Supporting information for

Hyperfine structure-tunneling coupling in *trans*-1,2-cyclohexanediamine revealed by rotational spectroscopy

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S1 Path parameterization

When parameterizing the $3N - 6 = 60$ internal coordinates of the molecule in terms of η, with $-1 \leq \eta \leq +1$, two types of parameterization need to be considered. For pairs of internal coordinates q_i and q_j which are exchanged by the (12)(34)(56)(78) symmetry operation, that is (12)(34)(56)(78) $q_i = q_j$ like the two dihedral angles τ_1 and τ_2 or the distances r_{15} and r_{26}, the following parameterization is taken:

$$q_i = f_i(\eta) \quad \text{and} \quad q_j = f_j(\eta), \tag{1}$$

where the functions $f_i(\eta)$ and $f_j(\eta)$ are such that $f_i(\eta) = f_j(-\eta)$. For internal coordinate q_i invariant under the (12)(34)(56)(78) symmetry operation, that is (12)(34)(56)(78) $q_i = q_i$ like the dihedral angle $\tau = \angle \mathrm{N_5C_7C_8N_6}$ or of the distance r_{78}, the following parameterization is taken:

$$q_i = f_i(\eta) \tag{2}$$

where the function $f_i(\eta)$ is an even function of η.

When solving Eqs. (33) of Hougen[1] in order to retrieve the Eulerian-type angles χ_2, θ_2, ϕ_2, all internal coordinates, except the two dihedral angles τ_1 and τ_2, were frozen to the values for the local minimum 3 corresponding to the $\eta = 0$, C_2 symmetry, Intermediate Configuration. The two dihedral angles τ_1 and τ_2 which were parameterized as follows:

$$\begin{cases} \tau_1 = (\tau_1^{\mathrm{eq}} + \tau_2^{\mathrm{eq}})/2 + \eta(\tau_2^{\mathrm{eq}} - \tau_1^{\mathrm{eq}})/2 \\ \tau_2 = (\tau_1^{\mathrm{eq}} + \tau_2^{\mathrm{eq}})/2 + \eta(\tau_1^{\mathrm{eq}} - \tau_2^{\mathrm{eq}})/2 \end{cases} \tag{3}$$

where τ_1^{eq} and τ_2^{eq} are introduced in Section 4.1 of the paper. This parameterization, although simple, is compatible with Eqs. (1) and (2).

References

[1] J. T. Hougen, *J. Mol. Spectrosc.*, 1985, **114**, 395–426.

