000
		1204.312, 1236.983, 1257.512	C	-1.15678	-1.95924	0.00000
		1265.769, 1371.736, 1407.083	H	1.12453	3.31120	0.00000
		1447.779, 1448.897, 1471.198	H	-2.26811	3.96265	0.00000
		1513.741, 1543.963, 1632.034	H	-3.36308	0.66943	0.00000
		1645.461, 1659.371, 3163.455	H	-3.28367	-1.81420	0.00000
		3166.371, 3173.82, 3179.535	H	-1.16416	-3.04397	0.00000
		3186.429, 3191.032, 3246.314	H	1.54377	-2.87660	0.00000
			H	3.49070	-1.38820	0.00000
			H	3.26753	1.07345	0.00000
TS7-trial-2	1.48915 , 1.20904, 0.66728	-822.2677, 157.163, 210.3379	C	0.52914	2.40135	0.00000
		234.8393, 353.0066, 420.4992	C	-0.80006	2.22003	0.00000
		452.8911, 469.6312, 514.8202	C	-1.23479	0.83897	0.00000
		540.3794, 549.6618, 572.6755	C	1.09948	1.02843	0.00000
		602.5868, 617.4639, 640.1934	C	0.00000	0.13303	0.00000
		666.466, 688.1323, 754.7173	C	2.36816	0.49249	0.00000
		767.5411, 805.3775, 810.9712	C	2.50965	-0.92551	0.00000
		838.3158, 855.7509, 923.8126	C	0.10136	-1.25769	0.00000
		932.9581, 979.5196, 989.6708	C	1.42706	-1.78282	0.00000
		1005.825, 1029.115, 1055.33	C	-2.40849	0.12356	0.00000
		1081.094, 1167.817, 1193.599	C	-2.33229	-1.29608	0.00000
		1202.799, 1233.185, 1254.592	C	-1.12822	-1.97627	0.00000
		1264.212, 1369.274, 1406.025	H	1.08152	3.32759	0.00000
		1445.108, 1448.951, 1469.861	H	-2.46920	4.05644	0.00000
		1513.59, 1542.68, 1630.423	H	-3.37115	0.62191	0.00000
		1644.506, 1658.469, 3164.026	H	-3.25708	-1.86154	0.00000
		3167.088, 3174.55, 3180.371	H	-1.12021	-3.06096	0.00000
		3186.935, 3191.768, 3246.961	H	1.58449	-2.85606	0.00000
			H	3.51099	-1.34137	0.00000
			H	3.25467	1.11714	0.00000

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS7-trial-3	1.48470, 1.20657, 0.66563	-749.0783, 155.4801, 209.1182	C	0.49671	2.40932	0.00000
		232.505, 346.105, 419.4741	C	-0.82740	2.20322	0.00000
		449.3895, 452.744, 499.7499	C	-1.24659	0.81874	0.00000
		514.2243, 532.0368, 542.3838	C	1.08660	1.04308	0.00000
		548.0892, 612.8604, 636.5252	C	0.00000	0.13187	0.00000
		663.6266, 683.6535, 750.3256	C	2.36297	0.52602	0.00000
		766.2124, 802.0074, 809.9104	C	2.52470	-0.88987	0.00000
		836.6228, 852.1524, 923.8765	C	0.12129	-1.25733	0.00000
		933.4542, 980.0955, 990.2535	C	1.45465	-1.76278	0.00000
		1002.108, 1028.336, 1055.051	C	-2.40940	0.08614	0.00000
		1078.665, 1167.113, 1191.586	C	-2.31176	-1.33201	0.00000
		1201.867, 1229.775, 1252.959	C	-1.09749	-1.99392	0.00000
		1262.869, 1367.272, 1405.1	H	1.03533	3.34366	0.00000
		1442.684, 1448.973, 1469.035	H	-2.68079	4.14127	0.00000
		1513.446, 1541.525, 1628.976	H	-3.37889	0.57103	0.00000
		1643.689, 1657.532, 3164.474	H	-3.22792	-1.91124	0.00000
		3167.663, 3175.171, 3180.929	H	-1.07324	-3.07835	0.00000
		3187.347, 3192.225, 3246.601	H	1.62763	-2.83361	0.00000
			H	3.53194	-1.29117	0.00000
			H	3.24024	1.16348	0.00000
TS7-trial-4	1.48021, 1.20392, 0.66392	-679.5415, 153.6305, 207.6712	C	0.46145	2.41688	0.00000
		230.2744, 338.5417, 408.4678	C	-0.85753	2.18635	0.00000
		425.0808, 427.0755, 456.084	C	-1.25845	0.79733	0.00000
		510.8991, 514.0371, 521.5396	C	1.07248	1.05864	0.00000
		546.6846, 610.4791, 633.6892	C	0.00000	0.13071	0.00000
		662.1898, 681.8817, 746.1927	C	2.35679	0.56190	0.00000
		765.4428, 799.6454, 809.1322	C	2.54030	-0.85137	0.00000
		835.5873, 849.8322, 923.9137	C	0.14273	-1.25652	0.00000
		933.8619, 980.5814, 990.7545	C	1.48395	-1.74081	0.00000
		998.9906, 1027.7, 1054.838	C	-2.40937	0.04641	0.00000
		1076.948, 1166.515, 1189.889	C	-2.28896	-1.36987	0.00000
		1201.294, 1226.955, 1251.995	C	-1.06422	-2.01221	0.00000
		1261.752, 1365.694, 1404.302	H	0.98565	3.35949	0.00000
		1440.606, 1448.947, 1468.597	H	-2.90708	4.21195	0.00000
		1513.306, 1540.345, 1627.754	H	-3.38618	0.51635	0.00000
		1643.007, 1656.643, 3164.787	H	-3.19576	-1.96358	0.00000
		3168.108, 3175.688, 3181.2	H	-1.02271	-3.09609	0.00000
		3187.664, 3192.396, 3245.466	H	1.67357	-2.80881	0.00000
			H	3.55363	-1.23697	0.00000
			H	3.22395	1.21297	0.00000

