Supplementary Material

NaK bound-free and bound-bound $4\,^3\Sigma^+ \rightarrow a\,^3\Sigma^+$ emission

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TABLE I: Comparison of the IPA potentials (in cm^{-1}) for the NaK $4\,^3\Sigma^+$ state determined by Burns *et al.* [J. Chem. Phys. **119** 4743–4754 (2003)] and in the present work. The asymptotic limits ($R \to \infty$) for both potentials are 26300.580 cm^{-1}.

R (Å)	Burns *et al.*	present	R (Å)	Burns *et al.*	present	R (Å)	Burns *et al.*	present
3.02	30014.488	27791.667	4.70	24131.977	24132.511	6.38	25278.139	25282.668
3.05	29164.013	27510.574	4.73	24152.511	24153.458	6.41	25303.283	25307.094
3.08	28453.357	27249.544	4.76	24173.582	24175.064	6.44	25326.354	25329.631
3.11	27859.534	27006.381	4.79	24194.774	24196.889	6.47	25347.827	25350.919
3.14	27363.336	26779.047	4.82	24215.506	24218.305	6.50	25368.691	25371.974
3.17	26948.715	26565.923	4.85	24235.601	24239.083	6.53	25389.997	25393.639
3.20	26602.257	26365.818	4.88	24255.041	24259.148	6.56	25412.466	25416.357
3.23	26312.758	26178.086	4.91	24274.001	24278.620	6.59	25435.730	25439.538
3.26	26070.853	26002.335	4.94	24292.412	24297.395	6.62	25458.810	25462.131
3.29	25868.718	25837.872	4.97	24310.130	24315.315	6.65	25480.774	25483.407
3.32	25699.825	25683.617	5.00	24326.990	24332.220	6.68	25501.110	25503.246
3.35	25555.662	25538.533	5.03	24342.776	24347.920	6.71	25519.846	25521.988
3.38	25421.281	25401.646	5.06	24357.364	24362.310	6.74	25537.753	25540.448
3.41	25293.417	25272.294	5.09	24370.632	24375.302	6.77	25555.753	25559.358
3.44	25172.972	25150.341	5.12	24382.523	24386.880	6.80	25573.910	25578.111
3.47	25060.837	25035.747	5.15	24392.943	24396.989	6.83	25591.903	25595.741
3.50	24957.349	24928.517	5.18	24402.148	24405.935	6.86	25609.570	25611.979
3.53	24861.155	24828.569	5.21	24410.467	24414.095	6.89	25627.129	25627.654
3.56	24771.625	24735.580	5.24	24418.267	24421.880	6.92	25644.510	25643.582
3.59	24688.514	24649.258	5.27	24425.948	24429.717	6.95	25660.659	25659.504
3.62	24611.319	24569.349	5.30	24433.835	24437.989	6.98	25674.592	25675.114
3.65	24538.951	24495.666	5.33	24442.351	24447.080	7.01	25686.962	25690.488
3.68	24470.444	24428.159	5.36	24451.814	24457.276	7.04	25699.214	25705.841
3.71	24404.851	24366.824	5.39	24462.415	24468.747	7.07	25712.769	25721.273