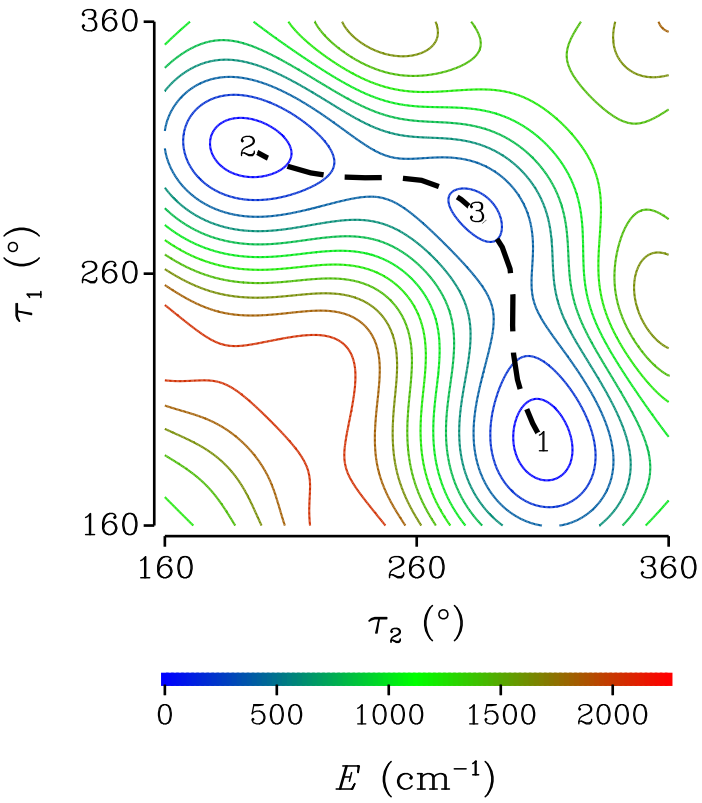

Figure S1: The relaxed two-dimensional potential energy surface of CDA as a function of the dihedral angles τ_1 and τ_2. Only the portion the portion of the surface with $160° \leq \tau_1, \tau_2 \leq 360°$ is shown. Contour lines corresponding to equally spaced energy values with a spacing of 200 cm^{-1} are drawn from 100 to 2300 cm^{-1}. The tunneling path connecting stationary points 1 and 2 is plotted with a dashed line.

Table S1: Observed minus calculated table[a]

F'	I'	F''	I''	F^b	O−C[c]	F'	I'	F''	I''	F^b	O−C[c]	F'	I'	F''	I''	F^b	O−C[c]
						2	2	2	2	4631.5194	−10.0						
				$1_{01},0 \leftarrow 0_{00},0$		2	1	1	1	4631.8549	−9.7					$2_{02},1 \leftarrow 1_{10},0$	
						3	2	2	2	4632.0560	−1.2						
1	2	0	0	3143.4131	2.6	1	1	1	1	4632.1282	22.9	0	2	1	2	4505.3456	−3.4
1	2	2	2	3143.4131	2.6	1	2	2	2	4632.6120	13.8	2	0	1	2	4505.4983	4.5
1	1	1	1	3143.4957	−14.9	1	2	0	0	4632.6120	13.8	1	2	1	2	4505.6109	3.0
3	2	2	2	3143.6126	−3.0							4	2	3	2	4506.1555	−11.5
										$1_{10},1 \leftarrow 0_{00},0$		3	1	2	1	4506.5734	16.1
				$1_{01},1 \leftarrow 0_{00},1$								3	2	2	2	4507.0598	1.7
						0	1	1	1	4673.6725	−2.9	2	2	2	2	4507.1542	−4.3
3	2	2	2	3143.6126	2.6	2	2	2	2	4673.8840	16.0	1	1	0	1	4507.2085	2.3
2	1	1	1	3143.6785	12.7	1	0	0	0	4673.9330	2.8						
1	0	2	2	3143.7577	7.7	1	0	2	2	4673.9330	2.8					$2_{12},0 \leftarrow 1_{01},1$	
1	0	0	0	3143.7577	7.7	2	1	1	1	4674.2070	3.8						
						3	2	2	2	4674.3480	0.6	2	0	2	2	6386.6254	−7.8
				$1_{11},0 \leftarrow 0_{00},1$		1	2	0	0	4675.0480	−4.7	1	2	1	0	6386.7041	33.6
						1	2	2	2	4675.0480	−4.7	2	1	1	1	6386.8461	16.4
1	2	0	0	3937.1600	−1.9							2	0	1	2	6386.8889	−9.3
1	2	2	2	3937.1600	−1.9					$2_{02},0 \leftarrow 1_{01},0$		4	2	3	2	6387.0050	9.1
1	1	1	1	3937.4892	−5.7							3	1	2	1	6387.1453	−2.0
3	2	2	2	3937.6296	0.3	4	2	3	2	5994.6136	−15.6	1	1	0	1	6387.2174	24.6
2	1	1	1	3937.7475	−4.4	3	1	2	1	5994.7407	7.8	3	2	2	2	6387.3100	10.5
2	2	2	2	3938.0050	4.1	3	2	2	2	5994.8165	4.8	2	2	1	0	6387.4894	3.3
0	1	1	1	3938.1360	8.5	2	2	1	0	5994.9573	−3.5						
																$2_{12},1 \leftarrow 1_{01},0$	
				$1_{11},1 \leftarrow 0_{00},0$						$2_{02},1 \leftarrow 1_{01},1$							
												4	2	3	2	6429.2627	4.7
1	2	0	0	3979.4612	1.9	4	2	3	2	5994.6136	−0.6	3	1	2	1	6429.5045	4.0
1	2	2	2	3979.4612	1.9	3	1	2	1	5994.7407	−15.3	3	2	2	2	6429.6430	−10.6
1	1	1	1	3979.7996	0.5	3	2	2	2	5994.8165	−18.3						
3	2	2	2	3979.9137	−0.2											$2_{11},0 \leftarrow 1_{01},1$	
2	1	1	1	3980.0387	−1.9					$2_{02},0 \leftarrow 1_{10},1$							
2	2	2	2	3980.2942	4.2							2	2	1	0	8469.3592	9.6
0	1	1	1	3980.4149	2.1	0	2	1	2	4462.9000	−15.7	3	2	2	2	8469.4671	−2.8
						2	0	1	2	4463.0247	−11.9	1	1	1	1	8469.6155	−6.0
				$1_{10},0 \leftarrow 0_{00},1$		4	2	3	2	4463.9001	2.7	3	1	2	1	8469.7372	2.5
						3	2	2	2	4464.6656	−11.1	4	2	3	2	8469.9718	0.4
0	1	1	1	4631.3805	−4.7	1	1	0	1	4464.7975	−10.7						