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS7-trial-5	1.47589, 1.20099, 0.66216	-612.8405, 151.6116, 205.9491	C	0.42332	2.42405	0.00000
		228.174, 330.4052, 362.9657	C	-0.89039	2.16912	0.00000
		375.5861, 421.4647, 449.8738	C	-1.27040	0.77467	0.00000
		499.6888, 512.5968, 513.7141	C	1.05699	1.07519	0.00000
		545.7365, 608.6697, 631.4094	C	0.00000	0.12961	0.00000
		661.402, 680.8734, 742.4474	C	2.34948	0.60033	0.00000
		764.9994, 797.9302, 808.6416	C	2.55638	-0.80972	0.00000
		834.9708, 848.3989, 923.9437	C	0.16578	-1.25513	0.00000
		934.1918, 980.99, 991.1819	C	1.51500	-1.71666	0.00000
		996.4469, 1027.239, 1054.725	C	-2.40828	0.00426	0.00000
		1075.788, 1166.041, 1188.553	C	-2.26370	-1.40968	0.00000
		1200.955, 1224.702, 1251.436	C	-1.02820	-2.03105	0.00000
		1260.865, 1364.513, 1403.622	H	0.93231	3.37510	0.00000
		1438.926, 1448.871, 1468.449	H	-3.15066	4.26377	0.00000
		1513.188, 1539.025, 1626.76	H	-3.39285	0.45774	0.00000
		1642.438, 1655.859, 3164.933	H	-3.16029	-2.01864	0.00000
		3168.467, 3176.091, 3181.355	H	-0.96833	-3.11406	0.00000
		3187.871, 3192.477, 3243.791	H	1.72244	-2.78133	0.00000
			H	3.57598	-1.17841	0.00000
			H	3.20556	1.26584	0.00000
TS7-trial-6	1.47174, 1.19779, 0.66035	-551.5418, 149.3576, 203.858	C	0.38301	2.43067	0.00000
		226.1442, 316.3334, 321.2499	C	-0.92522	2.15135	0.00000
		329.587, 420.9856, 446.7391	C	-1.28226	0.75098	0.00000
		494.8643, 505.0385, 513.6902	C	1.04039	1.09243	0.00000
		545.0854, 607.2051, 629.5583	C	0.00000	0.12858	0.00000
		661.0399, 680.2166, 739.1632	C	2.34106	0.64062	0.00000
		764.7745, 796.6759, 808.3875	C	2.57251	-0.76561	0.00000
		834.6224, 847.5292, 923.9916	C	0.19000	-1.25313	0.00000
		934.4577, 981.3337, 991.5454	C	1.54719	-1.69065	0.00000
		994.4217, 1026.97, 1054.737	C	-2.40615	-0.03968	0.00000
		1075.02, 1165.677, 1187.529	C	-2.23635	-1.45076	0.00000
		1200.785, 1222.903, 1251.158	C	-0.99001	-2.05003	0.00000
		1260.189, 1363.713, 1403.044	H	0.87600	3.39028	0.00000
		1437.657, 1448.759, 1468.484	H	-3.40638	4.29910	0.00000
		1513.11, 1537.621, 1625.976	H	-3.39866	0.39618	0.00000
		1641.969, 1655.2, 3164.932	H	-3.12199	-2.07551	0.00000
		3168.791, 3176.394, 3181.534	H	-0.91094	-3.13179	0.00000
		3187.989, 3192.626, 3241.809	H	1.77333	-2.75151	0.00000
			H	3.59839	-1.11641	0.00000
			H	3.18527	1.32109	0.00000

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS7-trial-7	1.46883, 1.19384, 0.65857	-494.9354, 146.801, 201.2727	C	0.33516	2.43787	0.00000
		224.0429, 274.7286, 288.3889	C	-0.96652	2.13088	0.00000
		313.9406, 420.8985, 443.8966	C	-1.29535	0.72357	0.00000
		492.2426, 498.8444, 513.7973	C	1.02035	1.11296	0.00000
		544.6736, 605.9943, 628.0492	C	0.00000	0.12794	0.00000
		660.9458, 679.7577, 736.2162	C	2.33016	0.68842	0.00000
		764.734, 795.7613, 808.3292	C	2.59046	-0.71274	0.00000
		834.4453, 846.9999, 924.0969	C	0.21848	-1.24963	0.00000
		934.7376, 981.6467, 991.8863	C	1.58446	-1.65874	0.00000
		992.8048, 1026.847, 1054.841	C	-2.40240	-0.09047	0.00000
		1074.465, 1165.418, 1186.724	C	-2.20319	-1.49769	0.00000
		1200.716, 1221.567, 1251.119	C	-0.94466	-2.07088	0.00000
		1259.647, 1363.229, 1402.565	H	0.80922	3.40714	0.00000
		1436.763, 1448.629, 1468.647	H	-3.70434	4.28170	0.00000
		1513.078, 1536.068, 1625.373	H	-3.40385	0.32454	0.00000
		1641.597, 1654.707, 3164.786	H	-3.07564	-2.14069	0.00000
		3169.078, 3176.584, 3181.55	H	-0.84312	-3.15074	0.00000
		3188.013, 3192.666, 3239.641	H	1.83262	-2.71467	0.00000
			H	3.62335	-1.04235	0.00000
			H	3.16006	1.38621	0.00000
TS7-trial-8	1.46760, 1.18895, 0.65683	-442.9747, 143.6231, 197.9133	C	-0.27932	2.44547	0.00000
		220.9846, 237.4065, 255.681	C	1.01434	2.10704	0.00000
		305.4567, 420.9068, 441.0614	C	1.30964	0.69218	0.00000
		490.5685, 493.9276, 513.8819	C	-0.99650	1.13697	0.00000
		544.3332, 604.9937, 626.7924	C	0.00000	0.12787	0.00000
		660.9956, 679.4153, 733.5253	C	-2.31621	0.74420	0.00000
		764.8265, 795.0794, 808.2927	C	-2.60987	-0.65031	0.00000
		834.357, 846.6564, 924.2447	C	-0.25137	-1.24412	0.00000
		934.9895, 981.9256, 991.5074	C	-1.62680	-1.62013	0.00000
		992.208, 1026.784, 1054.955	C	2.39661	-0.14845	0.00000
		1074.043, 1165.272, 1186.109	C	2.16352	-1.55049	0.00000
		1200.666, 1220.514, 1251.223	C	0.89160	-2.09317	0.00000
		1259.11, 1362.88, 1402.163	H	-0.73107	3.42551	0.00000
		1436.094, 1448.532, 1468.77	H	4.04486	4.19756	0.00000
		1513.069, 1534.535, 1624.838	H	3.40787	0.24225	0.00000
		1641.304, 1654.295, 3164.609	H	3.02028	-2.21423	0.00000
		3169.353, 3176.673, 3181.282	H	0.76402	-3.17025	0.00000
		3187.999, 3192.587, 3237.474	H	-1.90037	-2.66977	0.00000
			H	-3.65033	-0.95515	0.00000
			H	-3.12909	1.46171	0.00000

