

## Supplementary Material - Figures

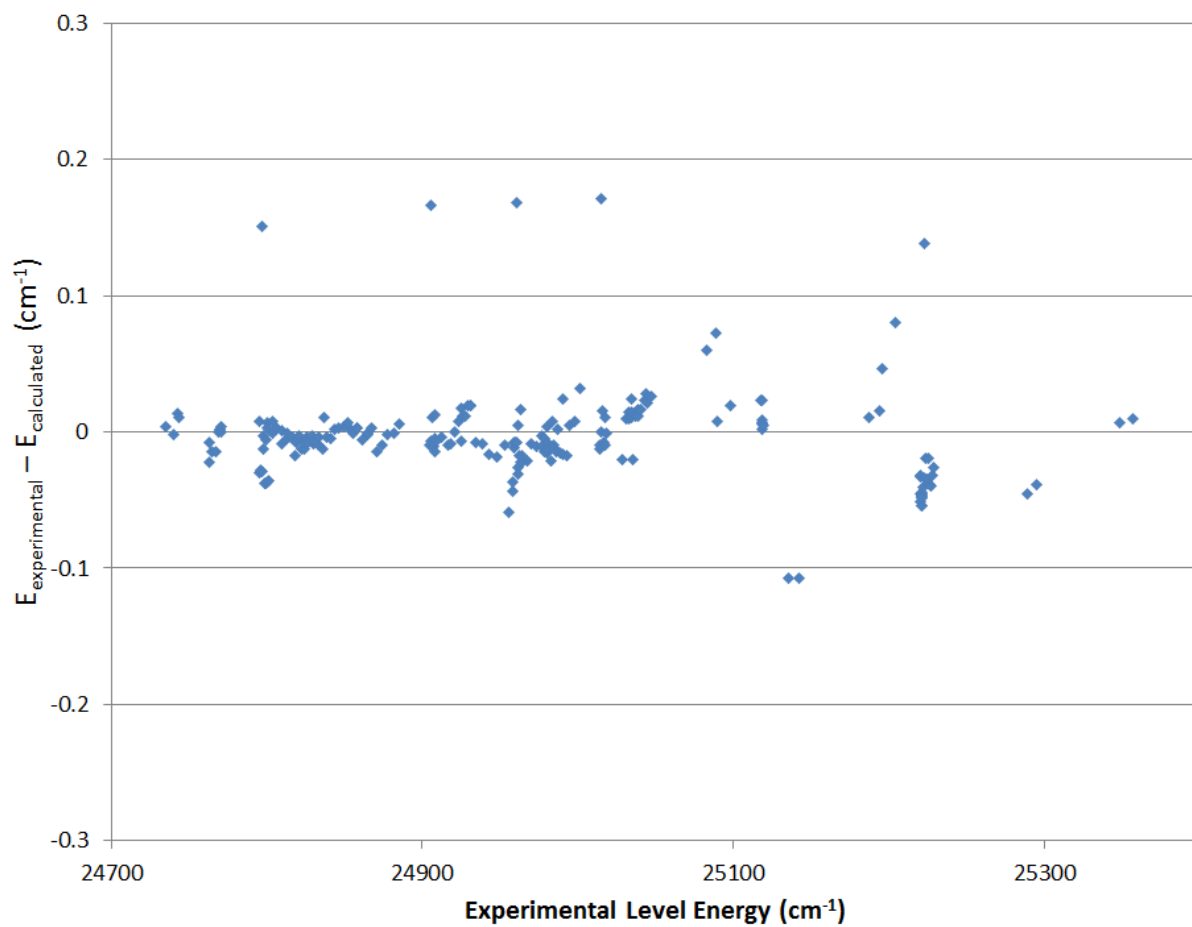


Figure 1. Differences of experimental level energies and energies calculated with the best fit IPA potential.

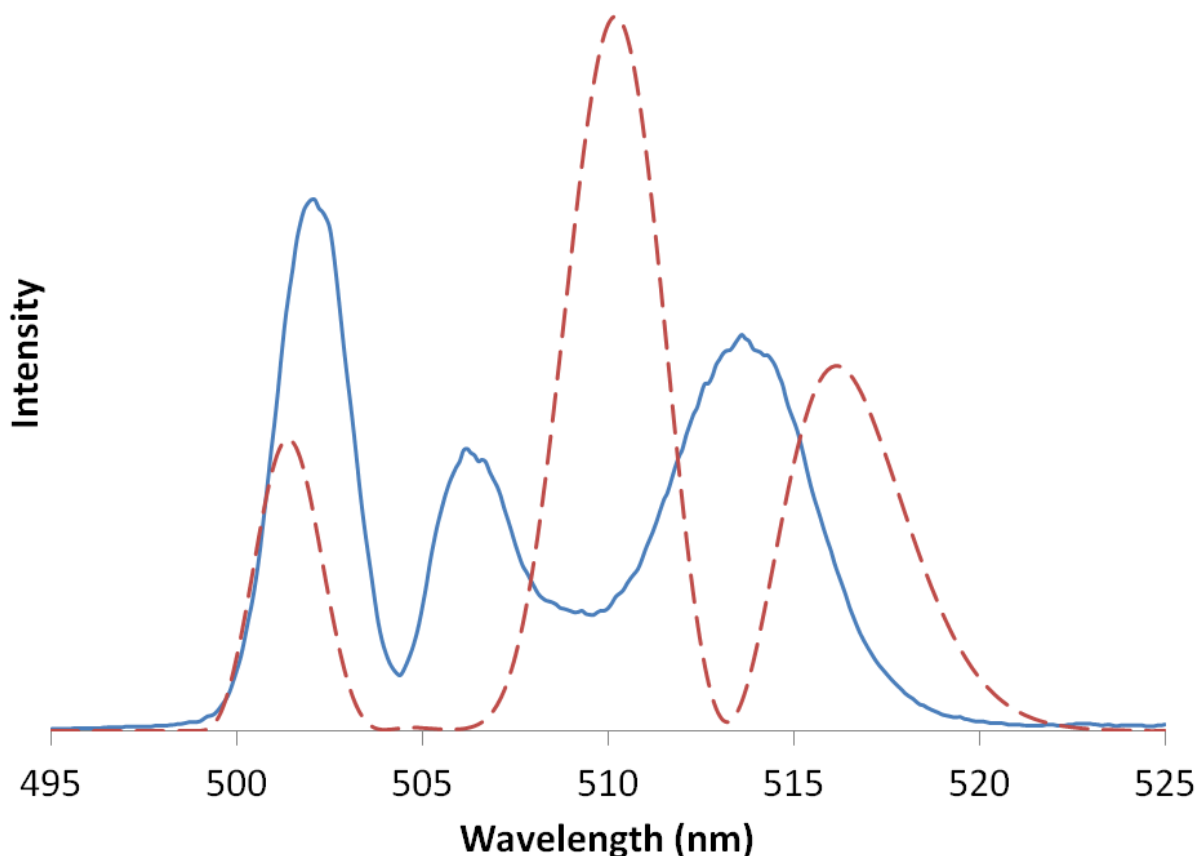


Figure 2. Comparison of experimental (solid – blue) and simulated (dashed – red)  $12(0^+)(1, 43) \rightarrow 1(a)^3\Sigma^+$  triplet emission calculated using a mixture of wavefunctions from the next nearest neighbor pair of levels  $12(0^+)(1, 43)$  and  $11(0^+)(4, 43)$ . Note that inclusion of the  $11(0^+)(v = 4)$  wavefunction causes the simulated emission spectrum to extend to longer wavelengths than is observed for the experimental spectrum. Inclusion of wavefunction contributions from even higher vibrational levels of the  $11(0^+)$  state would further exacerbate this situation. The reduced  $\chi^2$  value of the best fit to the experimental spectrum is 155.1, which is  $\sim 14.3$  times larger than that obtained for the fit shown in Fig. 7(b) based on the mixing of pure  $12(0^+)(1, 43)$  and  $11(0^+)(3, 43)$  vibrational wavefunctions.

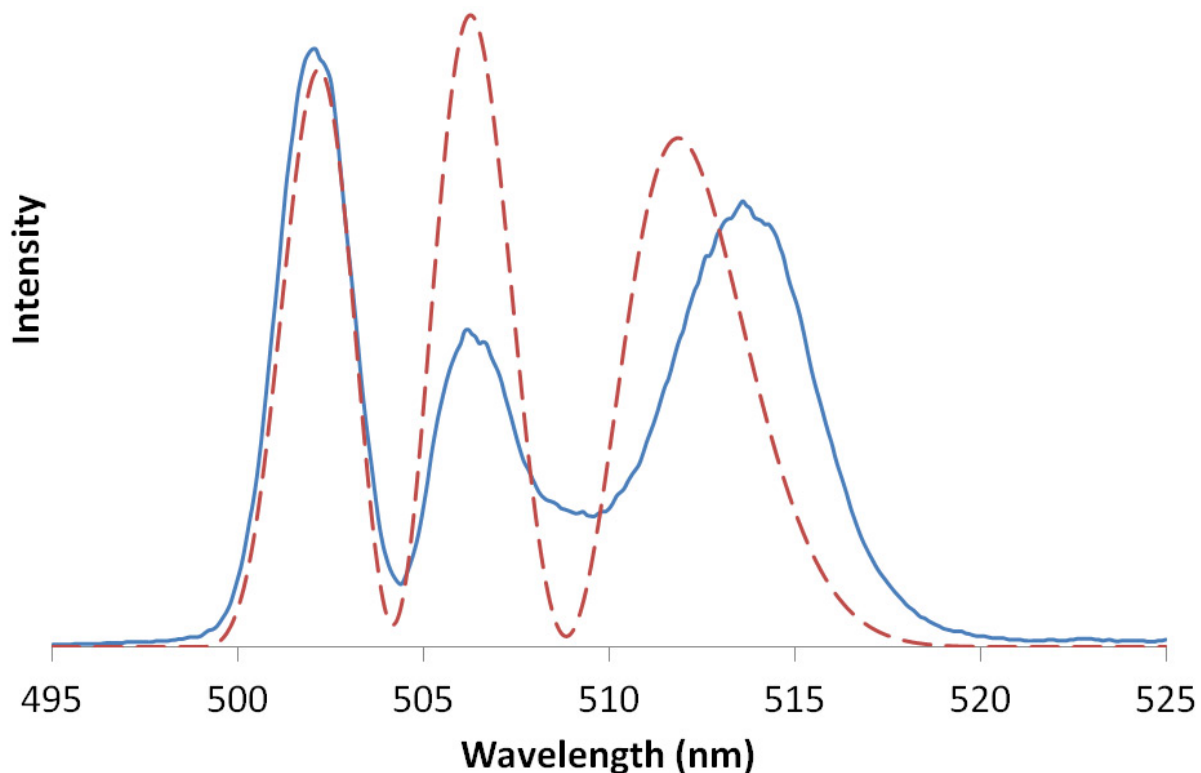


Figure 3. Comparison of experimental (solid – blue) and simulated (dashed – red)  $12(0^+) (1, 43) \rightarrow 1(a)^3\Sigma^+$  triplet emission calculated using a mixture of pure  $12(0^+) (1, 43)$  and  $11(0^+) (2, 43)$  wavefunctions. The generally poor level of agreement is evident regardless of the values chosen for  $\theta$  and  $(a_2/b_2)$ . The reduced  $\chi^2$  value of the best fit to the experimental spectrum is 34.44, which is  $\sim 3.18$  times larger than that obtained for the fit shown in Fig. 7(b) based on the mixing of pure  $12(0^+) (1, 43)$  and  $11(0^+) (3, 43)$  vibrational wavefunctions.