3.74	24341.840	24311.484	5.42	24474.245	24481.566	7.10	25726.378	25735.660
3.77	24282.788	24261.671	5.45	24487.760	24496.101	7.13	25739.522	25747.075
3.80	24229.311	24216.878	5.48	24502.130	24511.620	7.16	25752.227	25757.453
3.83	24182.354	24176.615	5.51	24517.524	24528.230	7.19	25764.593	25767.593
3.86	24142.055	24140.406	5.54	24534.213	24546.100	7.22	25776.631	25777.504
3.89	24107.613	24107.804	5.57	24553.002	24565.869	7.25	25788.350	25787.190
3.92	24077.851	24078.510	5.60	24574.367	24587.877	7.28	25799.760	25796.658
3.95	24051.766	24052.329	5.63	24597.731	24611.541	7.31	25810.871	25805.914
3.98	24028.553	24028.968	5.66	24621.756	24635.620	7.34	25821.691	25814.962
4.01	24007.568	24007.789	5.69	24645.866	24659.644	7.37	25832.230	25823.810
4.04	23988.407	23988.437	5.72	24670.298	24683.942	7.40	25842.495	25832.461
4.07	23970.968	23970.885	5.75	24695.520	24709.014	7.43	25852.495	25840.921
4.10	23955.615	23955.509	5.78	24721.912	24735.221	7.46	25862.238	25849.195
4.13	23946.743	23946.678	5.81	24749.449	24762.490	7.49	25871.731	25857.288
4.16	23943.455	23943.465	5.84	24777.634	24790.282	7.52	25880.981	25865.204
4.19	23941.517	23941.612	5.87	24806.099	24818.216	7.55	25889.997	25872.948
4.22	23940.508	23940.669	5.90	24834.875	24846.354	7.58	25898.784	25880.524
4.25	23942.672	23942.858	5.93	24863.780	24874.575	7.61	25907.349	25887.938
4.28	23947.206	23947.378	5.96	24892.387	24902.523	7.64	25915.700	25895.191
4.31	23953.616	23953.744	5.99	24920.603	24930.147	7.67	25923.841	25902.290
4.34	23961.269	23961.333	6.02	24948.679	24957.704	7.70	25931.779	25909.238
4.37	23969.758	23969.745	6.05	24976.995	24985.531	7.73	25939.521	25916.037
4.40	23979.001	23978.904	6.08	25005.797	25013.821	7.76	25947.070	25922.694
4.43	23989.319	23989.141	6.11	25034.877	25042.360	7.79	25954.434	25929.209
4.46	24000.848	24000.605	6.14	25063.724	25070.672	7.82	25961.616	25935.589
4.49	24013.575	24013.298	6.17	25091.675	25098.158	7.85	25968.623	25941.834
4.52	24027.452	24027.182	6.20	25118.404	25124.549	7.88	25975.460	25947.950
4.55	24042.452	24042.227	6.23	25144.416	25150.383	7.91	25982.130	25953.939
4.58	24058.514	24058.357	6.26	25170.492	25176.402	7.94	25988.639	25959.804
4.61	24075.549	24075.479	6.29	25197.054	25202.907	7.97	25994.991	25965.548
4.64	24093.490	24093.543	6.32	25224.148	25229.801	8.00	26001.191	25971.174
4.67	24112.307	24112.551	6.35	25251.429	25256.633			

