

Electronic Spectroscopy of Resonantly Stabilized Aromatic Radicals: 1-Indanyl and Methyl Substituted Analogues

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Scaling Factor: The scaling factors are determined as the ratio of experimental and calculated vibrational frequencies. The values for the D_0 and D_1 state of 1-indanyl radical are obtained at the B3LYP/6-311++g(2d,p) level of theory using the current set of data (Table S1). The average factor of 0.981 ± 0.005 for the ground state is close to the Computational Chemistry Comparison and Benchmark Database (CCCBDB) value of 0.97.¹ For the D_1 state it is estimated as 0.966 ± 0.008 .

Table S1. Experimental and calculated vibrational frequencies (cm^{-1}) in $D_1(A'')$ and $D_0(A'')$ states of 1-indanyl radical ($\text{C}_9\text{H}_9\text{-A}$). Ratios of experimental and calculated values are given.

Vibration	Excited State			Ground State		
	D ₁ (A'')	Experiment	Ratio	D ₀ (A'')	Experiment ²	Ratio
ν ₃₁	369	355	0.962	384	377	0.980
ν ₃₀	506	490	0.968	536	529	0.987
ν ₂₉	562	537	0.956	593	583	0.983
ν ₂₈	702	684	0.974	713	700	0.981
ν ₂₇	792	755	0.954	807	794	0.984
ν ₂₅	905	871	0.962	920	865	0.940
ν ₂₄	985	964	0.978	1032	1016	0.985
ν ₁₉	1201	1166	0.971	1248	1211	0.971
ν ₁₈	1241	1201	0.968	1206	1183	0.981
Average			0.966	Average		0.981

Table S2. Rotational constants (cm^{-1}) of D_0 and D_1 states of $\text{C}_{10}\text{H}_{11}$ isomers calculated at B3LYP/6-311++g(2d,p) and TD-B3LYP/6-311++g(2d,p) level of theory, respectively.

$\text{C}_{10}\text{H}_{11}\text{-A}$			$\text{C}_{10}\text{H}_{11}\text{-B}$		
	$D_0(A'')$	$D_1(A'')$		$D_0(A'')$	$D_1(A'')$
<i>A</i>	0.081	0.080	<i>A</i>	0.070	0.070
<i>B</i>	0.041	0.042	<i>B</i>	0.046	0.046
<i>C</i>	0.028	0.028	<i>C</i>	0.028	0.028
$\text{C}_{10}\text{H}_{11}\text{-C}$			$\text{C}_{10}\text{H}_{11}\text{-D}$		
	$D_0(A'')$	$D_1(A'')$		$D_0(A'')$	$D_1(A'')$
<i>A</i>	0.069	0.068	<i>A</i>	0.108	0.106
<i>B</i>	0.047	0.047	<i>B</i>	0.033	0.033
<i>C</i>	0.028	0.028	<i>C</i>	0.026	0.026
$\text{C}_{10}\text{H}_{11}\text{-E}$			$\text{C}_{10}\text{H}_{11}\text{-F}$		
	$D_0(A)$	$D_1(A)$		$D_0(A)$	$D_1(A)$
<i>A</i>	0.112	0.109	<i>A</i>	0.096	0.096
<i>B</i>	0.032	0.033	<i>B</i>	0.038	0.038
<i>C</i>	0.026	0.026	<i>C</i>	0.028	0.028
$\text{C}_{10}\text{H}_{11}\text{-G}$			$\text{C}_{10}\text{H}_{11}\text{-H}$		
	$D_0(A'')$	$D_1(A'')$		$D_0(A'')$	$D_1(A'')$
<i>A</i>	0.153	0.149	<i>A</i>	0.161	0.156
<i>B</i>	0.019	0.019	<i>B</i>	0.021	0.021
<i>C</i>	0.017	0.017	<i>C</i>	0.019	0.019
$\text{C}_{10}\text{H}_{11}\text{-I}$			$\text{C}_{10}\text{H}_{11}\text{-J}$		
	$D_0(A'')$	$D_1(A'')$		$D_0(A'')$	$D_1(A'')$
<i>A</i>	0.161	0.158	<i>A</i>	0.152	0.150
<i>B</i>	0.021	0.021	<i>B</i>	0.023	0.023
<i>C</i>	0.019	0.019	<i>C</i>	0.020	0.020