## Supplementary Material Table I – Experimental NaCs $2(A)^1\Sigma^+$ Level Energies

Table of NaCs  $2(A)^1\Sigma^+$  level energies determined in this work and in the work of Ashman *et al.* (J. Chem. Phys. **136**, 114313, 2012).  $v'$  and  $J'$  denote the  $2(A)^1\Sigma^+$  vibrational and rotational quantum numbers, respectively.  $v''$  and  $J''$  denote the ground  $1(X)^1\Sigma^+$  vibrational and rotational quantum numbers, respectively. The ground state level energies are calculated with the experimental Dunham coefficients of Docenko *et al.* (Eur. Phys. J. D **31**, 205-211, 2004), which are reported to be accurate to  $\pm 0.003 \text{ cm}^{-1}$ . We assign an uncertainty of  $\pm 0.01 \text{ cm}^{-1}$  to the pump laser frequency, hence the  $2(A)^1\Sigma^+$  level energies are also accurate to  $\sim 0.01 \text{ cm}^{-1}$ . The final column indicates whether the level energy was measured in this work (\*), or by Ashman *et al.* (blank).

$v'$	$J'$	$v''$	$J''$	Ground State Level Energy ( $\text{cm}^{-1}$ )	Pump Laser Frequency ( $\text{cm}^{-1}$ )	$2(A)^1\Sigma^+$ Level Energy ( $\text{cm}^{-1}$ )	Note
9	13	0	14	61.513	11019.23	11080.74	*
9	14	0	15	63.249	11018.76	11082.01	*
9	14	0	13	59.893	11022.11	11082.00	*
9	15	0	16	65.100	11018.27	11083.36	*
9	15	0	14	61.513	11021.85	11083.36	*
9	16	0	17	67.067	11017.75	11084.82	*
9	16	0	15	63.249	11021.57	11084.82	*
9	17	0	18	69.149	11017.22	11086.37	*
9	17	0	16	65.100	11021.26	11086.36	*
9	17	0	18	69.149	11017.21	11086.36	*
9	17	0	16	65.100	11021.26	11086.36	*
9	18	0	19	71.347	11016.66	11088.00	*
9	18	0	17	67.067	11020.94	11088.01	*
9	19	0	20	73.660	11016.08	11089.74	*
9	19	0	18	69.149	11020.59	11089.74	*
9	20	0	0	71.347	11020.23	11091.58	*
9	22	0	21	76.089	11019.45	11095.54	*
9	23	0	22	78.633	11019.03	11097.67	*
9	23	0	24	84.066	11013.60	11097.67	*
9	24	0	23	81.292	11018.60	11099.89	*
9	24	0	25	86.956	11012.93	11099.89	*
9	25	0	24	84.066	11018.15	11102.22	*
9	25	0	26	89.961	11012.26	11102.22	*
9	26	0	25	86.956	11017.69	11104.64	*
9	26	0	27	93.081	11011.56	11104.64	*
9	27	0	26	89.961	11017.22	11107.18	*
9	27	0	28	96.316	11010.86	11107.17	*

9	28	0	27	93.081	11016.73	11109.81	*
9	28	0	29	99.666	11010.14	11109.81	*
9	29	0	28	96.316	11016.23	11112.55	*
9	29	0	30	103.131	11009.41	11112.54	*
9	30	0	29	99.666	11015.73	11115.39	*
9	30	0	31	106.711	11008.68	11115.39	*
9	31	0	30	103.131	11015.21	11118.34	*
9	31	0	32	110.406	11007.93	11118.34	*
9	32	0	33	114.215	11007.18	11121.40	*
9	33	0	34	118.140	11006.43	11124.57	*
12	22	0	21	76.089	11171.51	11247.60	*
12	23	0	22	78.633	11171.18	11249.81	*
12	24	0	23	81.292	11170.79	11252.08	*
12	26	0	27	93.081	11163.70	11256.78	*
12	26	0	25	86.956	11169.82	11256.77	*
12	27	0	28	96.316	11162.89	11259.20	*
12	27	0	26	89.961	11169.24	11259.20	*
12	28	0	29	99.666	11162.01	11261.68	*
12	28	0	27	93.081	11168.59	11261.67	*
12	29	0	30	103.131	11161.07	11264.20	*
12	29	0	28	96.316	11167.88	11264.20	*
12	30	0	31	106.711	11160.06	11266.78	*
12	30	0	29	99.666	11167.11	11266.78	*
12	31	0	32	110.406	11159.01	11269.41	*
12	31	0	30	103.131	11166.28	11269.41	*
12	32	0	33	114.215	11157.89	11272.11	*
12	32	0	31	106.711	11165.40	11272.11	*
12	33	0	32	110.406	11164.46	11274.87	*
12	33	0	34	118.140	11156.73	11274.87	*
12	34	0	35	122.179	11155.49	11277.67	*
12	34	0	33	114.215	11163.45	11277.67	*
12	35	0	36	126.332	11154.25	11280.59	*
12	35	0	34	118.140	11162.45	11280.59	*
12	36	0	37	130.600	11152.95	11283.55	*
12	36	0	35	122.179	11161.38	11283.56	*
12	37	0	38	134.982	11151.61	11286.59	*
12	37	0	36	126.332	11160.26	11286.59	*
12	38	0	39	139.479	11150.23	11289.70	*
12	38	0	37	130.600	11159.11	11289.71	*
12	39	0	40	144.090	11148.80	11292.89	*
12	39	0	38	134.982	11157.91	11292.90	*
12	40	0	41	148.816	11147.34	11296.16	*
12	40	0	39	139.479	11156.69	11296.17	*

12	41	0	42	153.655	11145.85	11299.51	*
12	41	0	40	144.090	11155.42	11299.51	*
12	41	0	42	153.655	11145.85	11299.50	*
12	42	0	41	148.816	11154.12	11302.93	*
12	42	0	43	158.609	11144.32	11302.93	*
12	43	0	42	153.655	11152.79	11306.44	*
12	43	0	44	163.676	11142.76	11306.43	*
12	44	0	43	158.609	11151.42	11310.03	*
12	44	0	45	168.858	11141.17	11310.02	*
12	45	0	44	163.676	11150.03	11313.71	*
12	45	0	46	174.153	11139.55	11313.70	*
12	46	0	45	168.858	11148.60	11317.46	*
12	46	0	47	179.562	11137.89	11317.45	*
12	47	0	46	174.153	11147.15	11321.30	*
12	47	0	48	185.085	11136.21	11321.30	*
12	48	0	47	179.562	11145.67	11325.23	*
12	48	0	47	179.562	11145.66	11325.23	*
12	49	0	48	185.085	11144.16	11329.24	*
12	50	0	49	190.721	11142.63	11333.35	*
12	51	0	50	196.470	11141.08	11337.55	*
12	52	0	51	202.333	11139.51	11341.84	*
12	53	0	52	208.310	11137.92	11346.23	*
12	54	0	53	214.399	11136.31	11350.71	*
14	1	0	2	49.706	11296.42	11346.13	*
14	2	0	3	50.053	11296.22	11346.27	*
14	3	0	4	50.517	11296.01	11346.53	*
14	4	0	5	51.095	11295.76	11346.86	*
14	5	0	6	51.790	11295.48	11347.27	*
14	6	0	7	52.601	11295.17	11347.77	*
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14	10	0	9	54.569	11296.06	11350.63	*
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14	15	0	14	61.513	11294.53	11356.04	
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14	16	0	15	63.249	11294.14	11357.39	

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14	17	0	16	65.100	11293.71	11358.81	
14	17	0	18	69.149	11289.66	11358.81	
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14	20	0	19	71.347	11292.27	11363.61	
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14	22	0	21	76.089	11291.17	11367.26	
14	22	0	23	81.292	11285.97	11367.26	
14	23	0	22	78.633	11290.58	11369.21	
14	23	0	24	84.066	11285.15	11369.22	
14	24	0	23	81.292	11289.97	11371.26	
14	24	0	25	86.956	11284.31	11371.27	
14	25	0	24	84.066	11289.34	11373.41	
14	25	0	24	84.066	11289.34	11373.41	
14	25	0	26	89.961	11283.45	11373.41	
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14	26	0	25	86.956	11288.69	11375.65	
14	26	0	27	93.081	11282.56	11375.64	
14	26	0	27	93.081	11282.57	11375.65	
14	27	0	26	89.961	11288.02	11377.98	
14	27	0	26	89.961	11288.02	11377.98	
14	27	0	28	96.316	11281.67	11377.98	
14	28	0	27	93.081	11287.34	11380.42	
14	28	0	27	93.081	11287.34	11380.42	
14	28	0	29	99.666	11280.75	11380.42	
14	28	0	29	99.666	11280.75	11380.42	
14	29	0	28	96.316	11286.64	11382.96	
14	29	0	28	96.316	11286.64	11382.96	
14	29	0	30	103.131	11279.83	11382.96	
14	29	0	30	103.131	11279.83	11382.96	
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14	30	0	29	99.666	11285.94	11385.61	
14	30	0	31	106.711	11278.89	11385.60	
14	30	0	31	106.711	11278.89	11385.60	
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14	31	0	30	103.131	11285.23	11388.36	
14	31	0	32	110.406	11277.95	11388.35	
14	31	0	32	110.406	11277.95	11388.36	