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS7-trial-9	1.47225, 1.18143, 0.65545	-394.9788, 139.2306, 192.7602	C	-0.20062	2.45578	0.00000
		202.8918, 213.0449, 234.1532	C	1.08067	2.07338	0.00000
		297.2469, 420.944, 438.2094	C	1.32811	0.64947	0.00000
		489.4318, 489.9316, 513.7465	C	-0.96202	1.17190	0.00000
		543.8888, 604.0955, 625.765	C	0.00000	0.12985	0.00000
		661.0924, 679.1516, 730.5001	C	-2.29426	0.82373	0.00000
		764.991, 794.5185, 808.0891	C	-2.63432	-0.56014	0.00000
		834.2791, 846.4295, 924.5291	C	-0.29702	-1.23298	0.00000
		935.4878, 982.2352, 990.5838	C	-1.68434	-1.56244	0.00000
		992.647, 1026.707, 1054.995	C	2.38622	-0.22707	0.00000
		1073.689, 1165.198, 1185.651	C	2.10628	-1.62050	0.00000
		1200.557, 1219.882, 1251.336	C	0.81674	-2.11999	0.00000
		1258.522, 1362.478, 1401.718	H	-0.61984	3.45033	0.00000
		1435.447, 1448.56, 1468.579	H	4.50448	3.90219	0.00000
		1513.074, 1532.786, 1624.196	H	3.40989	0.13048	0.00000
		1640.965, 1653.824, 3164.672	H	2.94020	-2.31267	0.00000
		3169.462, 3176.771, 3179.835	H	0.65293	-3.19216	0.00000
		3188.022, 3192.119, 3235.347	H	-1.99318	-2.60224	0.00000
			H	-3.68443	-0.82989	0.00000
			H	-3.08267	1.56803	0.00000
TS8-trial-1	1.44218, 1.18174, 0.65214	-777.9102, 168.0204, 189.1782	C	0.60063	2.41301	0.00011
		217.9333, 276.8749, 303.2542	C	-0.88284	2.17420	0.00007
		329.8726, 418.9539, 455.8732	C	-1.24884	0.83567	0.00001
		478.6717, 486.8347, 507.3233	C	1.11547	0.97205	0.00007
		535.132, 574.4181, 633.2285	C	0.00511	0.11352	0.00001
		659.1831, 675.6444, 739.7706	C	2.38188	0.42353	0.00007
		773.699, 803.3936, 808.0356	C	2.50564	-0.98731	0.00002
		836.9812, 860.0562, 894.8323	C	0.09305	-1.28777	0.00005
		930.9534, 972.4491, 980.6776	C	1.40478	-1.82715	0.00004
		999.8123, 1012.961, 1050.346	C	-2.43952	0.08977	0.00005
		1066.231, 1125.016, 1134.301	C	-2.35201	-1.31354	0.00011
		1175.401, 1189.135, 1211.895	C	-1.14325	-2.00157	0.00011
		1238.389, 1261.084, 1305.449	H	-2.60593	4.09667	0.00009
		1359.462, 1381.718, 1403.753	H	-3.40422	0.58196	0.00005
		1443.071, 1455.227, 1461.911	H	-3.27363	-1.88576	0.00015
		1512.69, 1573.576, 1617.573	H	-1.13824	-3.08588	0.00015
		1636.378, 3018.712, 3042.448	H	1.54423	-2.90306	0.00009
		3159.382, 3162.31, 3170.032	H	3.49953	-1.42139	0.00002
		3179.284, 3183.179, 3193.349	H	3.27250	1.04242	0.00012
			H	0.93259	2.97435	0.88107
			H	0.93256	2.97428	0.88136