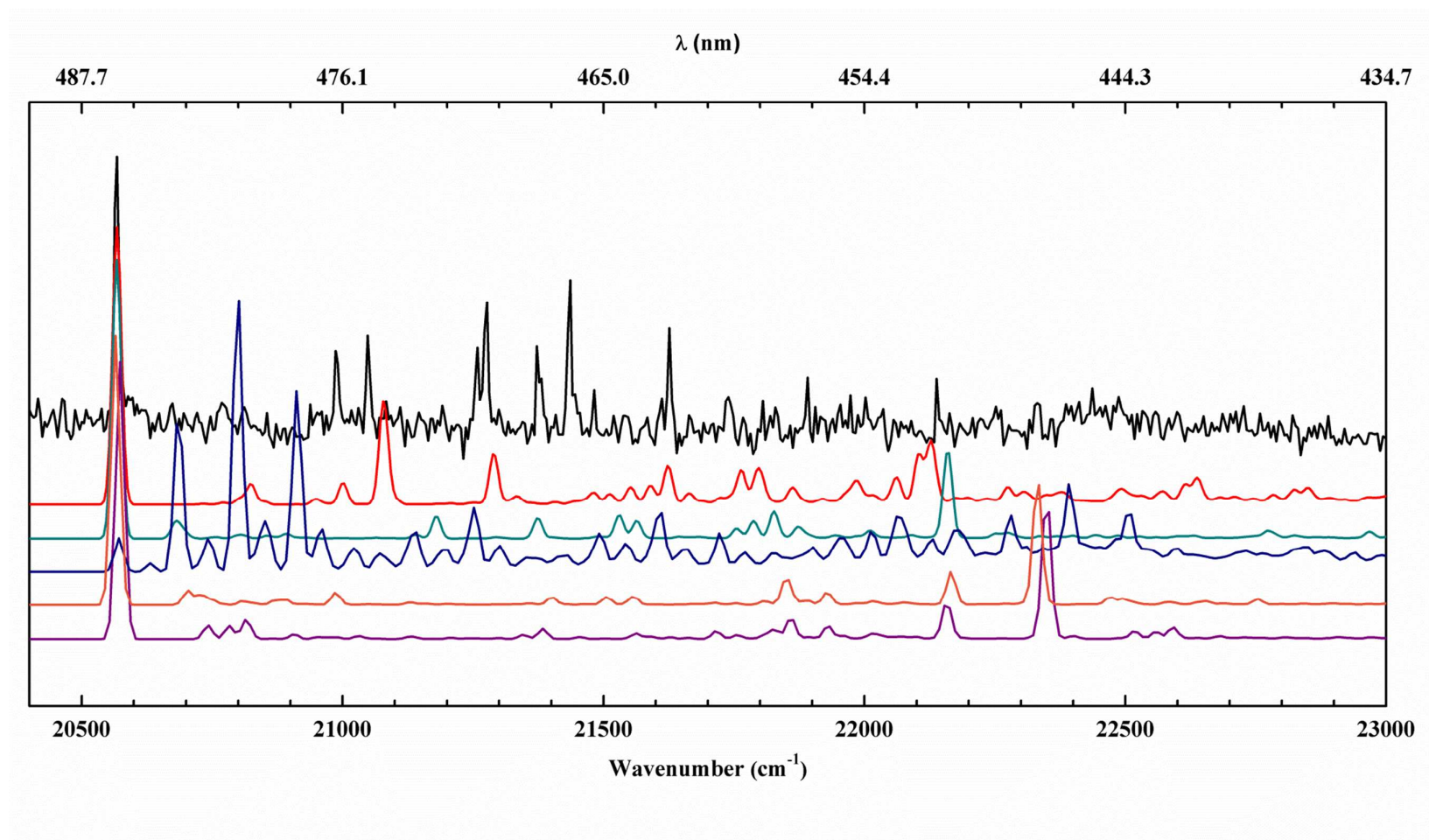


Figure S1. R2C2PI spectrum at $m/z = 131$ amu ($C_{10}H_{11}$) (black) and the Franck-Condon simulations ($T_{\text{vib}} = 0\text{K}$) of isomers $C_{10}H_{11}$ -A (red), $C_{10}H_{11}$ -G (green), $C_{10}H_{11}$ -H (blue), $C_{10}H_{11}$ -I (orange) and $C_{10}H_{11}$ -J (violet).