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14	35	0	34	118.140	11282.39	11400.53	
14	35	0	36	126.332	11274.19	11400.52	
14	36	0	35	122.179	11281.71	11403.88	
14	36	0	37	130.600	11273.28	11403.88	
14	37	0	36	126.332	11281.04	11407.37	
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14	42	0	41	148.816	11278.02	11426.83	
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14	43	0	42	153.655	11277.49	11431.15	
14	43	0	44	163.676	11267.47	11431.14	
14	43	0	44	163.676	11267.47	11431.15	
14	44	0	43	158.609	11276.99	11435.60	
14	44	0	45	168.858	11266.74	11435.60	
14	44	0	45	168.858	11266.74	11435.60	
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14	45	0	46	174.153	11266.04	11440.19	
14	46	0	45	168.858	11276.06	11444.92	
14	46	0	47	179.562	11265.35	11444.91	
14	47	0	46	174.153	11275.62	11449.78	
14	47	0	48	185.085	11264.69	11449.78	
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14	47	0	48	185.085	11264.70	11449.78	
14	48	0	47	179.562	11275.21	11454.78	
14	48	0	49	190.721	11264.05	11454.77	
14	48	0	49	190.721	11264.06	11454.78	
14	48	0	49	190.721	11264.06	11454.78	
14	49	0	48	185.085	11274.82	11459.91	
14	49	0	50	196.470	11263.44	11459.91	



14	49	0	50	196.470	11263.44	11459.91	
14	49	0	50	196.470	11263.46	11459.93	
14	50	0	49	190.721	11274.46	11465.18	
14	50	0	51	202.333	11262.84	11465.18	
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14	51	0	52	208.310	11262.29	11470.59	
14	51	0	52	208.310	11262.29	11470.60	
14	52	0	51	202.333	11273.83	11476.17	
14	52	0	53	214.399	11261.77	11476.16	
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14	52	0	53	214.399	11261.77	11476.17	
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14	53	0	54	220.602	11260.20	11480.80	
14	53	0	54	220.602	11260.20	11480.80	
14	54	0	53	214.399	11272.32	11486.72	
14	54	0	53	214.399	11272.33	11486.73	
14	54	0	55	226.917	11259.81	11486.72	
14	54	0	55	226.917	11259.81	11486.73	
14	55	0	54	220.602	11272.08	11492.68	
14	55	0	54	220.602	11272.08	11492.68	
14	55	0	56	233.345	11259.33	11492.68	
14	55	0	56	233.345	11259.33	11492.68	
14	56	0	55	226.917	11271.76	11498.68	
14	56	0	55	226.917	11271.76	11498.68	
14	56	0	57	239.886	11258.79	11498.68	
14	56	0	57	239.886	11258.79	11498.68	
14	57	0	56	233.345	11271.41	11504.76	
14	57	0	56	233.345	11271.41	11504.76	
14	57	0	58	246.540	11258.22	11504.76	
14	57	0	58	246.540	11258.22	11504.76	
14	58	0	57	239.886	11271.04	11510.92	
14	58	0	57	239.886	11271.04	11510.92	
14	58	0	59	253.306	11257.61	11510.92	
14	58	0	59	253.306	11257.61	11510.92	
14	59	0	58	246.540	11270.63	11517.17	
14	59	0	58	246.540	11270.63	11517.17	
14	59	0	60	260.185	11256.98	11517.17	
14	59	0	60	260.185	11256.98	11517.17	
14	60	0	59	253.306	11270.19	11523.50	
14	60	0	59	253.306	11270.19	11523.50	

14	60	0	61	267.176	11256.32	11523.50	
14	60	0	61	267.176	11256.33	11523.50	
14	61	0	60	260.185	11269.72	11529.91	
14	61	0	62	274.279	11255.63	11529.90	
14	62	0	61	267.176	11269.19	11536.37	
14	62	0	63	281.494	11254.87	11536.37	
14	63	0	62	274.279	11268.59	11542.87	
14	63	0	64	288.822	11254.05	11542.87	
14	64	0	63	281.494	11267.90	11549.39	
14	64	0	65	296.261	11253.13	11549.39	
14	65	0	64	288.822	11267.06	11555.88	
14	65	0	66	303.811	11252.07	11555.88	
14	66	0	65	296.261	11266.04	11562.30	
14	66	0	67	311.474	11250.83	11562.30	
14	67	0	68	319.248	11249.36	11568.60	
14	67	0	68	319.248	11249.36	11568.60	
14	68	0	69	327.133	11247.63	11574.76	
14	68	0	69	327.133	11247.63	11574.77	
14	69	0	70	335.129	11245.67	11580.80	
14	70	0	71	343.237	11243.52	11586.75	
14	71	0	72	351.455	11241.20	11592.66	
16	44	0	45	168.858	11375.67	11544.52	
18	1	0	2	49.706	11524.80	11574.50	
18	2	0	3	50.054	11524.61	11574.66	
18	2	0	3	50.054	11524.61	11574.66	
18	3	0	2	49.706	11525.18	11574.89	
18	3	0	4	50.517	11524.38	11574.89	
18	3	0	4	50.517	11524.38	11574.89	
18	4	0	3	50.054	11525.15	11575.20	
18	4	0	5	51.096	11524.11	11575.21	
18	4	0	5	51.096	11524.11	11575.21	
18	5	0	4	50.517	11525.08	11575.60	
18	5	0	6	51.790	11523.81	11575.60	
18	5	0	6	51.790	11523.81	11575.60	
18	6	0	5	51.096	11524.97	11576.07	
18	6	0	7	52.601	11523.46	11576.06	
18	6	0	7	52.601	11523.47	11576.07	
18	7	0	6	51.790	11524.82	11576.61	
18	7	0	6	51.790	11524.83	11576.62	
18	7	0	8	53.527	11523.09	11576.61	
18	7	0	8	53.527	11523.09	11576.61	
18	8	0	7	52.601	11524.64	11577.24	
18	8	0	7	52.601	11524.64	11577.24	

18	8	0	9	54.569	11522.67	11577.24	
18	8	0	9	54.569	11522.67	11577.24	
18	9	0	8	53.527	11524.42	11577.95	
18	9	0	8	53.527	11524.42	11577.95	
18	9	0	10	55.726	11522.22	11577.95	
18	9	0	10	55.726	11522.22	11577.95	
18	10	0	9	54.569	11524.16	11578.73	
18	10	0	9	54.569	11524.16	11578.73	
18	10	0	11	56.999	11521.73	11578.73	
18	10	0	11	56.999	11521.73	11578.73	
18	11	0	10	55.726	11523.87	11579.59	
18	11	0	10	55.726	11523.87	11579.59	
18	11	0	12	58.388	11521.20	11579.59	
18	11	0	12	58.388	11521.21	11579.60	
18	12	0	11	56.999	11523.53	11580.53	
18	12	0	11	56.999	11523.54	11580.53	
18	12	0	13	59.893	11520.64	11580.53	
18	12	0	13	59.893	11520.65	11580.54	
18	13	0	12	58.388	11523.16	11581.55	
18	13	0	12	58.388	11523.16	11581.55	
18	13	0	14	61.513	11520.04	11581.55	
18	13	0	14	61.513	11520.04	11581.55	
18	14	0	13	59.893	11522.75	11582.65	
18	14	0	13	59.893	11522.75	11582.65	
18	14	0	15	63.249	11519.40	11582.65	
18	14	0	15	63.249	11519.40	11582.65	
18	15	0	14	61.513	11522.31	11583.82	
18	15	0	14	61.513	11522.31	11583.82	
18	15	0	16	65.100	11518.73	11583.83	
18	15	0	16	65.100	11518.73	11583.83	
18	16	0	15	63.249	11521.83	11585.08	
18	16	0	15	63.249	11521.83	11585.08	
18	16	0	17	67.067	11518.01	11585.08	
18	16	0	17	67.067	11518.01	11585.08	
18	17	0	16	65.100	11521.31	11586.41	
18	17	0	16	65.100	11521.31	11586.41	
18	17	0	18	69.149	11517.26	11586.41	
18	17	0	18	69.149	11517.26	11586.41	
18	18	0	17	67.067	11520.76	11587.82	
18	18	0	17	67.067	11520.76	11587.83	
18	18	0	19	71.347	11516.48	11587.82	
18	18	0	19	71.347	11516.48	11587.83	
18	19	0	18	69.149	11520.16	11589.31	

18	19	0	18	69.149	11520.17	11589.31	
18	19	0	20	73.660	11515.65	11589.31	
18	19	0	20	73.660	11515.65	11589.31	
18	20	0	19	71.347	11519.53	11590.88	
18	20	0	19	71.347	11519.54	11590.88	
18	20	0	21	76.089	11514.79	11590.88	
18	20	0	21	76.089	11514.80	11590.89	
18	21	0	20	73.660	11518.87	11592.53	
18	21	0	20	73.660	11518.87	11592.53	
18	21	0	22	78.633	11513.89	11592.52	
18	22	0	21	76.089	11518.17	11594.26	
18	22	0	21	76.089	11518.17	11594.26	
18	22	0	23	81.292	11512.96	11594.25	
18	23	0	22	78.633	11517.43	11596.06	
18	23	0	22	78.633	11517.43	11596.07	
18	23	0	24	84.066	11511.99	11596.06	
18	24	0	23	81.292	11516.66	11597.95	
18	24	0	23	81.292	11516.66	11597.95	
18	24	0	25	86.956	11510.98	11597.94	
18	24	0	25	86.956	11510.99	11597.95	
18	25	0	24	84.066	11515.85	11599.92	
18	25	0	24	84.066	11515.85	11599.92	
18	25	0	26	89.961	11509.95	11599.91	
18	25	0	26	89.961	11509.95	11599.91	
18	26	0	25	86.956	11515.00	11601.95	
18	26	0	25	86.956	11515.01	11601.96	
18	26	0	27	93.081	11508.87	11601.95	
18	26	0	27	93.081	11508.88	11601.96	
18	27	0	26	89.961	11514.12	11604.08	
18	27	0	28	96.316	11507.76	11604.08	
18	27	0	28	96.316	11507.77	11604.09	
18	28	0	27	93.081	11513.20	11606.28	
18	28	0	29	99.666	11506.62	11606.28	
18	28	0	29	99.666	11506.63	11606.29	
18	29	0	28	96.316	11512.25	11608.57	
18	29	0	30	103.131	11505.44	11608.57	
18	29	0	30	103.131	11505.45	11608.58	
18	30	0	29	99.666	11511.27	11610.94	
18	30	0	29	99.666	11511.28	11610.95	
18	30	0	31	106.711	11504.23	11610.94	
18	31	0	30	103.131	11510.26	11613.39	
18	31	0	30	103.131	11510.26	11613.40	
18	31	0	32	110.406	11502.98	11613.39	