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
		-588.61, 167.8195, 188.7507	C	0.53610	2.42651	0.00011
		208.6086, 230.2328, 242.8459	C	-0.94143	2.14931	0.00007
		284.6616, 418.8458, 456.2642	C	-1.26918	0.79980	0.00001
		478.9308, 482.6197, 507.2196	C	1.09016	1.00022	0.00006
		535.1916, 575.2147, 633.5984	C	0.00363	0.11170	0.00001
		659.6612, 676.9051, 739.954	C	2.37107	0.48666	0.00007
		773.8241, 803.3314, 808.6322	C	2.53359	-0.92032	0.00002
		839.3644, 859.9616, 894.8198	C	0.13014	-1.28670	0.00005
		930.6665, 972.2927, 980.5064	C	1.45617	-1.79000	0.00004
		998.7985, 1012.23, 1049.996	C	-2.43891	0.02130	0.00005
TS8-trial-2	1.43639, 1.17993, 0.65040	1066.186, 1125.677, 1133.831	C	-2.31311	-1.37925	0.00011
		1175.498, 1188.969, 1211.525	C	-1.08614	-2.03405	0.00011
		1238.39, 1260.675, 1304.834	H	-2.86022	4.16322	0.00010
		1359.456, 1379.251, 1403.84	H	-3.41717	0.48597	0.00005
		1442.926, 1455.027, 1461.649	H	-3.21881	-1.97638	0.00015
		1512.454, 1573.142, 1617.245	H	-1.05156	-3.11783	0.00015
		1636.476, 3017.514, 3040.989	H	1.62492	-2.86171	0.00008
		3159.241, 3161.765, 3169.893	H	3.53902	-1.32697	0.00002
		3178.999, 3183.085, 3192.874	H	3.24438	1.12975	0.00012
			H	0.85352	2.99653	0.88097
			H	0.85348	2.99646	0.88126
		-445.1541, 157.721, 168.2399	C	0.46774	2.43892	0.00011
		179.0869, 190.4552, 223.3856	C	-1.00207	2.12091	0.00007
		285.5184, 418.8665, 456.5081	C	-1.28964	0.76153	0.00001
		479.257, 480.9645, 507.4735	C	1.06265	1.02928	0.00006
		535.4053, 575.7183, 633.8515	C	0.00210	0.10988	0.00001
		660.0192, 678.1071, 740.0958	C	2.35779	0.55294	0.00007
		773.9327, 803.5907, 809.0339	C	2.56092	-0.84881	0.00002
		841.3067, 859.8621, 894.7281	C	0.16908	-1.28435	0.00005
		930.3452, 972.2277, 980.3922	C	1.50905	-1.74921	0.00004
		998.2791, 1011.952, 1049.846	C	-2.43643	-0.05053	0.00005
TS8-trial-3	1.43070, 1.17795, 0.64863	1066.198, 1126.162, 1133.679	C	-2.27038	-1.44697	0.00011
		1175.653, 1188.907, 1211.522	C	-1.02522	-2.06633	0.00011
		1238.587, 1260.582, 1304.554	H	-3.12431	4.21527	0.00011
		1359.608, 1377.777, 1403.954	H	-3.42798	0.38510	0.00006
		1442.983, 1454.937, 1461.51	H	-3.15859	-2.06986	0.00015
		1512.322, 1573.035, 1617.048	H	-0.95967	-3.14868	0.00015
		1636.772, 3016.617, 3039.86	H	1.70861	-2.81562	0.00008
		3159.036, 3161.432, 3169.853	H	3.57767	-1.22632	0.00002
		3178.804, 3182.95, 3192.559	H	3.21220	1.22096	0.00012
			H	0.76929	3.01777	0.88089
			H	0.76925	3.01770	0.88117

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
		-362.7356, 105.1516, 114.6625	C	0.39731	2.44985	0.00011
		120.1622, 168.3465, 211.1821	C	-1.06279	2.08918	0.00007
		233.818, 421.1111, 437.5193	C	-1.30965	0.72157	0.00001
		466.6287, 471.2782, 504.8246	C	1.03359	1.05844	0.00006
		523.3626, 554.8406, 630.8418	C	0.00062	0.10813	0.00001
		657.7052, 681.5392, 753.663	C	2.34224	0.62060	0.00007
		777.8671, 797.3852, 802.2383	C	2.58669	-0.77454	0.00002
		851.1427, 855.2598, 922.1526	C	0.20878	-1.28060	0.00005
		947.6707, 956.9692, 987.4637	C	1.56190	-1.70563	0.00004
		1011.987, 1028.336, 1050.904	C	-2.43197	-0.12406	0.00005
TS8-trial-4	1.42509, 1.17583, 0.64684	1066.372, 1097.515, 1136.334	C	-2.22477	-1.51503	0.00011
		1175.767, 1192.014, 1213.714	C	-0.96192	-2.09744	0.00011
		1237.953, 1250.915, 1314.963	H	-3.39254	4.25603	0.00011
		1360.801, 1389.114, 1403.976	H	-3.43606	0.28185	0.00006
		1428.098, 1462.494, 1480.145	H	-3.09423	-2.16384	0.00015
		1523.869, 1605.188, 1623.983	H	-0.86457	-3.17740	0.00015
		1644.318, 3030.549, 3061.398	H	1.79291	-2.76568	0.00008
		3159.491, 3165.3, 3170.914	H	3.61414	-1.12190	0.00002
		3183.174, 3185.143, 3199.976	H	3.17655	1.31354	0.00012
			H	0.68187	3.03734	0.88086
			H	0.68184	3.03726	0.88114
		-258.1643, 90.0284, 99.8646	C	0.32276	2.45918	0.00011
		168.3111, 189.9157, 224.0338	C	-1.12596	2.05417	0.00007
		286.5861, 419.1748, 456.9528	C	-1.32945	0.67907	0.00001
		479.7179, 480.1571, 508.4401	C	1.00205	1.08831	0.00006
		535.9612, 576.3483, 634.1012	C	-0.00094	0.10638	0.00000
		660.4652, 679.7622, 740.2365	C	2.32370	0.69144	0.00007
		774.2924, 804.3457, 809.4695	C	2.61137	-0.69543	0.00002
		843.8314, 859.6105, 894.6757	C	0.25040	-1.27527	0.00005
		929.9945, 972.3983, 980.3673	C	1.61605	-1.65792	0.00004
		998.1794, 1011.998, 1050.006	C	-2.42492	-0.20117	0.00005
TS8-trial-5	1.41942, 1.17356, 0.64498	1066.379, 1127.466, 1133.969	C	-2.17457	-1.58508	0.00011
		1176.083, 1188.997, 1212.45	C	-0.89433	-2.12809	0.00011
		1239.241, 1261.17, 1304.569	H	-3.67239	4.27932	0.00011
		1360.235, 1376.82, 1404.223	H	-3.44127	0.17296	0.00006
		1443.614, 1455.211, 1461.296	H	-3.02349	-2.26056	0.00015
		1512.308, 1573.54, 1617.456	H	-0.76359	-3.20452	0.00015
		1637.327, 3015.82, 3038.786	H	1.88006	-2.71026	0.00008
		3158.251, 3161.626, 3169.621	H	3.64911	-1.01078	0.00002
		3178.722, 3182.389, 3192.429	H	3.13610	1.40993	0.00012
			H	0.58926	3.05523	0.88082
			H	0.58922	3.05515	0.88110