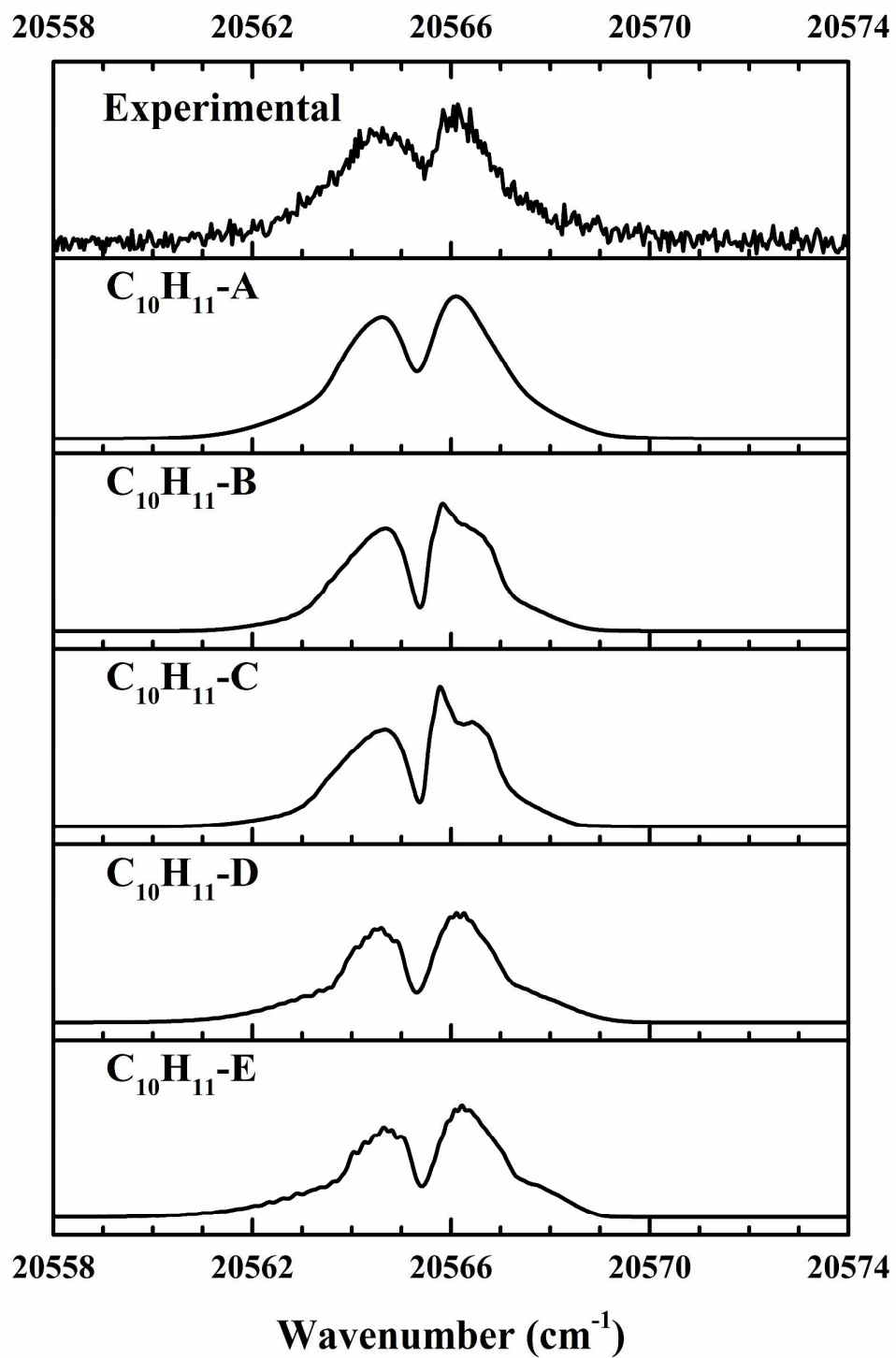


Figure S2. The b-type rotational contour obtained for the $D_1 \leftarrow D_0$ origin band of $C_{10}H_{11}$ -A, B, C, D and E isomers at $T=15$ K.