Determination of Density of States

The reviewer suggested that we could find an expression for the density of states (DOS) by differentiating the WKB energy formula,

$$v + \tfrac{1}{2} = \frac{\sqrt{2\mu}}{\pi\hbar} \int_{R_1(v)}^{R_2(v)} \sqrt{E - V(R) - J(J+1)\hbar^2/(2\mu R^2)}\, dR, \tag{1}$$

to obtain

$$\frac{dv}{dE} = \frac{\sqrt{\mu/2}}{\pi\hbar} \int_{R_1(E)}^{R_2(E)} \frac{dR}{\sqrt{E - V(R) - J(J+1)\hbar^2/(2\mu R^2)}}. \tag{2}$$

The reviewer suggested evaluating this integral using gaussian quadrature. The integrand is singular at both endpoints of the integration since $R_1(E)$ and $R_2(E)$ are the zeros of the argument of the square root in the denominator, but one can indeed efficiently evaluate the integral by isolating the factor that leads to the singularity. We rewrite the integral as

$$\frac{dv}{dE} = \frac{\sqrt{\mu/2}}{\pi\hbar} \int_{R_1}^{R_2} \frac{1}{\sqrt{(R - R_1)(R_2 - R)}} g(R)\, dR, \tag{3}$$

where the function $g(R)$ is

$$g(R) = \frac{\sqrt{(R - R_1)(R_2 - R)}}{\sqrt{E - V(R) - J(J+1)\hbar^2/(2\mu R^2)}}\, dR, \tag{4}$$

which behaves nicely at each endpoint. (Our notation here doesn't show the dependence of R_1 and R_2 on E.) Changing the variable of integration in Eq. (3) leads to

$$\frac{dv}{dE} = \frac{\sqrt{\mu/2}}{\pi\hbar} \int_{-1}^{+1} \frac{g\left(R(x)\right)\, dx}{\sqrt{1 - x^2}}, \tag{5}$$

where

$$R(x) = \tfrac{1}{2}\left[(R_2 - R_1)x + R_2 + R_1\right] \tag{6}$$

The integral in Eq.(5) is the standard form for Gauss-Chebyshev quadrature of the first kind; we used the venerable code GAUSSQ (available from netlib.org) to evaluate the points and weights.

We compared the values of dv/dE obtained from Eq. (5) with the values calculated using the fitting technique described in the manuscript. $V(R)$ was the potential for the $a\,^3\Sigma^+$ state, and $J = 36$. As the reviewer suggested, we evaluated dv/dE at the calculated bound and quasibound levels of the potential. For each vibrational energy we evaluated the turning points R_1 and R_2 using the routine ZEROIN (also available from netlib.org) and then we calculated the WKB phase integral [Eq. (1)] and dv/dE. We used several different numbers of quadrature points (`nquad`) to assess convergence. In the pages that follow, the results are tabulated and then discussed.

Table of Numerical Results

nquad = 4

v	E(cm^1)	wkbphase	dvde	original dvde
0	5127.6930	.4979488426	.0477283315	.0476873664
1	5147.9608	1.4990311210	.0511776816	.0511021967
2	5166.8352	2.5004634921	.0550575158	.0549991462
3	5184.3292	3.5012718938	.0595394275	.0594948825
4	5200.4523	4.5016247846	.0647992241	.0647805270
5	5215.2007	5.5011608051	.0711100671	.0711267444
6	5228.5674	6.4998710887	.0788737633	.0789215383
7	5240.5345	7.4978412159	.0887407015	.0888215543
8	5251.0724	8.4942610367	.1018103029	.1019383766
9	5260.1376	9.4889628377	.1201655311	.1203196647
10	5267.6718	10.4821662923	.1480725262	.1482964918
11	5273.6030	11.4728035755	.1957825063	.1957150211
12	5277.8392	12.4616423828	.2968219920	.3019857978

nquad = 7

v	E(cm^1)	wkbphase	dvde	original dvde
0	5127.6930	.4979690714	.0477262405	.0476873664
1	5147.9608	1.4991624289	.0511757513	.0511021967
2	5166.8352	2.5003623089	.0550603764	.0549991462
3	5184.3292	3.5012021573	.0595369968	.0594948825
4	5200.4523	4.5018282628	.0647988247	.0647805270
5	5215.2007	5.5018609958	.0711119061	.0711267444
6	5228.5674	6.5014279576	.0788761884	.0789215383
7	5240.5345	7.5007668304	.0887466107	.0888215543
8	5251.0724	8.4996587765	.1018132672	.1019383766
9	5260.1376	9.4985180767	.1201602963	.1203196647
10	5267.6718	10.4976016381	.1480573393	.1482964918
11	5273.6030	11.4963364900	.1957282893	.1957150211
12	5277.8392	12.4928155342	.2966812260	.3019857978

nquad = 12

v	E(cm^1)	wkbphase	dvde	original dvde
0	5127.6930	.4979690843	.0477262729	.0476873664
1	5147.9608	1.4991696433	.0511757539	.0511021967
2	5166.8352	2.5004132119	.0550598008	.0549991462
3	5184.3292	3.5012967279	.0595376928	.0594948825
4	5200.4523	4.5018563767	.0647993789	.0647805270
5	5215.2007	5.5019209590	.0711131174	.0711267444
6	5228.5674	6.5015283427	.0788740710	.0789215383
7	5240.5345	7.5007898620	.0887511020	.0888215543
8	5251.0724	8.4996041477	.1018006363	.1019383766
9	5260.1376	9.4983133326	.1201609871	.1203196647
10	5267.6718	10.4971170112	.1480734763	.1482964918
11	5273.6030	11.4957920843	.1957338350	.1957150211
12	5277.8392	12.4922518403	.2967092419	.3019857978