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
		-202.2775, 68.7083, 75.2336	C	0.24598	2.46655	0.00011
		168.4848, 189.9915, 224.6011	C	-1.18949	2.01603	0.00007
		286.9545, 419.3385, 457.2051	C	-1.34844	0.63483	0.00000
		479.7093, 480.164, 508.5525	C	0.96879	1.11813	0.00006
		536.0629, 576.6574, 634.1772	C	-0.00245	0.10475	0.00000
		660.5555, 680.0752, 740.2211	C	2.30248	0.76361	0.00007
		774.5339, 804.3466, 809.5762	C	2.63413	-0.61336	0.00002
		844.4067, 859.4295, 894.7447	C	0.29283	-1.26821	0.00005
		930.0017, 972.589, 980.44	C	1.66998	-1.60705	0.00004
		998.2265, 1011.98, 1050.093	C	-2.41522	-0.28005	0.00005
TS8-trial-6	1.41381, 1.17108, 0.64307	1066.51, 1128.41, 1134.069	C	-2.12086	-1.65532	0.00011
		1176.218, 1189.138, 1212.914	C	-0.82400	-2.15721	0.00011
		1239.442, 1261.558, 1304.603	H	-3.96005	4.28590	0.00012
		1360.334, 1376.534, 1404.341	H	-3.44308	0.06123	0.00006
		1443.749, 1455.298, 1461.268	H	-2.94782	-2.35752	0.00015
		1512.36, 1573.618, 1617.733	H	-0.65893	-3.22891	0.00015
		1637.273, 3015.655, 3038.537	H	1.96757	-2.65039	0.00008
		3158.054, 3161.77, 3169.528	H	3.68137	-0.89555	0.00002
		3178.655, 3182.214, 3191.978	H	3.09160	1.50760	0.00012
			H	0.49351	3.07079	0.88080
			H	0.49347	3.07071	0.88109
		-95.6783, 30.8536, 34.4679	C	0.00838	2.47477	0.00011
		168.223, 190.5955, 223.4885	C	-1.37644	1.88578	0.00006
		287.7284, 419.5974, 457.3906	C	-1.39788	0.49532	0.00000
		479.1157, 479.6468, 507.8277	C	0.86062	1.20407	0.00006
		535.8778, 576.9673, 634.1876	C	-0.00632	0.10021	0.00000
		660.6052, 680.115, 739.9579	C	2.22271	0.98198	0.00007
		774.4887, 803.6659, 809.529	C	2.68798	-0.35578	0.00002
		844.711, 858.9362, 894.5874	C	0.42216	-1.23704	0.00005
		930.0057, 972.7651, 980.4947	C	1.82599	-1.43931	0.00004
		997.684, 1011.798, 1049.858	C	-2.36945	-0.52019	0.00006
TS8-trial-7	1.39765, 1.16224, 0.63706	1066.648, 1129.461, 1133.669	C	-1.94166	-1.86002	0.00011
		1175.92, 1189.226, 1213.316	C	-0.60174	-2.23171	0.00011
		1238.892, 1261.799, 1304.388	H	-4.86131	4.19705	0.00015
		1359.888, 1375.846, 1404.167	H	-3.42597	-0.28193	0.00006
		1443.141, 1454.917, 1461.53	H	-2.69561	-2.64007	0.00015
		1512.353, 1572.949, 1617.372	H	-0.33170	-3.28192	0.00015
		1636.769, 3015.665, 3038.574	H	2.22432	-2.44848	0.00008
		3158.959, 3161.525, 3170.066	H	3.75790	-0.53359	0.00003
		3178.04, 3182.892, 3191.482	H	2.93491	1.79994	0.00012
			H	0.19572	3.10028	0.88082
			H	0.19570	3.10020	0.88109

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
		-73.6822, 23.8884, 26.1265	C	-0.07071	2.47243	0.00011
		168.0415, 190.7565, 222.8751	C	-1.43553	1.83842	0.00006
		287.927, 419.3565, 457.2062	C	-1.41118	0.44797	0.00000
		479.1676, 479.4517, 507.9577	C	0.82271	1.23033	0.00006
		535.9891, 576.7449, 634.1775	C	-0.00745	0.09858	0.00000
		660.594, 680.2419, 739.9317	C	2.19129	1.05306	0.00007
		774.248, 803.8209, 809.5127	C	2.70032	-0.26872	0.00002
		844.8301, 859.003, 894.3424	C	0.46473	-1.22391	0.00005
		929.8784, 972.6462, 980.399	C	1.87444	-1.38003	0.00004
		997.4202, 1011.794, 1049.765	C	-2.34899	-0.59879	0.00006
TS8-trial-8	1.39241, 1.15890, 0.63497	1066.357, 1128.754, 1133.669	C	-1.87752	-1.92386	0.00011
		1175.929, 1189.012, 1212.881	C	-0.52613	-2.25152	0.00011
		1238.951, 1261.379, 1304.276	H	-5.16545	4.13767	0.00016
		1359.852, 1375.845, 1404.125	H	-3.41276	-0.39535	0.00006
		1443.199, 1454.984, 1461.331	H	-2.60551	-2.72819	0.00015
		1512.303, 1573.008, 1617.185	H	-0.22193	-3.29233	0.00015
		1636.893, 3015.579, 3038.518	H	2.30563	-2.37559	0.00008
		3158.896, 3161.598, 3169.805	H	3.77551	-0.41123	0.00003
		3178.082, 3182.797, 3191.961	H	2.87632	1.89393	0.00012
			H	0.09618	3.10368	0.88082
			H	0.09616	3.10360	0.88109
		-59.9863, 18.5955, 21.3923	C	-0.14813	2.46760	0.00011
		167.926, 190.794, 222.6456	C	-1.49191	1.79010	0.00006
		288.1108, 419.0698, 456.9785	C	-1.42266	0.40110	0.00000
		479.3676, 479.3908, 508.1603	C	0.78474	1.25488	0.00006
		536.1003, 576.4717, 634.2031	C	-0.00848	0.09694	0.00000
		660.5934, 680.3907, 739.9141	C	2.15829	1.12188	0.00007
		774.0995, 804.0519, 809.5416	C	2.70970	-0.18281	0.00002
		844.9572, 859.154, 894.1395	C	0.50614	-1.20968	0.00005
		929.7694, 972.4739, 980.3102	C	1.92012	-1.32020	0.00004
		997.3739, 1011.763, 1049.787	C	-2.32636	-0.67523	0.00006
TS8-trial-9	1.38723, 1.15536, 0.63283	1066.098, 1127.869, 1133.745	C	-1.81243	-1.98440	0.00011
		1176.037, 1188.822, 1212.193	C	-0.45123	-2.26856	0.00011
		1239.188, 1260.859, 1304.291	H	-5.46761	4.06724	0.00016
		1359.936, 1375.874, 1404.191	H	-3.39613	-0.50619	0.00006
		1443.337, 1455.059, 1461.109	H	-2.51421	-2.81172	0.00015
		1512.233, 1573.198, 1617.194	H	-0.11384	-3.29910	0.00015
		1637.014, 3015.438, 3038.395	H	2.38328	-2.30130	0.00008
		3158.677, 3161.573, 3169.413	H	3.78893	-0.29058	0.00003
		3178.211, 3182.565, 3192.265	H	2.81592	1.98435	0.00012
			H	-0.00152	3.10386	0.88082
			H	-0.00154	3.10378	0.88110