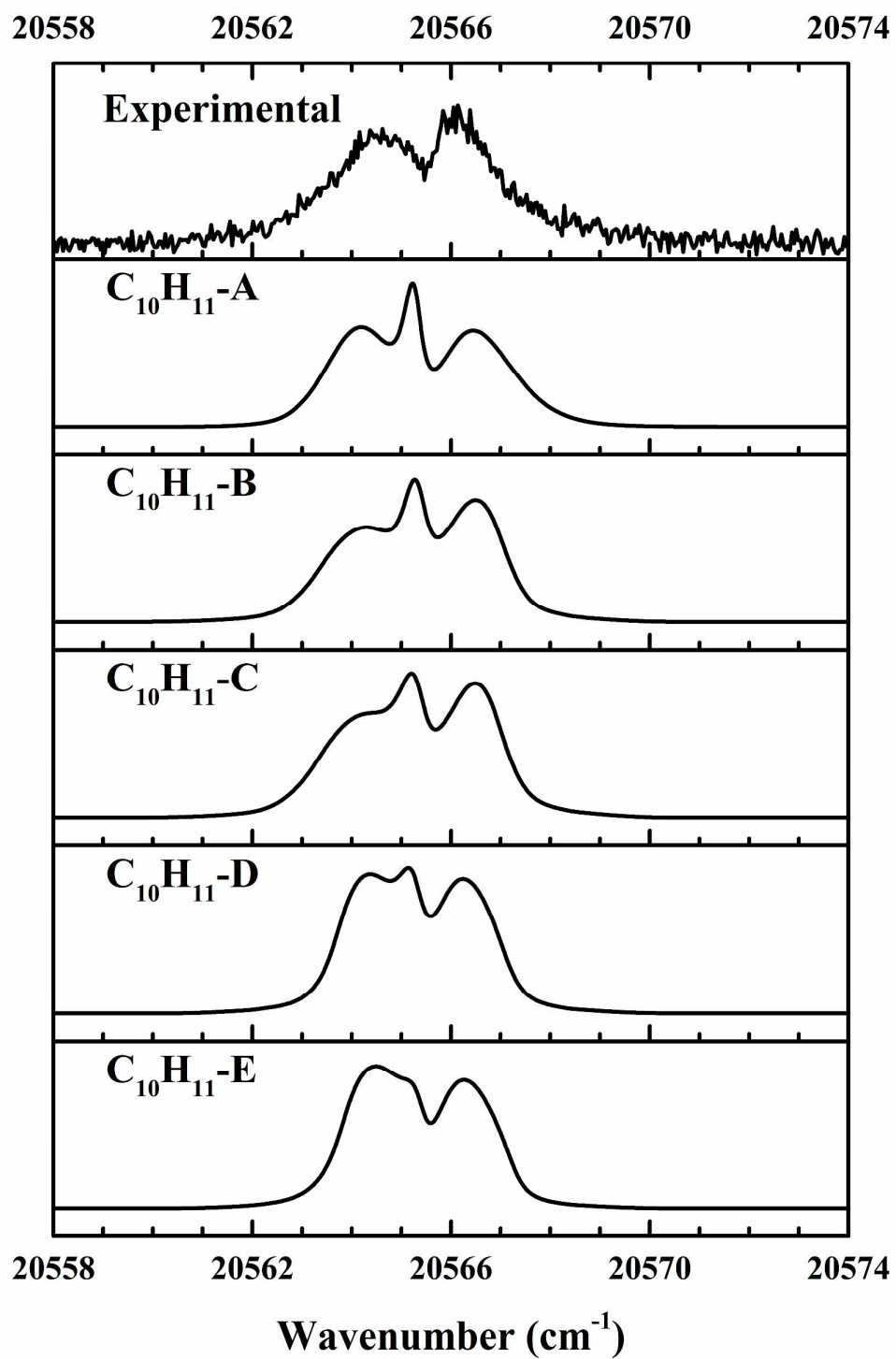


Figure S3. The a-type rotational contour obtained for the D₁←D₀ origin band of C₁₀H₁₁-A, B, C, D and E isomers at T=15 K.