[a]Hyperfine components are assigned with the hyperfine quantum numbers F and I.
[b]The observed frequency is given in this column in MHz.
[c]The observed minus calculated residual is given in this column in kHz.

Table S1: Observed minus calculated table[a] (continued)

F'	I'	F''	I''	F^b	O−C[c]	F'	I'	F''	I''	F^b	O−C[c]	F'	I'	F''	I''	F^b	O−C[c]
						4	2	4	2	2082.9869	11.5	3	2	2	2	9406.2874	7.3
				$2_{11},1 \leftarrow 1_{01},0$		2	1	2	1	2083.1836	−26.7	2	0	1	0	9406.4218	15.5
						2	0	2	0	2083.3390	−9.4	1	1	0	1	9406.4742	8.5
2	2	2	2	8511.6650	10.9												
2	2	1	0	8511.6650	−6.6					$2_{11},1 \leftarrow 2_{12},1$						$2_{21},1 \leftarrow 1_{10},0$	
1	1	0	1	8511.7700	13.4												
3	2	2	2	8511.7700	−9.7	2	2	2	2	2081.8600	10.7	2	0	1	2	9447.7499	4.7
3	2	3	2	8511.8935	−3.6	3	2	3	2	2082.1540	27.9	3	2	3	2	9448.1234	4.3
1	1	1	1	8512.0386	3.9	3	1	3	1	2082.5630	19.5	4	2	3	2	9448.2230	−3.1
4	2	3	2	8512.2738	23.5	4	2	4	2	2082.9869	−5.4	3	1	2	1	9448.3696	−3.9
1	2	1	2	8512.5534	3.6	2	1	2	1	2083.1836	9.4	3	2	2	2	9448.6316	−15.3
						2	0	2	0	2083.3390	−3.7	1	1	0	1	9448.8237	4.7
				$2_{11},0 \leftarrow 2_{02},1$													
										$2_{21},0 \leftarrow 1_{11},1$						$2_{21},0 \leftarrow 2_{12},1$	
2	2	2	2	2474.4090	−2.7												
3	2	3	2	2474.6248	−10.2	1	1	0	1	10099.7237	−4.6	2	2	2	2	4506.5780	2.8
3	1	3	1	2474.9746	−4.1	3	2	2	2	10099.8680	9.9	3	1	3	1	4507.0741	11.3
4	2	4	2	2475.3570	−0.1	3	1	2	1	10100.1541	−15.3	3	2	4	2	4507.2735	−0.9
2	1	2	1	2475.4930	−6.1	4	2	3	2	10100.3830	8.0	4	2	4	2	4507.4266	11.4
2	0	2	0	2475.6360	−6.3	2	1	1	1	10100.5030	−3.1	2	0	2	0	4507.6490	−9.3
												1	2	0	2	4507.8222	10.1
				$2_{11},1 \leftarrow 2_{02},0$						$2_{21},1 \leftarrow 1_{11},0$							
																$2_{21},1 \leftarrow 2_{12},0$	
2	2	2	2	2516.7190	8.2	3	2	2	2	10142.1579	−17.5						
3	2	2	2	2516.8500	13.6	2	0	2	2	10142.3376	−4.9	2	2	2	2	4548.8873	−1.0
3	2	3	2	2516.9730	5.1	3	1	2	1	10142.4798	−6.4	3	1	3	1	4549.4127	−12.3
1	1	1	1	2517.0750	13.4	4	2	3	2	10142.6506	−3.4	3	2	4	2	4549.5613	−9.1
3	1	3	1	2517.3230	11.9	2	1	1	1	10142.8262	−7.8	4	2	4	2	4549.6613	−16.1
3	2	2	0	2517.4375	14.1	2	0	1	2	10143.1755	−6.0	2	0	2	0	4549.9619	4.4
4	2	4	2	2517.6260	4.9							1	2	0	2	4550.1430	0.9
2	1	2	1	2517.8160	−6.4					$2_{21},0 \leftarrow 1_{10},1$							
2	0	2	0	2517.9290	−2.5											$2_{21},0 \leftarrow 2_{11},1$	
						1	2	1	2	9405.2374	4.7						
				$2_{11},0 \leftarrow 2_{12},0$		1	1	1	1	9405.5126	8.1	4	2	4	2	2424.4230	0.0
						2	1	1	1	9405.6600	−8.5	3	1	3	1	2424.5355	16.1
2	2	2	2	2081.8600	−3.5	3	2	3	2	9405.8030	2.3	2	2	2	2	2424.7169	−9.0
3	2	3	2	2082.1540	−16.3	4	2	3	2	9405.9410	−0.5						
3	1	3	1	2082.5630	−24.4	2	2	1	0	9406.1859	3.1						