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS9-trial-1	1.38536, 1.16290, 0.64858	-352.7689, 170.2282, 183.449	C	1.15783	2.03723	0.17131
		199.4936, 227.9391, 238.6644	C	-0.30639	2.40683	0.15760
		305.8006, 421.0363, 449.7374	C	-1.00592	1.06506	0.05686
		471.0132, 479.7191, 510.3629	C	1.30070	0.64841	0.09940
		550.1044, 568.7003, 630.0262	C	-0.01389	0.07874	0.03514
		661.3887, 686.9925, 697.2809	C	2.40329	-0.22916	0.09388
		757.3178, 780.5807, 811.0738	C	2.15916	-1.60503	0.02697
		830.7088, 859.6135, 890.2755	C	-0.27017	-1.30146	0.03653
		915.1508, 936.0542, 962.4184	C	0.87147	-2.14426	0.03937
		985.9942, 994.1285, 1036.38	C	-2.32753	0.67277	0.00582
		1055.06, 1072.18, 1129.24	C	-2.62376	-0.71296	0.08280
		1139.043, 1181.067, 1198.364	C	-1.63776	-1.68194	0.09703
		1226.793, 1228.484, 1253.689	H	-3.13795	1.39324	0.00345
		1293.344, 1350.433, 1384.249	H	-3.66298	-1.01818	0.13182
		1413.132, 1426.566, 1439.787	H	-1.90600	-2.73112	0.15451
		1469.321, 1484.931, 1529.054	H	0.74636	-3.22014	0.09682
		1598.895, 1628.066, 1645.66	H	3.00471	-2.28362	0.01832
		3002.628, 3061.173, 3165.26	H	3.41843	0.14767	0.12175
		3168.259, 3175.517, 3182.315	H	1.95561	2.75862	0.27624
		3187.756, 3196.921, 3237.115	H	2.46293	3.52188	2.70962
			H	-0.54168	3.07518	0.67686
			H	-0.58151	2.95106	1.07217
TS9-trial-2	1.38232, 1.16114, 0.64772	-333.422, 169.9339, 178.4529	C	1.19072	2.01510	0.17997
		194.8364, 217.6583, 228.8377	C	-0.26640	2.41020	0.15971
		302.86, 420.875, 449.2951	C	-0.98902	1.08081	0.05774
		470.8849, 479.835, 510.2597	C	1.31017	0.62563	0.10473
		549.9309, 568.2228, 630.0695	C	-0.01411	0.07797	0.03650
		661.402, 686.9733, 698.9594	C	2.39833	-0.27115	0.09742
		757.0729, 780.3389, 810.9448	C	2.13081	-1.64208	0.02649
		830.7748, 859.7036, 890.2023	C	-0.29341	-1.29749	0.03854
		914.7333, 936.3163, 962.4088	C	0.83393	-2.15946	0.04210
		986.1261, 994.2771, 1036.359	C	-2.31731	0.71102	0.00741
		1055.336, 1072.262, 1129.325	C	-2.63675	-0.66915	0.08689
		1138.629, 1181.122, 1197.923	C	-1.66706	-1.65469	0.10161
		1227.063, 1228.233, 1253.805	H	-3.11539	1.44515	0.00150
		1293.42, 1351.294, 1383.94	H	-3.68088	-0.95676	0.13787
		1413.009, 1427.098, 1439.008	H	-1.95299	-2.69905	0.16153
		1469.559, 1484.98, 1529.13	H	0.69080	-3.23292	0.10212
		1597.909, 1628.024, 1645.062	H	2.96465	-2.33500	0.01673
		3003.769, 3056.641, 3165.361	H	3.41966	0.08830	0.12809
		3168.549, 3175.599, 3182.526	H	2.00091	2.72350	0.28017
		3187.838, 3196.963, 3234.816	H	2.61635	3.56355	2.73308
			H	-0.48572	3.07999	0.67851
			H	-0.53680	2.96292	1.07045