18	32	0	31	106.711	11509.21	11615.92	
18	32	0	31	106.711	11509.21	11615.92	
18	32	0	33	114.215	11501.71	11615.92	
18	33	0	32	110.406	11508.13	11618.53	
18	33	0	32	110.406	11508.13	11618.53	
18	33	0	34	118.140	11500.39	11618.53	
18	34	0	33	114.215	11507.01	11621.22	
18	34	0	33	114.215	11507.01	11621.23	
18	34	0	35	122.179	11499.05	11621.22	
18	35	0	34	118.140	11505.86	11624.00	
18	35	0	34	118.140	11505.87	11624.01	
18	35	0	36	126.332	11497.67	11624.00	
18	36	0	35	122.179	11504.68	11626.86	
18	36	0	37	130.600	11496.26	11626.86	
18	37	0	36	126.332	11503.48	11629.81	
18	37	0	38	134.983	11494.82	11629.80	
18	38	0	37	130.600	11502.23	11632.83	
18	38	0	39	139.479	11493.36	11632.84	
18	39	0	38	134.983	11500.97	11635.95	
18	39	0	40	144.090	11491.86	11635.95	
18	40	0	39	139.479	11499.67	11639.15	
18	40	0	41	148.816	11490.34	11639.15	
18	41	0	40	144.090	11498.35	11642.44	
18	41	0	42	153.655	11488.79	11642.44	
18	42	0	41	148.816	11497.00	11645.82	
18	42	0	43	158.609	11487.21	11645.82	
18	43	0	42	153.655	11495.63	11649.29	
18	43	0	44	163.676	11485.61	11649.29	
18	44	0	43	158.609	11494.24	11652.85	
18	44	0	45	168.858	11483.99	11652.85	
18	45	0	44	163.676	11492.83	11656.50	
18	45	0	46	174.153	11482.35	11656.50	
18	46	0	45	168.858	11491.40	11660.26	
18	46	0	47	179.562	11480.69	11660.25	
18	47	0	46	174.153	11489.95	11664.10	
18	47	0	48	185.085	11479.02	11664.10	
18	48	0	47	179.562	11488.48	11668.05	
18	48	0	49	190.721	11477.33	11668.05	
18	49	0	48	185.085	11487.01	11672.09	
18	49	0	50	196.470	11475.62	11672.09	
18	50	0	49	190.721	11485.52	11676.25	
18	50	0	51	202.333	11473.92	11676.25	
18	51	0	50	196.470	11484.04	11680.51	

18	51	0	52	208.310	11472.20	11680.51	
18	52	0	51	202.333	11482.55	11684.88	
18	52	0	53	214.399	11470.49	11684.88	
18	53	0	52	208.310	11481.06	11689.37	
18	54	0	53	214.399	11479.58	11693.98	
18	55	0	54	220.602	11478.10	11698.71	
18	56	0	55	226.917	11476.64	11703.56	
18	57	0	56	233.345	11475.20	11708.54	
18	58	0	57	239.886	11473.78	11713.66	
18	59	0	58	246.540	11472.38	11718.92	
18	60	0	59	253.306	11471.01	11724.32	
21	4	0	3	50.054	11685.40	11735.45	
21	5	0	4	50.517	11685.34	11735.86	
21	6	0	5	51.096	11685.26	11736.36	
21	6	0	7	52.601	11683.76	11736.36	
21	7	0	6	51.790	11685.15	11736.94	
21	7	0	8	53.527	11683.41	11736.93	
21	8	0	7	52.601	11685.00	11737.60	
21	8	0	9	54.569	11683.03	11737.60	
21	9	0	8	53.527	11684.81	11738.34	
21	9	0	10	55.726	11682.61	11738.34	
21	10	0	9	54.569	11684.60	11739.17	
21	10	0	11	56.999	11682.17	11739.16	
21	11	0	10	55.726	11684.34	11740.07	
21	11	0	12	58.388	11681.68	11740.07	
21	12	0	11	56.999	11684.06	11741.06	
21	12	0	13	59.893	11681.16	11741.05	
21	13	0	12	58.388	11683.73	11742.12	
21	13	0	14	61.513	11680.61	11742.12	
21	14	0	13	59.893	11683.37	11743.26	
21	14	0	13	59.893	11683.37	11743.27	
21	14	0	15	63.249	11680.01	11743.26	
21	14	0	15	63.249	11680.02	11743.27	
21	15	0	14	61.513	11682.98	11744.50	
21	15	0	16	65.100	11679.39	11744.49	
21	16	0	15	63.249	11682.55	11745.80	
21	16	0	17	67.067	11678.73	11745.80	
21	17	0	16	65.100	11682.09	11747.19	
21	18	0	17	67.067	11681.59	11748.65	
21	19	0	18	69.149	11681.05	11750.19	
21	20	0	19	71.347	11680.47	11751.82	
21	21	0	20	73.660	11679.86	11753.52	
21	22	0	21	76.089	11679.21	11755.30	

21	23	0	22	78.633	11678.52	11757.15	
21	35	0	36	126.332	11659.00	11785.33	
21	36	0	37	130.600	11657.57	11788.17	
21	37	0	38	134.983	11656.10	11791.09	
21	38	0	39	139.479	11654.60	11794.08	
21	39	0	40	144.090	11653.05	11797.14	
21	40	0	41	148.816	11651.47	11800.29	
21	41	0	40	144.090	11659.42	11803.51	
21	41	0	42	153.655	11649.85	11803.50	
21	42	0	41	148.816	11657.99	11806.80	
21	42	0	43	158.609	11648.19	11806.80	
21	43	0	42	153.655	11656.52	11810.18	
21	43	0	44	163.676	11646.50	11810.18	
21	44	0	43	158.609	11655.01	11813.62	
21	44	0	43	158.609	11655.02	11813.63	
21	44	0	45	168.858	11644.76	11813.62	
21	44	0	45	168.858	11644.77	11813.63	
21	45	0	44	163.676	11653.49	11817.17	
21	45	0	46	174.153	11643.01	11817.16	
21	46	0	45	168.858	11651.93	11820.79	
21	46	0	47	179.562	11641.22	11820.78	
21	47	0	46	174.153	11650.33	11824.49	
21	48	0	47	179.562	11648.71	11828.27	
21	49	0	48	185.085	11647.07	11832.16	
21	50	0	49	190.721	11645.41	11836.13	
21	51	0	50	196.470	11643.73	11840.20	
21	52	0	51	202.333	11642.06	11844.39	
23	32	0	31	106.711	11777.07	11883.78	*
23	33	0	32	110.406	11776.12	11886.52	*
23	34	0	33	114.215	11775.11	11889.33	*
23	35	0	34	118.140	11774.07	11892.20	*
23	36	0	35	122.179	11772.97	11895.15	*
23	37	0	36	126.332	11771.83	11898.16	*
23	38	0	37	130.600	11770.64	11901.24	*
23	39	0	38	134.982	11769.40	11904.39	*
23	40	0	39	139.479	11768.12	11907.60	*
23	41	0	40	144.090	11766.78	11910.87	*
23	42	0	41	148.816	11765.40	11914.22	*
23	43	0	42	153.655	11763.97	11917.63	*
23	44	0	43	158.609	11762.49	11921.10	*
23	45	0	44	163.676	11760.97	11924.65	*
23	46	0	45	168.858	11759.41	11928.26	*
23	47	0	46	174.153	11757.79	11931.94	*

23	48	0	47	179.562	11756.12	11935.68	*
23	49	0	48	185.085	11754.42	11939.50	*
23	50	1	49	288.375	11655.01	11943.38	
23	50	1	51	299.940	11643.43	11943.37	
23	50	0	49	190.721	11752.66	11943.38	*
23	51	0	50	196.470	11750.85	11947.32	*
23	52	0	51	202.333	11749.00	11951.33	*
25	9	1	8	151.740	11787.99	11939.73	
25	10	1	9	152.777	11787.94	11940.71	
25	11	1	10	153.930	11787.87	11941.80	
25	12	1	11	155.198	11787.79	11942.99	
25	13	1	12	156.582	11787.69	11944.27	
25	14	1	13	158.080	11787.57	11945.65	
25	15	1	14	159.694	11787.43	11947.13	
25	15	1	16	163.266	11783.86	11947.13	
25	16	1	15	161.422	11787.28	11948.70	
25	16	1	17	165.225	11783.48	11948.70	
25	17	1	16	163.266	11787.11	11950.37	
25	17	1	18	167.299	11783.07	11950.37	
25	18	0	17	67.067	11885.08	11952.14	
25	18	1	17	165.225	11786.91	11952.14	
25	18	1	19	169.488	11782.65	11952.14	
25	19	0	18	69.149	11884.85	11954.00	
25	19	1	18	167.299	11786.70	11954.00	
25	20	0	19	71.347	11884.61	11955.96	
25	20	0	21	76.089	11879.87	11955.96	
25	20	1	19	169.488	11786.47	11955.96	
25	20	1	21	174.210	11781.75	11955.96	
25	21	0	20	73.660	11884.35	11958.01	
25	21	0	22	78.633	11879.37	11958.00	
25	21	1	20	171.792	11786.21	11958.00	
25	21	1	22	176.744	11781.26	11958.00	
25	22	0	21	76.089	11884.06	11960.15	
25	22	0	23	81.292	11878.86	11960.15	
25	22	1	21	174.210	11785.94	11960.15	
25	22	1	23	179.393	11780.75	11960.14	
25	23	0	22	78.633	11883.75	11962.38	
25	23	0	24	84.066	11878.31	11962.38	
25	23	1	22	176.744	11785.63	11962.38	
25	23	1	24	182.156	11780.22	11962.38	
25	24	0	23	81.292	11883.41	11964.70	
25	24	0	25	86.956	11877.75	11964.70	
25	24	1	23	179.393	11785.31	11964.70	