[a]Hyperfine components are assigned with the hyperfine quantum numbers F and I.
[b]The observed frequency is given in this column in MHz.
[c]The observed minus calculated residual is given in this column in kHz.

Table S1: Observed minus calculated table[a] (continued)

F'	I'	F''	I''	F^b	O−C[c]	F'	I'	F''	I''	F^b	O−C[c]	F'	I'	F''	I''	F^b	O−C[c]
						3	2	2	2	9741.1111	11.3	5	2	5	2	4211.5890	7.2
			$2_{21},1 \leftarrow 2_{11},0$									3	1	3	1	4211.7200	15.5
									$2_{20},0 \leftarrow 2_{12},1$			3	0	3	0	4211.7690	−8.4
1	2	0	2	2466.4736	3.3							1	2	1	2	4211.9890	6.1
2	0	2	0	2466.6057	−3.5	2	2	2	2	4798.9251	−5.1						
4	2	4	2	2466.6874	−14.6	3	2	2	2	4799.0244	−6.1				$3_{12},1 \leftarrow 3_{03},0$		
3	1	3	1	2466.8220	−15.5	3	2	3	2	4799.1725	−9.2						
3	2	3	2	2466.9534	−0.3	1	2	2	2	4799.4004	−11.1	3	2	3	2	4252.7390	10.2
2	2	2	2	2467.0244	−0.5	3	1	3	1	4799.5991	12.5	4	2	4	2	4253.1551	8.6
1	2	2	2	2467.2413	−7.4	4	2	4	2	4800.0674	9.8	2	1	2	1	4253.2762	2.5
						2	1	2	1	4800.2002	−3.3	4	1	4	1	4253.4330	1.4
			$2_{20},0 \leftarrow 1_{11},1$			2	0	2	0	4800.3784	−6.7	5	2	5	2	4253.7940	−11.7
												1	2	1	2	4254.2140	7.7
3	2	2	2	10392.2680	−10.3				$2_{20},1 \leftarrow 2_{12},0$								
4	2	3	2	10393.0100	−7.4										$3_{22},0 \leftarrow 2_{11},1$		
2	1	1	1	10393.1760	−11.4	2	2	2	2	4841.2620	0.5						
2	0	1	2	10393.5910	−13.0	2	2	3	2	4841.4385	−6.9	3	0	2	0	11855.1457	−0.8
0	2	1	2	10393.7379	−10.7	3	2	3	2	4841.5858	8.7	2	2	1	2	11855.2209	13.9
						3	1	3	1	4841.9742	−7.3	5	2	4	2	11855.3112	9.8
			$2_{20},1 \leftarrow 1_{11},0$			4	2	4	2	4842.3180	−5.6	4	1	3	1	11855.4802	3.7
						2	1	2	1	4842.5880	6.1	4	2	3	2	11855.6709	16.5
3	2	2	2	10434.6074	−20.9	2	0	2	0	4842.7020	2.8	3	2	2	2	11855.7798	−0.1
3	2	3	2	10435.0067	6.8												
4	2	3	2	10435.3070	6.8				$2_{20},0 \leftarrow 2_{11},1$						$3_{22},1 \leftarrow 2_{11},0$		
2	1	1	1	10435.5350	−9.7												
2	0	1	2	10435.9364	13.3	3	2	3	2	2717.0489	−6.7	5	2	4	2	11897.5529	−10.8
0	2	1	2	10436.0380	−6.2	4	2	4	2	2717.0877	22.4	4	1	3	1	11897.7363	−8.3
			$2_{20},0 \leftarrow 1_{10},1$						$2_{20},1 \leftarrow 2_{11},0$						$3_{22},0 \leftarrow 3_{13},1$		
1	2	1	2	9697.8861	−10.4	4	2	4	2	2759.3461	−2.1	3	2	3	2	5704.5904	−6.6
2	0	1	2	9697.9997	−10.9	3	2	3	2	2759.4111	4.4	4	2	4	2	5704.8258	−13.7
2	1	1	1	9698.3387	−11.1							4	1	4	1	5705.0580	0.1
3	2	2	2	9698.6967	−3.6				$3_{12},0 \leftarrow 3_{03},1$			2	2	2	2	5705.2356	−20.5
2	1	2	1	9698.7741	−9.2							5	2	5	2	5705.4500	4.0
						3	2	3	2	4210.4760	−2.3	3	1	3	1	5705.5429	8.6
			$2_{20},1 \leftarrow 1_{10},0$			4	2	4	2	4210.8080	−2.4	1	2	1	2	5705.7430	−10.4
						2	1	2	1	4210.8780	20.8						
4	2	3	2	9740.8890	16.7	4	1	4	1	4211.0950	−0.9						