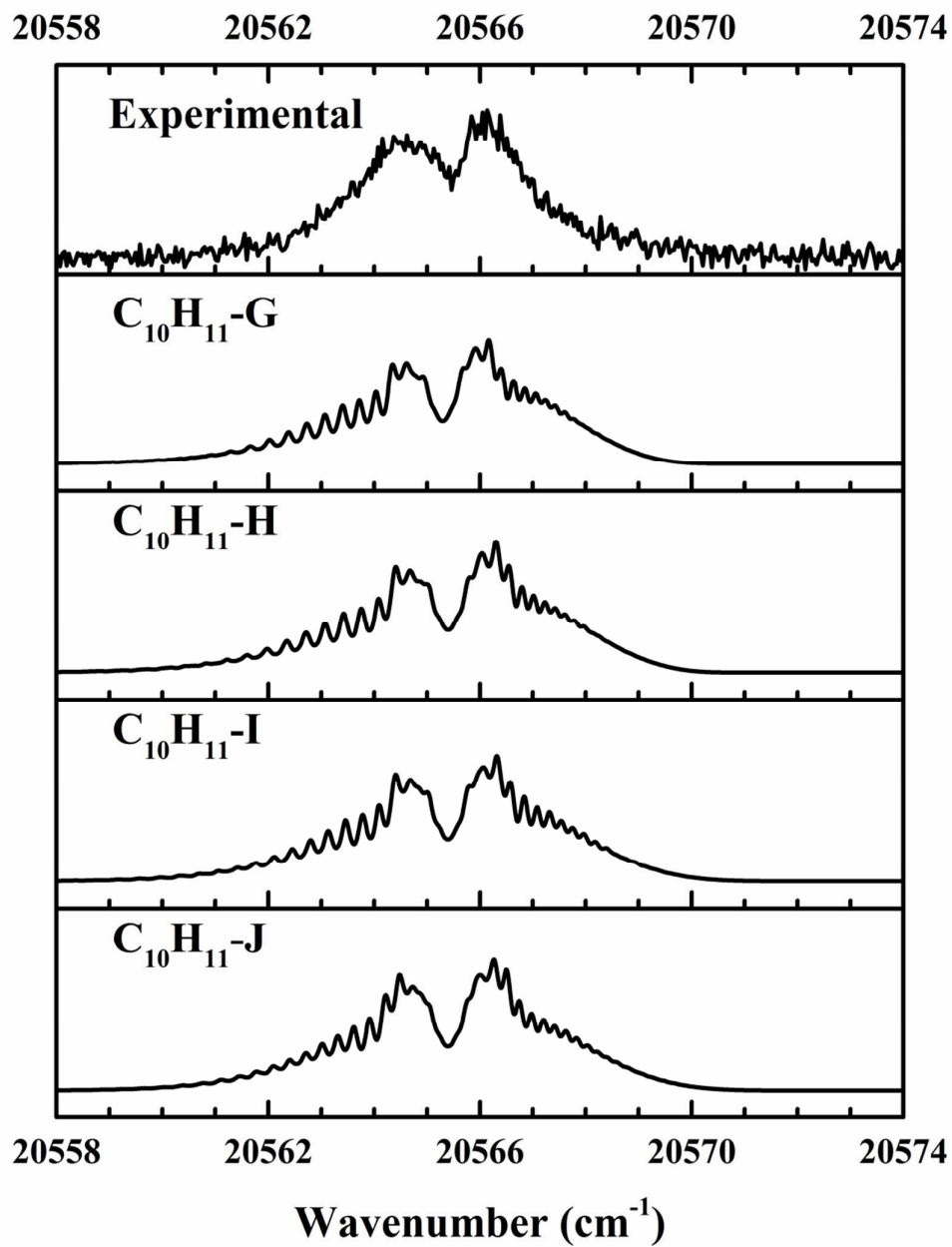


Figure S4. The b-type rotational contour obtained for the $D_1 \leftarrow D_0$ origin band of $C_{10}H_{11}$ -G, H, I and J isomers at $T=15$ K.