25	24	1	25	185.034	11779.67	11964.70	
25	25	0	24	84.066	11883.05	11967.11	
25	25	0	26	89.961	11877.15	11967.11	
25	25	1	24	182.156	11784.95	11967.11	
25	25	1	26	188.026	11779.08	11967.11	
25	25	1	24	182.156	11817.35	11999.50	
25	26	0	25	86.956	11882.66	11969.61	
25	26	0	27	93.081	11876.53	11969.61	
25	26	1	25	185.034	11784.58	11969.61	
25	26	1	27	191.134	11778.48	11969.61	
25	27	0	26	89.961	11882.24	11972.20	
25	27	0	28	96.316	11875.88	11972.20	
25	27	0	28	96.316	11875.88	11972.20	
25	27	1	26	188.026	11784.17	11972.19	
25	27	1	28	194.356	11777.77	11972.12	
25	28	0	27	93.081	11881.79	11974.87	
25	28	0	29	99.666	11875.20	11974.86	
25	28	1	27	191.134	11783.73	11974.86	
25	28	1	29	197.692	11777.17	11974.87	
25	29	0	28	96.316	11881.30	11977.62	
25	29	0	30	103.131	11874.49	11977.62	
25	29	1	28	194.356	11783.26	11977.61	
25	29	1	30	201.143	11776.47	11977.62	
25	30	0	29	99.666	11880.78	11980.45	
25	30	0	31	106.711	11873.74	11980.45	
25	30	1	29	197.692	11782.76	11980.45	
25	31	0	32	110.406	11872.95	11983.36	
25	31	1	30	201.143	11782.21	11983.36	
25	32	0	31	106.711	11879.64	11986.35	
25	32	0	33	114.215	11872.13	11986.35	
25	32	1	31	204.708	11781.64	11986.35	
25	33	0	32	110.406	11879.00	11989.41	
25	33	0	32	110.406	11879.01	11989.41	
25	33	0	34	118.140	11871.27	11989.41	
25	33	1	32	208.388	11781.02	11989.41	
25	34	0	33	114.215	11878.33	11992.54	
25	34	0	33	114.215	11878.33	11992.54	
25	34	0	35	122.179	11870.36	11992.54	
25	34	1	33	212.182	11780.36	11992.54	
25	35	0	34	118.140	11877.61	11995.75	
25	35	0	34	118.140	11877.61	11995.75	
25	35	0	36	126.332	11869.41	11995.74	
25	36	0	35	122.179	11876.84	11999.02	

25	36	0	35	122.179	11876.84	11999.02	
25	36	0	37	130.600	11868.42	11999.02	
25	37	0	36	126.332	11876.02	12002.36	
25	37	0	36	126.332	11876.02	12002.36	
25	37	0	38	134.983	11867.37	12002.36	
25	38	0	37	130.600	11875.16	12005.76	
25	38	0	39	139.479	11866.28	12005.76	
25	39	0	38	134.983	11874.24	12009.22	
25	39	0	40	144.090	11865.13	12009.22	
25	40	0	39	139.479	11873.26	12012.74	
25	40	0	41	148.816	11863.92	12012.74	
25	41	0	40	144.090	11872.23	12016.32	
25	41	0	42	153.655	11862.66	12016.32	
25	42	0	41	148.816	11871.14	12019.96	
25	42	0	43	158.609	11861.35	12019.96	
25	43	0	42	153.655	11869.99	12023.65	
25	44	0	43	158.609	11868.78	12027.39	
25	45	0	44	163.676	11867.37	12031.05	
25	46	0	45	168.858	11866.18	12035.04	
25	47	0	46	174.153	11864.79	12038.94	
25	48	0	47	179.562	11863.33	12042.89	
27	11	0	10	55.726	12189.13	12244.85	
27	11	0	12	58.388	12186.47	12244.85	
27	11	1	10	153.930	12090.93	12244.86	
27	11	1	12	156.582	12088.27	12244.85	
27	33	1	32	208.388	11877.40	12085.78	
27	34	1	33	212.182	11877.03	12089.21	
27	35	1	34	216.091	11876.64	12092.73	
27	36	1	35	220.113	11876.23	12096.34	
27	36	1	37	228.500	11867.84	12096.34	
27	37	1	36	224.250	11875.79	12100.04	
27	37	1	38	232.865	11867.17	12100.04	
27	38	1	37	228.500	11875.33	12103.83	
27	38	1	39	237.343	11866.49	12103.83	
27	39	1	38	232.865	11874.84	12107.70	
27	39	1	40	241.936	11865.77	12107.70	
27	40	1	39	237.343	11874.31	12111.66	
27	40	1	41	246.642	11865.01	12111.66	
27	41	1	40	241.936	11873.75	12115.69	
27	41	1	42	251.461	11864.22	12115.68	
27	42	1	41	246.642	11873.15	12119.79	
27	42	1	43	256.395	11863.40	12119.79	
27	43	1	42	251.461	11872.51	12123.97	

27	43	1	44	261.442	11862.53	12123.97	
27	44	1	43	256.395	11871.82	12128.21	
27	44	1	45	266.602	11861.61	12128.21	
27	45	1	44	261.442	11871.08	12132.52	
27	45	1	46	271.875	11860.64	12132.52	
27	46	1	45	266.602	11870.28	12136.88	
27	46	1	47	277.262	11859.62	12136.89	
27	47	1	46	271.875	11869.43	12141.30	
27	47	1	48	282.762	11858.54	12141.30	
27	48	1	47	277.262	11868.51	12145.77	
27	48	1	49	288.375	11857.39	12145.77	
27	49	1	48	282.762	11867.52	12150.28	
27	49	1	50	294.101	11856.18	12150.28	
27	50	1	49	288.375	11866.45	12154.83	
27	50	1	51	299.940	11854.89	12154.83	
27	51	1	50	294.101	11865.31	12159.42	
27	51	1	52	305.892	11853.52	12159.41	
27	52	1	51	299.940	11864.10	12164.04	
27	52	1	53	311.956	11852.08	12164.04	
27	53	1	52	305.892	11862.80	12168.69	
27	53	1	54	318.133	11850.56	12168.69	
27	54	1	53	311.956	11861.42	12173.38	
27	55	1	54	318.133	11859.96	12178.09	
27	56	1	55	324.423	11858.40	12182.83	
27	81	0	80	421.181	11900.11	12321.29	
27	81	0	82	439.712	11881.58	12321.29	
27	81	1	80	517.878	11803.42	12321.29	
27	81	1	82	536.331	11784.96	12321.29	
27	83	0	82	439.712	11897.41	12337.12	
27	83	0	84	458.680	11878.44	12337.12	
27	83	1	82	536.331	11800.79	12337.12	
27	83	1	84	555.219	11781.90	12337.12	
30	11	1	10	153.930	12260.46	12414.39	
30	11	1	12	156.582	12257.80	12414.38	
30	11	2	10	251.477	12162.91	12414.39	
30	11	2	12	254.118	12160.27	12414.38	
31	61	0	60	260.185	12146.13	12406.32	
31	61	0	62	274.279	12132.04	12406.32	
31	61	1	60	357.553	12048.76	12406.32	
31	61	1	62	371.589	12034.73	12406.32	
31	61	2	60	454.256	11952.06	12406.32	
31	61	2	62	468.232	11938.08	12406.32	
31	61	3	60	550.286	11856.03	12406.32	

31	61	3	62	564.204	11842.11	12406.32	
31	61	4	60	645.641	11760.68	12406.32	
31	61	4	62	659.498	11746.82	12406.31	
32	46	1	45	266.602	12144.79	12411.39	
32	47	1	46	271.875	12144.43	12416.31	
32	47	1	48	282.762	12133.54	12416.31	
32	48	1	47	277.262	12144.07	12421.34	
32	48	1	49	288.375	12132.96	12421.33	
32	49	1	48	282.762	12143.71	12426.47	
32	49	1	50	294.101	12132.37	12426.47	
32	50	1	49	288.375	12143.35	12431.72	
32	50	1	51	299.940	12131.78	12431.72	
32	51	1	50	294.101	12142.97	12437.07	
32	51	1	52	305.892	12131.18	12437.07	
32	52	1	51	299.940	12142.60	12442.54	
32	52	1	53	311.956	12130.58	12442.54	
32	53	1	52	305.892	12142.22	12448.11	
33	11	2	10	251.477	12268.51	12519.98	
33	11	2	12	254.118	12265.87	12519.98	
33	11	3	10	348.361	12171.61	12519.98	
33	11	3	12	350.991	12168.98	12519.97	
34	28	2	27	288.528	12193.34	12481.86	
34	28	2	29	295.059	12186.81	12481.86	
34	36	2	37	325.740	12176.98	12502.72	
34	37	2	38	330.086	12175.54	12505.62	
34	38	2	39	334.546	12174.04	12508.58	
34	39	2	40	339.120	12172.49	12511.61	
34	40	2	41	343.806	12170.89	12514.70	
34	41	2	42	348.606	12169.24	12517.85	
34	42	2	41	343.806	12177.25	12521.06	
34	42	2	43	353.519	12167.54	12521.06	
34	43	2	42	348.606	12175.73	12524.34	
34	43	2	44	358.545	12165.79	12524.34	
34	44	2	43	353.519	12174.16	12527.68	
34	44	2	45	363.684	12163.99	12527.68	
34	44	2	45	363.684	12163.99	12527.68	
34	45	2	44	358.545	12172.54	12531.08	
34	45	2	46	368.935	12162.14	12531.08	
34	45	2	46	368.935	12162.14	12531.08	
34	46	2	45	363.684	12170.87	12534.55	
34	46	2	47	374.300	12160.25	12534.55	
34	46	2	47	374.300	12160.25	12534.55	
34	47	2	46	368.935	12169.14	12538.08	