[a]Hyperfine components are assigned with the hyperfine quantum numbers F and I.
[b]The observed frequency is given in this column in MHz.
[c]The observed minus calculated residual is given in this column in kHz.

Table S1: Observed minus calculated table[a] (continued)

F'	I'	F''	I''	F^b	O−C[c]	F'	I'	F''	I''	F^b	O−C[c]	F'	I'	F''	I''	F^b	O−C[c]
						3	1	3	1	4759.6380	−15.7						
			$3_{22},1\leftarrow3_{13},0$			4	1	4	1	4759.8495	28.6	4	2	4	2	7309.8840	1.3
												5	2	5	2	7310.2862	18.5
3	2	3	2	5746.8501	7.5				$4_{14},0\leftarrow3_{13},0$			5	1	5	1	7310.4318	−2.6
4	2	4	2	5747.1758	1.2							3	2	3	2	7310.6259	−8.1
2	1	2	1	5747.2803	−3.4	6	2	5	2	10773.6372	−1.2	4	0	4	0	7310.7923	−11.3
4	1	4	1	5747.3857	−6.8	5	1	4	1	10773.6905	−1.3						
5	2	5	2	5747.6874	23.7										$4_{31},0\leftarrow4_{22},1$		
3	0	3	0	5747.8284	1.4				$4_{23},0\leftarrow4_{14},1$								
												6	2	6	2	4220.9999	−6.3
			$3_{31},0\leftarrow3_{21},1$			4	2	4	2	7267.7110	−15.5	5	2	5	2	4221.0767	17.1
						5	2	5	2	7267.9720	3.3	4	2	4	2	4221.1155	−2.4
3	1	3	1	4717.3360	−10.2	5	1	5	1	7268.1310	−4.8						
5	2	5	2	4717.4240	27.2	6	2	6	2	7268.5650	8.8				$4_{31},1\leftarrow4_{22},0$		
						2	2	2	2	7268.7600	−13.0						
			$3_{31},1\leftarrow3_{21},0$									6	2	6	2	4263.2553	−9.3
									$4_{23},1\leftarrow4_{14},0$								

[a]Hyperfine components are assigned with the hyperfine quantum numbers F and I.
[b]The observed frequency is given in this column in MHz.
[c]The observed minus calculated residual is given in this column in kHz.