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS9-trial-3	1.37932, 1.15933, 0.64681	-315.5931, 168.2976, 173.0575	C	1.22493	1.99145	0.18807
		191.04, 205.024, 224.8402	C	-0.22431	2.41313	0.16191
		300.8247, 420.7277, 448.9481	C	-0.97092	1.09717	0.05842
		470.7869, 479.9685, 510.0834	C	1.31974	0.60150	0.10969
		549.7295, 567.8384, 630.2169	C	-0.01429	0.07723	0.03762
		661.4117, 686.8942, 701.0163	C	2.39225	-0.31520	0.10093
		756.8687, 780.1246, 810.7422	C	2.10023	-1.68055	0.02628
		830.8499, 859.7602, 890.1363	C	-0.31779	-1.29282	0.04057
		914.3508, 936.5693, 962.4724	C	0.79410	-2.17474	0.04456
		986.2373, 994.4157, 1036.321	C	-2.30580	0.75126	0.00918
		1055.567, 1072.323, 1129.334	C	-2.64962	-0.62269	0.09113
		1138.253, 1181.16, 1197.532	C	-1.69744	-1.62537	0.10620
		1227.233, 1227.994, 1253.869	H	-3.09060	1.49956	0.00058
		1293.445, 1352.033, 1383.616	H	-3.69860	-0.89164	0.14403
		1412.881, 1427.648, 1438.304	H	-2.00189	-2.66434	0.16840
		1469.798, 1484.976, 1529.201	H	0.63207	-3.24537	0.10693
		1596.987, 1627.961, 1644.492	H	2.92146	-2.38834	0.01568
		3004.716, 3052.308, 3165.528	H	3.41980	0.02582	0.13435
		3168.788, 3175.704, 3182.679	H	2.04793	2.68570	0.28470
		3187.994, 3196.877, 3232.628	H	2.77996	3.59776	2.75241
			H	-0.42760	3.08477	0.67940
			H	-0.48892	2.97382	1.06937
TS9-trial-4	1.37633, 1.15749, 0.64593	-298.3124, 162.3268, 171.38	C	1.25765	1.96807	0.19546
		185.0555, 196.2708, 222.5194	C	-0.18355	2.41529	0.16455
		299.4348, 420.615, 448.6665	C	-0.95311	1.11274	0.05935
		470.6812, 480.1203, 509.8683	C	1.32860	0.57795	0.11450
		549.5177, 567.5269, 630.4139	C	-0.01447	0.07655	0.03890
		661.4207, 686.793, 703.1662	C	2.38556	-0.35773	0.10445
		756.6904, 779.9393, 810.5164	C	2.06995	-1.71730	0.02619
		830.9143, 859.7591, 890.0628	C	-0.34131	-1.28783	0.04252
		913.9824, 936.7968, 962.5525	C	0.75530	-2.18884	0.04694
		986.3292, 994.5254, 1036.282	C	-2.29392	0.79007	0.01089
		1055.765, 1072.404, 1129.266	C	-2.66125	-0.57741	0.09552
		1137.889, 1181.175, 1197.201	C	-1.72632	-1.59640	0.11090
		1227.214, 1227.835, 1253.856	H	-3.06561	1.55189	0.00256
		1293.455, 1352.672, 1383.285	H	-3.71461	-0.82818	0.15049
		1412.754, 1428.145, 1437.673	H	-2.04855	-2.62985	0.17547
		1470.053, 1484.936, 1529.247	H	0.57493	-3.25638	0.11163
		1596.15, 1627.883, 1643.96	H	2.87874	-2.43926	0.01484
		3005.468, 3048.445, 3165.727	H	3.41883	-0.03471	0.14065
		3168.961, 3175.824, 3182.778	H	2.09277	2.64832	0.28924
		3188.183, 3196.75, 3230.668	H	2.93836	3.62533	2.77476
			H	-0.37193	3.08895	0.67908
			H	-0.44181	2.98289	1.06945

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS9-trial-5	1.37347, 1.15554, 0.64512	-282.2793, 154.7023, 170.9588	C	1.28733	1.94617	0.20235
		175.0984, 193.2744, 220.8093	C	-0.14613	2.41671	0.16764
		298.4341, 420.5364, 448.4327	C	-0.93650	1.12686	0.06048
		470.5643, 480.2755, 509.6568	C	1.33636	0.55622	0.11932
		549.3126, 567.2645, 630.5879	C	-0.01469	0.07598	0.04037
		661.4304, 686.6939, 705.0881	C	2.37870	-0.39672	0.10821
		756.514, 779.7554, 810.3045	C	2.04146	-1.75060	0.02647
		830.9559, 859.7087, 889.9557	C	-0.36292	-1.28278	0.04436
		913.6001, 936.9673, 962.6179	C	0.71932	-2.20115	0.04908
		986.3767, 994.5821, 1036.259	C	-2.28240	0.82572	0.01264
		1055.915, 1072.505, 1129.132	C	-2.67128	-0.53542	0.10018
		1137.529, 1181.162, 1196.92	C	-1.75248	-1.56919	0.11574
		1227.059, 1227.748, 1253.783	H	-3.04181	1.59978	0.00464
		1293.49, 1353.188, 1382.963	H	-3.72837	-0.76933	0.15741
		1412.623, 1428.574, 1437.095	H	-2.09095	-2.59727	0.18281
		1470.296, 1484.882, 1529.279	H	0.52217	-3.26556	0.11606
		1595.387, 1627.772, 1643.504	H	2.83857	-2.48542	0.01452
		3005.976, 3044.935, 3165.953	H	3.41694	-0.09041	0.14722
		3169.078, 3175.97, 3182.843	H	2.13338	2.61328	0.29380
		3188.402, 3196.632, 3228.904	H	3.08873	3.64161	2.80476
			H	-0.32114	3.09251	0.67757
			H	-0.39816	2.98996	1.07067
TS9-trial-6	1.37061, 1.15356, 0.64437	-267.8854, 146.6147, 163.9158	C	1.31435	1.92554	0.20908
		171.178, 192.2097, 219.4253	C	-0.11162	2.41746	0.17132
		297.6469, 420.4745, 448.2195	C	-0.92100	1.13964	0.06180
		470.4425, 480.434, 509.4927	C	1.34318	0.53602	0.12400
		549.1362, 567.0265, 630.7262	C	-0.01488	0.07547	0.04181
		661.4357, 686.6209, 706.8869	C	2.37176	-0.43259	0.11202
		756.3343, 779.5699, 810.1522	C	2.01470	-1.78092	0.02691
		830.9505, 859.6316, 889.8194	C	-0.38276	-1.27782	0.04628
		913.2231, 937.107, 962.7055	C	0.68600	-2.21198	0.05119
		986.3987, 994.5898, 1036.233	C	-2.27125	0.85847	0.01424
		1056.041, 1072.619, 1128.99	C	-2.67989	-0.49649	0.10491
		1137.187, 1181.139, 1196.703	C	-1.77619	-1.54366	0.12074
		1226.897, 1227.686, 1253.694	H	-3.01912	1.64370	0.00640
		1293.531, 1353.682, 1382.649	H	-3.74018	-0.71481	0.16449
		1412.513, 1428.949, 1436.611	H	-2.12954	-2.56654	0.19044
		1470.528, 1484.89, 1529.305	H	0.47341	-3.27327	0.12047
		1594.77, 1627.627, 1643.135	H	2.80089	-2.52740	0.01456
		3006.295, 3041.815, 3166.124	H	3.41435	-0.14177	0.15381
		3169.163, 3176.092, 3182.883	H	2.17030	2.58032	0.29858
		3188.565, 3196.526, 3227.345	H	3.22763	3.65419	2.84087
			H	-0.27457	3.09553	0.67486
			H	-0.35768	2.99522	1.07306