34	47	2	48	379.777	12158.30	12538.08	
34	47	2	48	379.777	12158.30	12538.08	
34	47	2	48	379.777	12158.30	12538.08	
34	48	2	47	374.300	12167.37	12541.67	
34	48	2	49	385.367	12156.30	12541.67	
34	49	2	48	379.777	12165.55	12545.33	
34	49	2	50	391.069	12154.26	12545.33	
34	50	2	49	385.367	12163.69	12549.05	
34	50	2	49	385.367	12163.69	12549.06	
34	50	2	51	396.883	12152.17	12549.05	
34	51	2	50	391.069	12161.77	12552.84	
34	51	2	50	391.069	12161.77	12552.84	
34	51	2	52	402.810	12150.03	12552.84	
34	52	2	51	396.883	12159.82	12556.70	
34	52	2	51	396.883	12159.81	12556.70	
34	52	2	53	408.849	12147.85	12556.70	
34	53	2	52	402.810	12157.81	12560.62	
34	53	2	54	415.000	12145.62	12560.62	
34	54	2	53	408.849	12155.76	12564.61	
34	54	2	55	421.264	12143.34	12564.61	
34	55	2	54	415.000	12153.66	12568.66	
34	55	2	56	427.639	12141.02	12568.66	
34	56	0	55	226.917	12345.87	12572.79	
34	56	0	57	239.886	12332.90	12572.78	
34	56	1	55	324.423	12248.36	12572.78	
34	56	1	57	337.339	12235.44	12572.78	
34	56	2	55	421.264	12151.52	12572.78	
34	56	2	55	421.264	12151.52	12572.78	
34	56	2	57	434.125	12138.66	12572.78	
34	56	2	57	434.125	12138.66	12572.78	
34	56	3	55	517.434	12055.35	12572.78	
34	56	3	57	530.242	12042.54	12572.78	
34	57	2	56	427.639	12149.33	12576.97	
34	57	2	58	440.724	12136.25	12576.97	
34	58	2	57	434.125	12147.12	12581.24	
34	58	2	59	447.434	12133.81	12581.24	
34	59	2	58	440.724	12144.86	12585.58	
34	59	2	58	440.724	12144.86	12585.59	
34	60	2	59	447.434	12142.58	12590.01	
34	61	2	60	454.256	12140.28	12594.54	
34	62	2	61	461.188	12138.05	12599.24	
35	15	2	16	260.775	12263.38	12524.16	
35	15	3	14	354.077	12170.08	12524.16	

35	15	3	16	357.620	12166.54	12524.16	
35	68	2	67	505.117	12173.94	12679.05	
35	68	2	69	520.645	12158.41	12679.06	
35	87	1	86	574.542	12204.37	12778.91	
35	87	1	88	594.298	12184.62	12778.91	
35	87	1	88	594.298	12184.62	12778.92	
35	87	2	86	670.323	12108.59	12778.91	
35	87	2	88	689.993	12088.92	12778.92	
37	43	0	42	153.655	12538.36	12692.01	
37	43	0	44	163.676	12528.34	12692.01	
37	43	1	42	251.461	12440.55	12692.01	
37	43	1	44	261.442	12430.57	12692.01	
37	43	2	42	348.606	12343.40	12692.00	
37	43	2	44	358.545	12333.46	12692.00	
37	43	3	42	445.084	12246.92	12692.00	
37	43	3	44	454.981	12237.02	12692.00	
37	43	4	42	540.891	12151.11	12692.00	
37	43	4	44	550.745	12141.27	12692.01	
37	43	4	44	550.745	12141.27	12692.01	
37	43	5	42	636.022	12055.99	12692.01	
37	43	5	44	645.834	12046.18	12692.01	
37	43	6	42	730.474	11961.54	12692.01	
37	43	6	44	740.242	11951.77	12692.01	
37	43	7	42	824.241	11867.77	12692.01	
37	43	7	44	833.966	11858.04	12692.01	
37	43	8	42	917.319	11774.69	12692.01	
37	43	8	44	927.000	11765.01	12692.01	
37	43	9	42	1009.702	11682.31	12692.01	
37	43	9	44	1019.338	11672.68	12692.01	
37	43	10	42	1101.385	11590.63	12692.02	
37	43	10	44	1110.976	11581.04	12692.01	
37	43	11	42	1192.362	11499.65	12692.01	
37	43	11	44	1201.907	11490.11	12692.01	
37	43	12	42	1282.627	11409.39	12692.01	
37	43	12	44	1292.127	11399.89	12692.01	
37	43	13	42	1372.175	11319.84	12692.02	
37	43	13	44	1381.627	11310.39	12692.01	
37	43	15	42	1549.090	11142.92	12692.01	
37	43	15	44	1558.447	11133.57	12692.01	
37	68	2	69	520.645	12261.47	12782.11	
37	68	3	67	600.930	12181.19	12782.12	
37	68	3	69	616.392	12165.72	12782.11	
39	68	3	67	600.930	12301.67	12902.60	

39	68	3	69	616.392	12286.20	12902.60	
40	84	3	85	755.790	12275.74	13031.53	
40	84	4	83	831.390	12200.15	13031.54	
40	84	4	85	850.247	12181.29	13031.53	
41	108	3	107	992.190	12248.18	13240.37	
41	108	3	109	1016.194	12224.18	13240.37	
41	108	4	107	1085.587	12154.78	13240.36	
41	108	4	109	1109.481	12130.89	13240.37	

## Supplementary Material Table II – Experimental NaCs 12(0<sup>+</sup>) Level Energies

Table of NaCs 12(0<sup>+</sup>) level energies determined in this work.  $v$  and  $J$  denote the vibrational and rotational quantum numbers for a given state with unprimed, single primed, and double primed quantum numbers corresponding to the upper state [12(0<sup>+</sup>)], intermediate state [ $2(A)^1\Sigma^+$ ], and ground state [ $1(X)^1\Sigma^+$ ], respectively. For levels observed via transitions involving a collisional step, quantum numbers of the collisionally populated level are denoted with a subscript  $c$ . Transferred collisional energy is the energy gained or lost in the collision step  $2(A)^1\Sigma^+(v', J') + P \rightarrow 2(A)^1\Sigma^+(v'_c, J'_c) + P$ , where  $P$  is the collision partner. This energy is positive if the collisionally populated level lies above, and negative if it lies below, the initial level. The ground state level energies are calculated using the experimental Dunham coefficients of Docenko *et al.* (Eur. Phys. J. D **31**, 205-211, 2004), which are reported to be accurate to  $\pm 0.003$  cm<sup>-1</sup>. We assign an uncertainty of  $\pm 0.01$  cm<sup>-1</sup> to the pump and probe laser frequencies, hence the 12(0<sup>+</sup>) level energies are considered to be accurate to  $\sim 0.02$  cm<sup>-1</sup>.

Upper Level [12(0 <sup>+</sup> )]		Intermediate Level [2(A) <sup>1</sup> Σ <sup>+</sup> ]		Intermediate Level After Collision		Ground State Level [1(X) <sup>1</sup> Σ <sup>+</sup> ]		Ground State Level Energy (cm <sup>-1</sup> )	Pump Laser Frequency (cm <sup>-1</sup> )	Transferred Collisional Energy (cm <sup>-1</sup> )	Probe Laser Frequency (cm <sup>-1</sup> )	Upper State Level Energy (cm <sup>-1</sup> )
$v$	$J$	$v'$	$J'$	$v'_c$	$J'_c$	$v''$	$J''$					
0	33	12	34			0	33	114.215	11163.45		13456.98	24734.65
0	35	12	34			0	33	114.215	11163.45		13462.05	24739.72
0	43	14	44			0	45	168.858	11266.74		13327.32	24762.92
0	45	14	44			0	45	168.858	11266.74		13333.86	24769.45
1	0	14	1			0	2	49.706	11296.42		13396.80	24742.93
1	2	14	1			0	2	49.706	11296.42		13397.02	24743.15
1	23	14	26	14	24	0	25	86.956	11288.69	-4.38	13392.06	24763.32
1	24	14	26	14	25	0	25	86.956	11288.69	-2.24	13391.70	24765.10
1	25	14	26			0	25	86.956	11288.69		13391.31	24766.95
1	26	14	26	14	27	0	25	86.956	11288.69	2.34	13390.91	24768.89
1	27	14	26	14	28	0	25	86.956	11288.69	4.77	13390.47	24770.89
1	27	14	26			0	25	86.956	11288.69		13395.24	24770.88
1	37	14	44	14	38	0	45	168.858	11266.74	-24.61	13383.89	24794.88
1	38	14	44	14	39	0	45	168.858	11266.74	-20.86	13382.93	24797.67
1	39	14	44	14	38	0	45	168.858	11266.74	-24.61	13389.56	24800.55



1	39	14	44	14	40	0	45	168.858	11266.74	-16.97	13381.91	24800.55
1	40	14	44	14	41	0	45	168.858	11266.74	-12.94	13380.83	24803.49
1	40	14	44	14	39	0	45	168.858	11266.74	-20.86	13388.76	24803.50
1	41	14	44	14	40	0	45	168.858	11266.74	-16.97	13387.88	24806.51
1	42	14	44	14	41	0	45	168.858	11266.74	-12.94	13386.93	24809.59
1	42	14	44	14	43	0	45	168.858	11266.74	-4.45	13378.45	24809.60
1	43	14	44			0	45	168.858	11266.74		13377.16	24812.76
1	43	14	44	14	42	0	45	168.858	11266.74	-8.76	13385.93	24812.76
1	44	14	44	14	45	0	45	168.858	11266.74	4.59	13375.81	24815.99
1	44	14	44	14	43	0	45	168.858	11266.74	-4.45	13384.85	24815.99
1	45	14	44			0	45	168.858	11266.74		13383.70	24819.30
1	46	14	44	14	45	0	45	168.858	11266.74	4.59	13382.50	24822.68
1	47	14	44	14	46	0	45	168.858	11266.74	9.32	13381.22	24826.14
1	48	14	44	14	47	0	45	168.858	11266.74	14.18	13379.88	24829.66
1	49	14	44	14	48	0	45	168.858	11266.74	19.18	13378.48	24833.26
1	50	14	44	14	49	0	45	168.858	11266.74	24.33	13377.02	24836.95
2	5	14	10	14	6	0	9	54.569	11296.06	-2.85	13447.63	24795.41
2	6	14	10	14	7	0	9	54.569	11296.06	-2.27	13447.50	24795.86
2	7	14	10	14	8	0	9	54.569	11296.06	-1.42	13447.35	24796.56
2	8	14	10	14	9	0	9	54.569	11296.06	-0.85	13447.19	24796.97
2	9	14	10			0	9	54.569	11296.06		13447.03	24797.66
2	10	14	10	14	11	0	9	54.569	11296.06	0.90	13446.85	24798.37
2	11	14	10	14	12	0	9	54.569	11296.06	1.89	13446.67	24799.19
2	11	14	10	14		0	9	54.569	11296.06		13448.60	24799.22
2	12	14	10	14	13	0	9	54.569	11296.06	2.99	13446.47	24800.08
2	13	14	10	14	14	0	9	54.569	11296.06	4.16	13446.26	24801.05
2	24	14	26	14	23	0	25	86.956	11288.69	-6.43	13447.39	24816.60
2	25	14	26			0	25	86.956	11288.69		13442.80	24818.44
2	25	14	26	14	24	0	25	86.956	11288.69	-4.38	13447.19	24818.45
2	26	14	26	14	25	0	25	86.956	11288.69	-2.24	13446.98	24820.39
2	27	14	26			0	25	86.956	11288.69		13446.74	24822.38