Table S2: Predicted hyperfine patterns[a]

F'	I'	F''	I''	F^b	Int.[c]	F'	I'	F''	I''	F^b	Int.[c]
			$1_{10}, 0 \leftarrow 0_{00}, 1$						$1_{10}, 0 \leftarrow 0_{00}, 0$		
0	1	1	1	4631.3852	14.3	2	2	1	1	4652.6745	33.0
2	2	2	2	4631.5294	71.3	1	0	1	1	4652.7082	35.4
1	0	0	0	4631.5631	27.0	2	1	2	2	4653.0097	35.2
1	0	2	2	4631.5631	15.7	1	1	0	0	4653.2504	0.1
2	1	1	1	4631.8646	71.3	1	1	2	2	4653.2504	100.0
3	2	2	2	4632.0572	100.0	1	2	1	1	4653.7433	66.7
1	1	1	1	4632.1053	42.6						
1	2	2	2	4632.5982	26.9				$1_{10}, 1 \leftarrow 0_{00}, 1$		
1	2	0	0	4632.5982	15.8						
						2	2	1	1	4652.7229	34.5
			$1_{10}, 1 \leftarrow 0_{00}, 0$			1	0	1	1	4652.7851	28.8
						2	1	2	2	4653.0581	32.3
0	1	1	1	4673.6754	14.3	1	1	0	0	4653.4915	0.1
2	2	2	2	4673.8680	71.3	1	1	2	2	4653.4915	100.0
1	0	0	0	4673.9302	31.2	1	2	1	1	4653.9076	69.2
1	0	2	2	4673.9302	11.6						
2	1	1	1	4674.2032	71.3						
3	2	2	2	4674.3474	100.0						
1	1	1	1	4674.6366	42.6						
1	2	2	2	4675.0527	31.1						
1	2	0	0	4675.0527	11.7						

[a]Hyperfine components are assigned with the hyperfine quantum numbers F and I.
[b]Calculated frequencies are given in this column in MHz.
[c]Unitless relative intensities are given in this column.