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS9-trial-7	1.36775, 1.15150, 0.64364	-255.2283, 138.4278, 153.6343	C	1.33972	1.90565	0.21547
		171.0914, 191.6993, 218.2655	C	-0.07891	2.41775	0.17526
		296.9994, 420.433, 448.038	C	-0.90607	1.15159	0.06327
		470.3411, 480.5976, 509.37	C	1.34939	0.51674	0.12879
		548.9806, 566.8207, 630.8357	C	-0.01511	0.07497	0.04345
		661.4331, 686.5636, 708.3455	C	2.36466	-0.46660	0.11603
		756.1387, 779.3854, 810.0352	C	1.98880	-1.80935	0.02748
		830.9302, 859.5454, 889.6304	C	-0.40160	-1.27282	0.04813
		912.8087, 937.1877, 962.7634	C	0.65413	-2.22181	0.05328
		986.3835, 994.5536, 1036.22	C	-2.26017	0.88954	0.01590
		1056.134, 1072.72, 1128.829	C	-2.68752	-0.45926	0.10984
		1136.861, 1181.101, 1196.486	C	-1.79841	-1.51901	0.12588
		1226.75, 1227.598, 1253.595	H	-2.99696	1.68518	0.00831
		1293.607, 1354.044, 1382.346	H	-3.75063	-0.66266	0.17189
		1412.396, 1429.258, 1436.162	H	-2.16586	-2.53671	0.19835
		1470.711, 1484.899, 1529.327	H	0.42697	-3.27990	0.12488
		1594.168, 1627.467, 1642.829	H	2.76441	-2.56682	0.01472
		3006.486, 3039.106, 3166.254	H	3.41117	-0.19065	0.16073
		3169.23, 3176.17, 3182.936	H	2.20487	2.54850	0.30365
		3188.685, 3196.51, 3226.086	H	3.36231	3.66137	2.88073
			H	-0.23065	3.09822	0.67140
			H	-0.31907	2.99921	1.07617
TS9-trial-8	1.36486, 1.14942, 0.64298	-243.9762, 130.4937, 144.0849	C	1.36236	1.88731	0.22201
		171.0706, 191.4054, 217.2775	C	-0.04938	2.41757	0.17966
		296.433, 420.4016, 447.8751	C	-0.89245	1.16220	0.06488
		470.2616, 480.7639, 509.3037	C	1.35474	0.49919	0.13361
		548.861, 566.6253, 630.8931	C	-0.01531	0.07451	0.04507
		661.4323, 686.5343, 709.4728	C	2.35779	-0.49730	0.12019
		755.9404, 779.2035, 809.973	C	1.96503	-1.83476	0.02814
		830.8749, 859.4777, 889.4119	C	-0.41855	-1.26806	0.05010
		912.3975, 937.2296, 962.8196	C	0.62522	-2.23031	0.05546
		986.3461, 994.4852, 1036.211	C	-2.24977	0.91751	0.01743
		1056.222, 1072.821, 1128.704	C	-2.69393	-0.42546	0.11480
		1136.603, 1181.071, 1196.308	C	-1.81814	-1.49641	0.13117
		1226.642, 1227.512, 1253.519	H	-2.97640	1.72243	0.00996
		1293.693, 1354.39, 1382.072	H	-3.75939	-0.61533	0.17935
		1412.309, 1429.531, 1435.803	H	-2.19827	-2.50923	0.20652
		1470.864, 1484.982, 1529.355	H	0.38495	-3.28532	0.12948
		1593.682, 1627.316, 1642.581	H	2.73096	-2.60202	0.01504
		3006.54, 3036.73, 3166.315	H	3.40764	-0.23487	0.16785
		3169.297, 3176.203, 3182.991	H	2.23567	2.51923	0.30933
		3188.732, 3196.509, 3225.01	H	3.48452	3.66671	2.92740
			H	-0.19096	3.10042	0.66712
			H	-0.28425	3.00191	1.08009

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Table S3: Continued from previous page.

Species	Rotational Constants [GHz]	Frequencies [cm^{-1}]	Atom	Cartesian Coordinates [Å]		
				X	Y	Z
TS9-trial-9	1.36206, 1.14723, 0.64233	-232.8355, 123.0033, 135.287	C	1.38415	1.86922	0.22847
		171.0844, 191.2047, 216.5059	C	-0.02067	2.41711	0.18406
		295.9549, 420.3794, 447.743	C	-0.87908	1.17244	0.06638
		470.2026, 480.9413, 509.2816	C	1.35967	0.48202	0.13844
		548.7698, 566.4722, 630.9731	C	-0.01556	0.07412	0.04663
		661.4308, 686.5237, 710.5774	C	2.35060	-0.52713	0.12458
		755.7565, 779.0387, 809.9495	C	1.94144	-1.85923	0.02908
		830.8254, 859.4309, 889.1831	C	-0.43507	-1.26316	0.05209
		912.0137, 937.2503, 962.8576	C	0.59686	-2.23820	0.05752
		986.2914, 994.3967, 1036.199	C	-2.23931	0.94475	0.01913
		1056.305, 1072.917, 1128.613	C	-2.69979	-0.39232	0.11991
		1136.385, 1181.051, 1196.153	C	-1.83715	-1.47402	0.13654
		1226.553, 1227.435, 1253.468	H	-2.95592	1.75862	0.01180
		1293.777, 1354.706, 1381.826	H	-3.76735	-0.56895	0.18702
		1412.237, 1429.764, 1435.525	H	-2.22959	-2.48192	0.21481
		1470.98, 1485.111, 1529.384	H	0.34384	-3.29004	0.13393
		1593.271, 1627.181, 1642.378	H	2.69782	-2.63591	0.01579
		3006.562, 3034.571, 3166.313	H	3.40354	-0.27793	0.17523
		3169.373, 3176.177, 3183.063	H	2.26526	2.49034	0.31541
		3188.717, 3196.564, 3224.127	H	3.60856	3.66579	2.97492
			H	-0.15232	3.10228	0.66271
			H	-0.25037	3.00400	1.08413

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