2	28	14	26	14	27	0	25	86.956	11288.69	2.34	13446.47	24824.46
2	29	14	26	14	28	0	25	86.956	11288.69	4.77	13446.19	24826.61
2	30	14	26	14	29	0	25	86.956	11288.69	7.31	13445.88	24828.84
2	31	14	39	14	30	0	40	144.090	11270.65	-29.13	13445.53	24831.13
2	32	14	39	14	31	0	40	144.090	11270.65	-26.38	13445.15	24833.51
2	33	14	39	14	32	0	40	144.090	11270.65	-23.52	13444.72	24835.94
2	34	14	39	14	33	0	40	144.090	11270.65	-20.53	13444.27	24838.47
2	35	14	39	14	34	0	40	144.090	11270.65	-17.43	13443.76	24841.06
2	36	14	39	14	35	0	40	144.090	11270.65	-14.21	13443.21	24843.74
2	37	14	39	14	36	0	40	144.090	11270.65	-10.85	13442.59	24846.47
2	38	14	39	14	37	0	40	144.090	11270.65	-7.37	13441.92	24849.29
2	39	14	39	14	38	0	40	144.090	11270.65	-3.75	13441.19	24852.17
2	39	14	44	14	38	0	45	168.858	11266.74	-24.61	13441.19	24852.18
2	40	14	39			0	40	144.090	11270.65		13440.39	24855.13
2	40	14	44	14	39	0	45	168.858	11266.74	-20.86	13440.39	24855.13
2	41	14	39	14	40	0	40	144.090	11270.65	3.89	13439.53	24858.16
2	41	14	44	14	40	0	45	168.858	11266.74	-16.97	13439.53	24858.16
2	42	14	44	14	41	0	45	168.858	11266.74	-12.94	13438.60	24861.26
2	43	14	44			0	45	168.858	11266.74		13428.85	24864.44
2	43	14	44	14	42	0	45	168.858	11266.74	-8.76	13437.61	24864.44
2	44	14	44	14	43	0	45	168.858	11266.74	-4.45	13436.55	24867.70
2	45	14	44			0	45	168.858	11266.74		13435.41	24871.01
2	46	14	44	14	45	0	45	168.858	11266.74	4.59	13434.22	24874.41
2	47	14	44	14	46	0	45	168.858	11266.74	9.32	13432.97	24877.89
2	48	14	44	14	47	0	45	168.858	11266.74	14.18	13431.65	24881.43
2	49	14	44	14	48	0	45	168.858	11266.74	19.18	13430.28	24885.05
2	55	14	60	14	56	0	59	253.306	11270.20	-24.82	13409.58	24908.26
2	56	14	60	14	57	0	59	253.306	11270.20	-18.74	13407.63	24912.38
2	57	14	60	14	58	0	59	253.306	11270.20	-12.58	13405.65	24916.57
2	58	14	60	14	59	0	59	253.306	11270.20	-6.33	13403.68	24920.85
2	59	14	60			0	59	253.306	11270.20		13401.68	24925.18

2	61	14	60			0	59	253.306	11270.20		13410.57	24934.07
2	62	14	60	14	61	0	59	253.306	11270.20	6.40	13408.72	24938.63
2	63	14	60	14	62	0	59	253.306	11270.20	12.87	13406.88	24943.25
2	64	14	60	14	63	0	59	253.306	11270.20	19.37	13405.07	24947.94
2	65	14	60	14	64	0	59	253.306	11270.20	25.89	13403.33	24952.72
3	43	12	44			0	43	158.609	11151.39		13608.43	24918.43
3	45	12	44			0	43	158.609	11151.39		13615.04	24925.04
4	6	14	10	14	7	0	9	54.569	11296.06	-2.27	13556.33	24904.69
4	7	14	10	14	8	0	9	54.569	11296.06	-1.42	13556.19	24905.39
4	8	14	10	14	9	0	9	54.569	11296.06	-0.85	13556.04	24905.82
4	9	14	10			0	9	54.569	11296.06		13555.88	24906.50
4	10	14	10	14	11	0	9	54.569	11296.06	0.90	13555.71	24907.23
4	11	14	10			0	9	54.569	11296.06		13557.45	24908.07
4	11	14	10	14	12	0	9	54.569	11296.06	1.89	13555.53	24908.05
4	12	14	10	14	13	0	9	54.569	11296.06	2.99	13555.34	24908.95
4	23	14	26	14	24	0	25	86.956	11288.69	-4.38	13552.47	24923.73
4	24	14	26	14	25	0	25	86.956	11288.69	-2.24	13552.12	24925.53
4	25	14	26			0	25	86.956	11288.69		13551.75	24927.39
4	26	14	26	14	27	0	25	86.956	11288.69	2.34	13551.35	24929.34
4	27	14	26	14	28	0	25	86.956	11288.69	4.77	13550.93	24931.35
4	27	14	26			0	25	86.956	11288.69		13555.70	24931.35
4	37	14	44	14	38	0	45	168.858	11266.74	-24.61	13544.46	24955.45
4	38	14	39			0	40	144.090	11270.65		13543.56	24958.29
4	38	14	44	14	39	0	45	168.858	11266.74	-20.86	13543.55	24958.29
4	39	14	39	14	40	0	40	144.090	11270.65	3.89	13542.57	24961.20
4	39	14	44	14	40	0	45	168.858	11266.74	-16.97	13542.57	24961.20
4	40	14	44	14	41	0	45	168.858	11266.74	-12.94	13541.52	24964.18
4	41	14	44	14	42	0	45	168.858	11266.74	-8.76	13540.39	24967.22
4	42	14	44	14	43	0	45	168.858	11266.74	-4.45	13539.20	24970.35
4	43	14	44			0	45	168.858	11266.74		13537.94	24973.54
4	44	14	44	14	45	0	45	168.858	11266.74	4.59	13536.62	24976.81

4	45	14	44	14	46	0	45	168.858	11266.74	9.32	13535.24	24980.15
4	45	14	44			0	45	168.858	11266.74		13544.54	24980.13
4	46	14	44	14	47	0	45	168.858	11266.74	14.18	13533.79	24983.57
4	47	14	44	14	48	0	45	168.858	11266.74	19.18	13532.27	24987.04
4	48	14	44	14	49	0	45	168.858	11266.74	24.33	13530.69	24990.62
4	49	14	44	14	50	0	45	168.858	11266.74	29.58	13529.05	24994.23
4	50	14	44	14	51	0	45	168.858	11266.74	34.99	13527.34	24997.93
4	51	14	44	14	52	0	45	168.858	11266.74	40.57	13525.56	25001.73
4	59	14	60			0	59	253.306	11270.20		13511.01	25034.51
4	61	14	60			0	59	253.306	11270.20		13519.93	25043.43
5	4	14	10	14	5	0	9	54.569	11296.06	-3.36	13611.76	24959.03
5	5	14	10	14	6	0	9	54.569	11296.06	-2.85	13611.63	24959.41
5	6	14	10	14	7	0	9	54.569	11296.06	-2.27	13611.50	24959.85
5	7	14	10	14	8	0	9	54.569	11296.06	-1.42	13611.35	24960.55
5	8	14	10	14	9	0	9	54.569	11296.06	-0.85	13611.19	24960.97
5	9	14	10			0	9	54.569	11296.06		13611.03	24961.65
5	10	14	10	14	11	0	9	54.569	11296.06	0.90	13610.86	24962.38
5	11	14	10			0	9	54.569	11296.06		13612.60	24963.23
5	11	14	10	14	12	0	9	54.569	11296.06	1.89	13610.67	24963.19
5	12	14	10	14	13	0	9	54.569	11296.06	2.99	13610.48	24964.09
5	22	14	26	14	21	0	25	86.956	11288.69	-10.25	13611.74	24977.13
5	23	14	26	14	24	0	25	86.956	11288.69	-4.38	13607.58	24978.85
5	23	14	26	14	22	0	25	86.956	11288.69	-8.39	13611.58	24978.84
5	24	14	26	14	25	0	25	86.956	11288.69	-2.24	13607.22	24980.63
5	24	14	26	14	23	0	25	86.956	11288.69	-6.43	13611.41	24980.62
5	25	14	26			0	25	86.956	11288.69		13606.83	24982.47
5	26	14	26	14	25	0	25	86.956	11288.69	-2.24	13611.01	24984.42
5	26	14	26	14	27	0	25	86.956	11288.69	2.34	13606.44	24984.42
5	27	14	26			0	25	86.956	11288.69		13610.78	24986.42
5	27	14	26	14	28	0	25	86.956	11288.69	4.77	13606.00	24986.42
5	28	14	26	14	27	0	25	86.956	11288.69	2.34	13610.52	24988.50