nquad = 64

v	E(cm^1)	wkbphase	dvde	original dvde
0	5127.6930	.4979692663	.0477262644	.0476873664
1	5147.9608	1.4991706127	.0511757534	.0511021967
2	5166.8352	2.5004200110	.0550597818	.0549991462
3	5184.3292	3.5013031244	.0595376714	.0594948825
4	5200.4523	4.5018414715	.0647993862	.0647805270
5	5215.2007	5.5018511632	.0711132197	.0711267444
6	5228.5674	6.5014789675	.0788753332	.0789215383
7	5240.5345	7.5007735560	.0887492755	.0888215543
8	5251.0724	8.4997150475	.1018028650	.1019383766
9	5260.1376	9.4983463734	.1201668156	.1203196647
10	5267.6718	10.4970896195	.1480656222	.1482964918
11	5273.6030	11.4958269188	.1957193546	.1957150211
12	5277.8392	12.4923844877	.2967039990	.3019857978

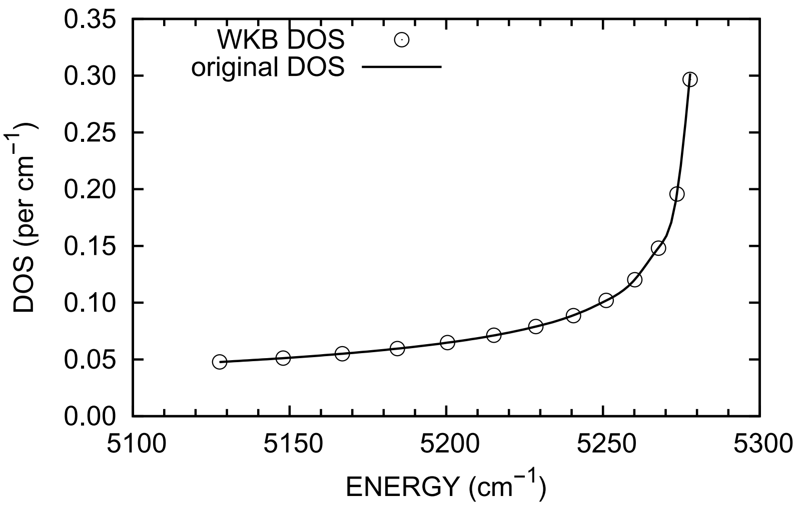

Figure 1. Density of states (DOS) for $J = 36$ calculated by the WKB method for and by the fitting method used in the manuscript. The solid lines generally pass through the center of the circles; a small offset can be discerned for the last point.

Examination of the results tabulated shows that the gaussian quadrature provides accurate results with very few points, and also that the WKB method and the original method we implemented are in excellent agreement. The values of the DOS calculated with seven or 12 quadrature points generally agree to four significant figures. For the true bound states ($v = 0$–11), the WKB DOS and our original DOS differ only in the fourth significant figure. The difference is slightly larger (about 2%) for $v = 12$, the quasibound state. We do not think that this small difference would affect our fitting results in any significant way.

The comparison is also shown graphically in Figure 1.

In the course of our tests, we noted an obscure but interesting point about the convergence of the integrals. Gaussian quadrature is known to be extremely accurate for polynomial-like functions. However, in the present case, we were limited to five or six significant figures of accuracy, even when using 64 quadrature points. We attribute this behavior to our use of cubic spline interpolation to evaluate the potential $V(R)$. The cubic spline is not the same polynomial in every interval, and thus the convergence was slower than our initial expectation.