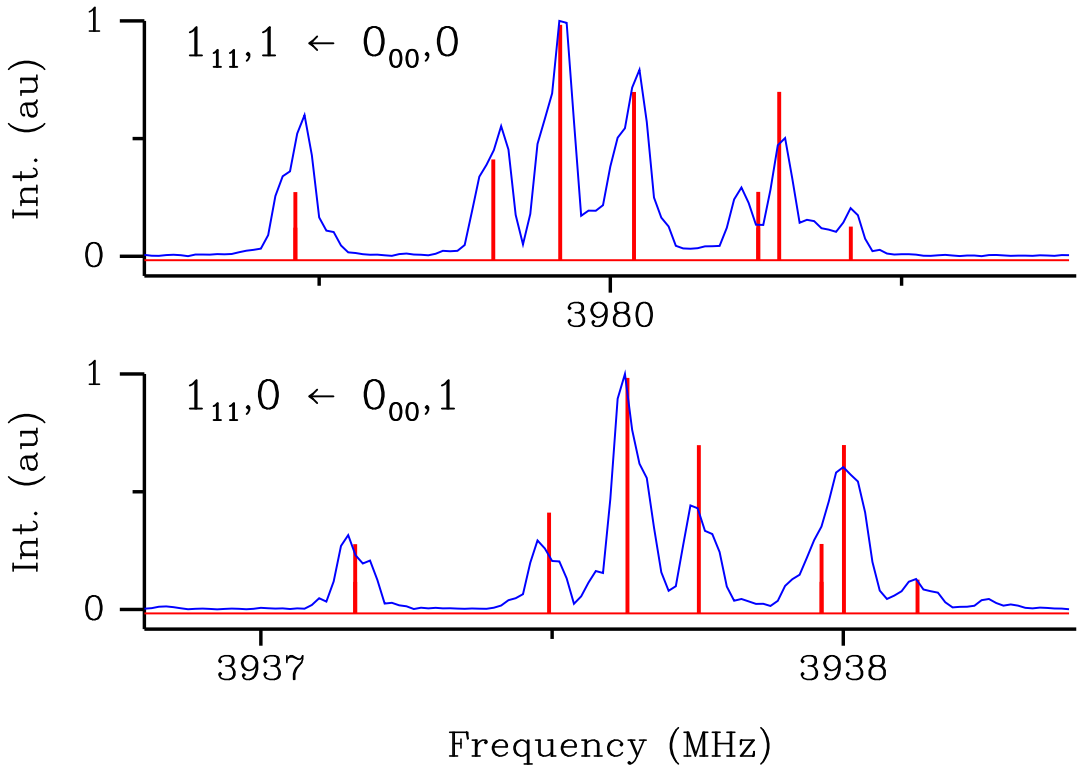

Figure S2: Comparisons between observed spectra and calculated stick spectra for the $1_{11},1 \leftarrow 0_{00},0$ and $1_{11},0 \leftarrow 0_{00},1$ transitions in the upper and lower panels, respectively. Both spectra are plotted as a function of the frequency in MHz.

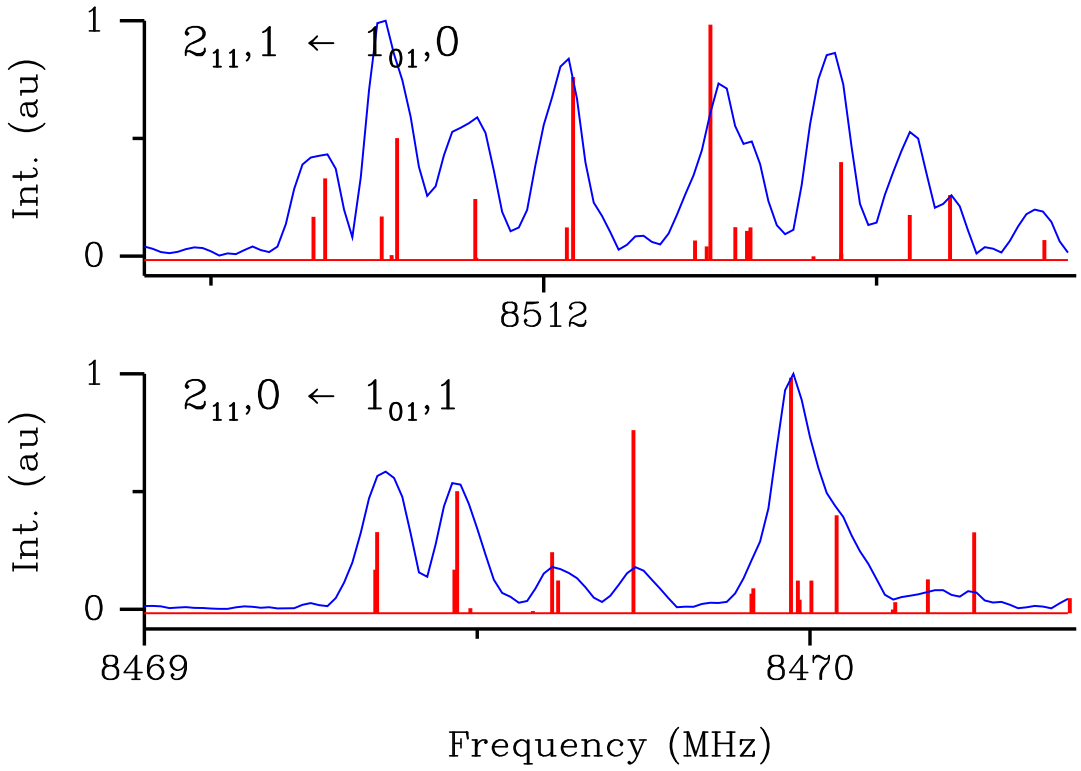

Figure S3: Comparisons between observed spectra and calculated stick spectra for the $2_{11},1 \leftarrow 1_{01},0$ and $2_{11},0 \leftarrow 1_{01},1$ transitions in the upper and lower panels, repectively. Both spectra are plotted as a function of the frequency in MHz.