5	29	14	26	14	28	0	25	86.956	11288.69	4.77	13610.24	24990.66
5	30	14	26	14	29	0	25	86.956	11288.69	7.31	13609.92	24992.88
5	43	14	44			0	45	168.858	11266.74		13592.94	25028.53
5	45	14	44			0	45	168.858	11266.74		13599.52	25035.11
5	59	14	60			0	59	253.306	11270.20		13565.79	25089.30
5	61	14	60			0	59	253.306	11270.20		13574.69	25098.19
6	5	14	10	14	6	0	9	54.569	11296.06	-2.85	13665.98	25013.76
6	6	14	10	14	7	0	9	54.569	11296.06	-2.27	13665.85	25014.21
6	7	14	10	14	8	0	9	54.569	11296.06	-1.42	13665.70	25014.90
6	8	14	10	14	9	0	9	54.569	11296.06	-0.85	13665.55	25015.33
6	9	14	10			0	9	54.569	11296.06		13665.38	25016.01
6	10	14	10	14	11	0	9	54.569	11296.06	0.90	13665.20	25016.73
6	11	14	10			0	9	54.569	11296.06		13666.93	25017.56
6	11	14	10	14	12	0	9	54.569	11296.06	1.89	13665.02	25017.54
6	12	14	10	14	13	0	9	54.569	11296.06	2.99	13664.82	25018.44
6	22	14	26	14	21	0	25	86.956	11288.69	-10.25	13666.01	25031.40
6	23	14	26	14	22	0	25	86.956	11288.69	-8.39	13665.85	25033.10
6	23	14	26	14	24	0	25	86.956	11288.69	-4.38	13661.84	25033.11
6	24	14	26	14	23	0	25	86.956	11288.69	-6.43	13665.66	25034.88
6	24	14	26	14	25	0	25	86.956	11288.69	-2.24	13661.48	25034.88
6	25	14	26	14	24	0	25	86.956	11288.69	-4.38	13665.47	25036.73
6	25	14	26			0	25	86.956	11288.69		13661.09	25036.73
6	26	14	26	14	25	0	25	86.956	11288.69	-2.24	13665.25	25038.66
6	26	14	26	14	27	0	25	86.956	11288.69	2.34	13660.67	25038.65
6	27	14	26			0	25	86.956	11288.69		13665.01	25040.65
6	28	14	26	14	27	0	25	86.956	11288.69	2.34	13664.74	25042.73
6	29	14	26	14	28	0	25	86.956	11288.69	4.77	13664.45	25044.87
6	30	14	26	14	29	0	25	86.956	11288.69	7.31	13664.13	25047.09
6	43	14	44			0	45	168.858	11266.74		13646.96	25082.56
6	45	14	44			0	45	168.858	11266.74		13653.51	25089.11
7	43	11	44			0	43	158.609	11107.34		13869.43	25135.38

7	45	11	44			0	43	158.609	11107.34		13875.93	25141.88
7	59	14	60			0	59	253.306	11270.20		13672.01	25195.51
7	61	14	60			0	59	253.306	11270.20		13680.81	25204.31
8	0	14	1			0	2	49.706	11296.42		13771.91	25118.04
8	1	14	1	14	2	0	2	49.706	11296.42	0.15	13771.82	25118.09
8	2	14	1	14	3	0	2	49.706	11296.42	0.40	13771.71	25118.24
8	2	14	1			0	2	49.706	11296.42		13772.13	25118.26
8	3	14	1	14	2	0	2	49.706	11296.42	0.15	13772.18	25118.46
8	4	14	1	14	3	0	2	49.706	11296.42	0.40	13772.22	25118.75
8	5	14	1	14	4	0	2	49.706	11296.42	0.73	13772.26	25119.12
8	43	18	44			0	43	158.609	11494.24		13534.33	25187.18
8	45	18	44			0	43	158.609	11494.24		13540.81	25193.66
10	0	14	1			0	2	49.706	11296.42		13874.22	25220.34
10	1	14	1	14	2	0	2	49.706	11296.42	0.15	13874.12	25220.40
10	2	14	1	14	3	0	2	49.706	11296.42	0.40	13874.02	25220.55
10	2	14	1			0	2	49.706	11296.42		13874.43	25220.56
10	3	14	1	14	4	0	2	49.706	11296.42	0.73	13873.91	25220.77
10	3	14	1	14	2	0	2	49.706	11296.42	0.15	13874.48	25220.76
10	4	14	1	14	5	0	2	49.706	11296.42	1.14	13873.78	25221.05
10	4	14	10	14	5	0	9	54.569	11296.06	-3.36	13873.78	25221.06
10	4	14	1	14	3	0	2	49.706	11296.42	0.40	13874.53	25221.06
10	5	14	1	14	6	0	2	49.706	11296.42	1.65	13873.64	25221.42
10	5	14	10	14	6	0	9	54.569	11296.06	-2.85	13873.65	25221.42
10	5	14	1	14	4	0	2	49.706	11296.42	0.73	13874.56	25221.42
10	6	14	10	14	7	0	9	54.569	11296.06	-2.27	13873.50	25221.86
10	7	14	10	14	8	0	9	54.569	11296.06	-1.42	13873.35	25222.55
10	8	14	10	14	9	0	9	54.569	11296.06	-0.85	13873.18	25222.96
10	9	14	10			0	9	54.569	11296.06		13873.00	25223.63
10	10	14	10	14	9	0	9	54.569	11296.06	-0.85	13874.56	25224.34
10	11	14	10			0	9	54.569	11296.06		13874.53	25225.16
10	12	14	10	14	11	0	9	54.569	11296.06	0.90	13874.48	25226.01

10	13	14	10	14	12	0	9	54.569	11296.06	1.89	13874.43	25226.95
10	14	14	10	14	13	0	9	54.569	11296.06	2.99	13874.36	25227.98
10	15	14	10	14	14	0	9	54.569	11296.06	4.16	13874.29	25229.07
10	43	14	44			0	45	168.858	11266.74		13853.31	25288.90
10	45	14	44			0	45	168.858	11266.74		13859.74	25295.34
10	59	14	60			0	59	253.306	11270.20		13824.83	25348.33
10	61	14	60			0	59	253.306	11270.20		13833.52	25357.02
12	41	18	42			0	41	148.816	11497.00		13732.65	25378.47
12	43	18	42			0	41	148.816	11497.00		13739.11	25384.92
13	43	18	44			0	43	158.609	11494.24		13786.23	25439.08
13	45	18	44			0	43	158.609	11494.24		13792.61	25445.46
14	43	18	44			0	43	158.609	11494.24		13835.96	25488.81
14	45	18	44			0	43	158.609	11494.24		13842.31	25495.16
22	43	29	44			1	45	266.602	11994.95		13653.82	25915.37
22	45	29	44			1	45	266.602	11994.95		13659.80	25921.35

## Supplementary Material Table III – NaCs 12(0<sup>+</sup>) RKR Potential Energy Curve

NaCs 12(0<sup>+</sup>) RKR potential energy curve determined in this work. To obtain the total absolute potential curve,  $T_e = 24671.019 \text{ cm}^{-1}$  must be added to each energy value. The more accurate IPA potential energy curve is given in Table II in the journal article and in Table IV of the Supplementary Material.

$v$	$R_{\min}$ (Å)	$R_{\max}$ (Å)	Energy (cm <sup>-1</sup> )
-0.4	4.7447	4.9202	4.4507
-0.2	4.6818	4.9830	13.5071
0	4.6397	5.0250	22.7599
0.2	4.6062	5.0584	32.1963
0.4	4.5778	5.0868	41.8044
0.6	4.5529	5.1117	51.5724
0.8	4.5306	5.1342	61.4886
1	4.5102	5.1547	71.5421
1.2	4.4914	5.1738	81.7219
1.4	4.4739	5.1917	92.0177
1.6	4.4575	5.2087	102.4191
1.8	4.4420	5.2248	112.9164
2	4.4272	5.2403	123.5001
2.2	4.4132	5.2552	134.1610
2.4	4.3997	5.2696	144.8903
2.6	4.3868	5.2836	155.6794
2.8	4.3743	5.2973	166.5202
3	4.3623	5.3107	177.4048
3.2	4.3506	5.3239	188.3256
3.4	4.3393	5.3368	199.2755
3.6	4.3283	5.3496	210.2476
3.8	4.3176	5.3622	221.2354
4	4.3071	5.3748	232.2326
4.2	4.2969	5.3872	243.2334
4.4	4.2869	5.3996	254.2321
4.6	4.2771	5.4119	265.2237
5	4.2581	5.4364	287.1658
6	4.2135	5.4975	341.5923
7	4.1725	5.5591	395.1057
8	4.1347	5.6214	447.5052
9	4.1004	5.6842	498.7958
10	4.0701	5.7466	549.1880
11	4.0445	5.8071	599.0983
12	4.0248	5.8642	649.1484
13	4.0118	5.9157	700.1662
14	4.0064	5.9601	753.1850



## Supplementary Material Table IV – NaCs 12(0<sup>+</sup>) IPA Potential Energy Curve

NaCs 12(0<sup>+</sup>) IPA potential energy curve determined in this work.

$R$ (Å)	Energy (cm <sup>-1</sup> )	$R$ (Å)	Energy (cm <sup>-1</sup> )
4.0066	25372.1902	4.9204	24675.7057
4.0120	25353.8388	4.9832	24685.5888
4.0249	25313.6700	5.0252	24694.8413
4.0447	25262.8959	5.0586	24704.7210
4.0702	25212.3998	5.0870	24715.0111
4.1006	25162.1021	5.1119	24725.0570
4.1349	25112.1539	5.1344	24734.6046
4.1727	25061.5645	5.1549	24743.7734
4.2137	25009.3151	5.1740	24752.9083
4.2583	24955.1027	5.1919	24762.1829
4.2773	24933.1528	5.2089	24773.3190
4.2871	24922.2078	5.2250	24783.9433
4.2971	24911.3020	5.2405	24794.7367
4.3073	24900.4408	5.2554	24805.6899
4.3178	24889.6251	5.2698	24816.7863
4.3285	24878.8374	5.2838	24828.0196
4.3395	24868.0960	5.2975	24839.3859
4.3508	24857.3999	5.3109	24850.8537
4.3625	24846.7576	5.3241	24862.3620
4.3745	24836.1676	5.3370	24873.8740
4.3870	24825.6479	5.3498	24885.3510
4.3999	24815.1958	5.3624	24896.7747
4.4134	24804.8180	5.3750	24908.1083
4.4274	24794.5197	5.3874	24919.3482
4.4422	24784.2999	5.3998	24930.4736
4.4577	24774.1712	5.4121	24941.4632
4.4741	24764.1546	5.4366	24962.9916
4.4916	24754.2386	5.4977	25014.7877
4.5104	24739.9024	5.5593	25065.4399
4.5308	24730.5804	5.6216	25115.7452
4.5531	24721.3148	5.6844	25169.3976
4.5780	24712.0850	5.7468	25228.9479
4.6064	24702.7850	5.8073	25288.2247
4.6399	24693.3421	5.8644	25344.1242
4.6820	24683.7029	5.9159	25391.9912
4.7449	24673.2199	5.9603	25430.4357
4.8327	24668.2803		