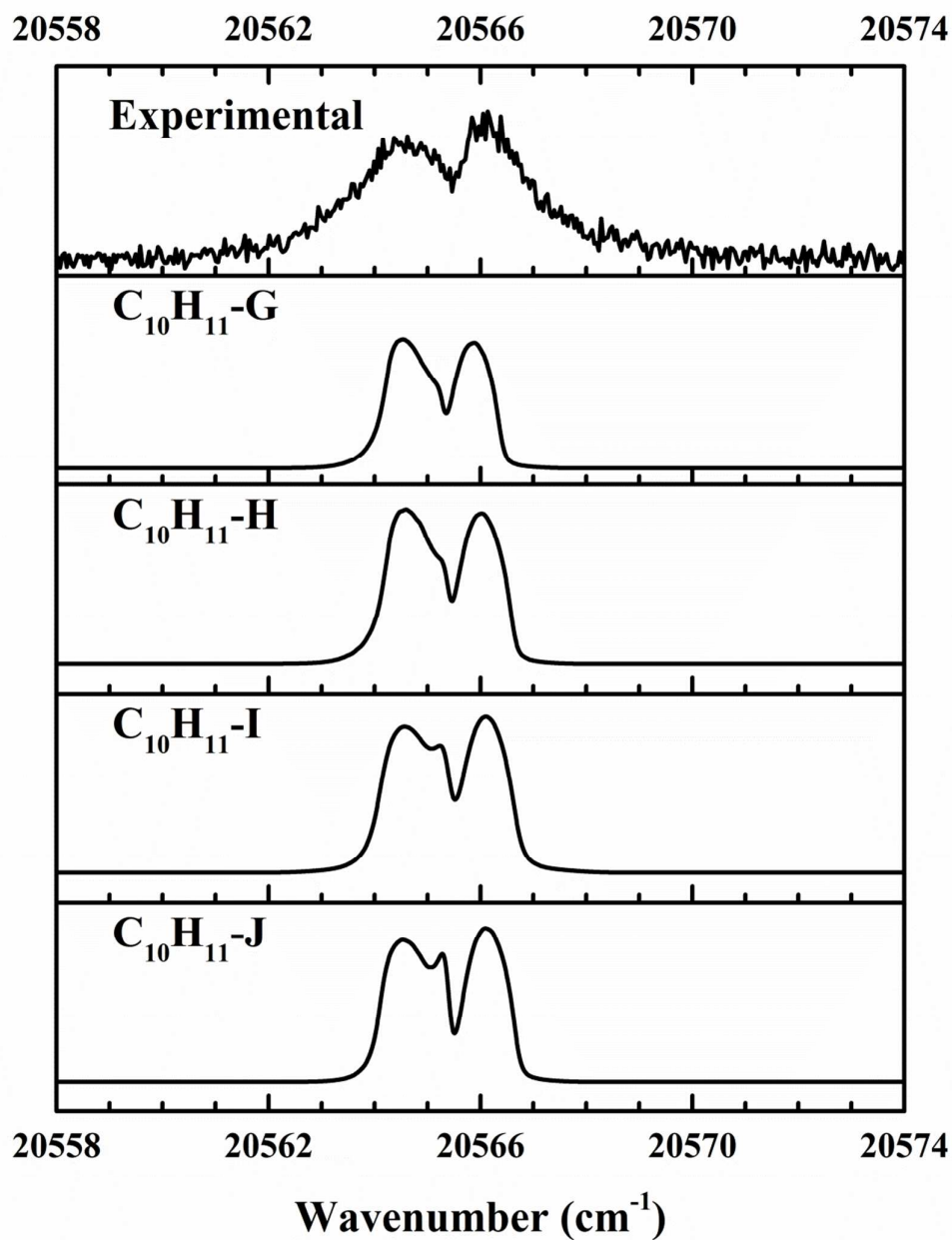


Figure S5. The a-type rotational contour obtained for the $D_1 \leftarrow D_0$ origin band of $C_{10}H_{11}$ -G, H, I and J isomers at $T=15$ K.

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- (1) Johnson, R. D. NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 16a, 2013.
- (2) Troy, T. P.; Nakajima, M.; Chalyavi, N.; Clady, R. G. C. R.; Nauta, K.; Kable, S. H.; Schmidt, T. W. Identification of the Jet-Cooled 1-Indanyl Radical by Electronic Spectroscopy, *J. Phys. Chem. A* **2009**, *113*, 10279-10283.