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An Empirical Potential Energy Surface for Water Accounting for States with High Angular Momentum

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A new empirical potential energy surface for water has been deduced using fully variational calculations and nonlinear least squares. The refinement was made starting from the previously published surface of Jensen (*J. Mol. Spectrosc.* **133**, 438, 1989), with 13 parameters being meaningfully determined from the data set. The new potential reproduces excited rotational energy levels more accurately than the previous surface. It has good extrapolation properties, while still offering useful predictions of the higher energy band origins. Suggestions are made as to how further improvements can be made to the surface. © 1994 Academic Press, Inc.

1. INTRODUCTION

With the development of efficient computational schemes for the variational calculation of rovibrational states in small molecules, these methods have been brought to the forefront of investigations into spectroscopic behavior and chemical reaction dynamics. There is still a growing literature reporting improved computational methods for small molecular systems (*1, 2*). Of equal importance is the determination of molecular potential energy surfaces which guide such computational work. In recent years, there have been several published empirically determined potential energy surfaces for several triatomic molecules including H_2O (*3–5*), H_2S (*4, 6*), H_2Se (*4, 7*), HCN (*8*), CO_2 (*9, 10*), and H_3^+ (*11, 12*).

Conventionally, rotationally resolved spectra of water have been analyzed using approaches based in perturbation theory (*13*). Such analyses have been suitable for the identification and assignment of transitions at low angular momentum; however, it becomes increasingly difficult to assign transitions at higher J and K_a levels in the ground vibrational state due to large contributions from centrifugal distortion. The reduced Hamiltonian of Watson (*14*) must be extended to very high order to satisfactorily reproduce the observed energy levels in these higher J states. Indeed, if such an analysis is extended beyond $J = 20$, a divergence in the perturbation series is encountered (*15*). In the region of the first triad of water ($2\nu_2$, ν_1, and ν_3), analysis becomes complicated by accidental degeneracies given rise to from Fermi and Coriolis resonances. These degeneracies become more commonplace for higher degrees of vibrational excitation. In order to account for the positions of energy levels to within their measurement accuracy, it becomes necessary to use an unphysical number of molecular constants. Other approaches have been reasonably successful at accelerating the convergence of Taylor series expansions using various approaches (*16, 17*).

Here we present the results of a least-squares refinement of the ground state potential energy surface with the starting point chosen as the previous result due to Jensen (*3*), which was derived from experimental data using the MORBID variational approach

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(*18*). This study, while including a variety of data for highly excited vibrational states, was based on rotation–vibration data involving $J \leqslant 2$ only. Due to parameter correlations it was not possible to freely adjust the equilibrium value of the bond angle supplement, and therefore it was constrained to its *ab initio* value. We have found that the inclusion of a variety of rotationally excited energy states as data in the least squares has allowed for the empirical determination of this quantity. This led to more meaningful values of all other parameters in the potential and serves as a better starting point for a truly predictive potential energy surface.

2. COMPUTATIONAL ASPECTS

All calculations were performed using Radau coordinates following the methods outlined in a previous paper (*19*). Finite basis representation (FBR), using the TRIATOM program suite (*20*), and one-dimensional discrete variable representation (DVR), using DVR1D (*21*) calculations, were performed for the states of interest. The FBR calculations used 800 functions (see Ref. (*19*)) for a given k value in the first step of the FBR calculations, with truncation to 1800 basis functions in the second step. For the computation of band origins, 40 DVR grid points in the bond angle were chosen for a calculation with 22 radial basis functions. These calculations ensured convergence to within 0.001 cm^{-1} for states below 10 000 cm^{-1}, and to within 0.1 cm^{-1} for band origins below 20 000 cm^{-1}.

TABLE I

Parameter Values for the Water Potential

Parameter	*ab initio*[a]	Jensen [b]	This Work
ρ_e / Degrees	75.56024	75.56024	75.4781(28)
r_e / Å	0.959166	0.95843(1)	0.958290(16)
a / Å^{-1}	2.226	2.22410(20)	2.2251(8)
$f_0^{(2)}$ / cm^{-1}	19618	18975.6(17)	18988.7(38)
$f_0^{(3)}$ / cm^{-1}	1551	1728(58)	1586.4(39)
$f_0^{(4)}$ / cm^{-1}		5154(86)	5003.5(93)
$f_1^{(1)}$ / cm^{-1}	−6159	−7171(52)	−7023(40)
$f_1^{(2)}$ / cm^{-1}		−3129(74)	−3138(36)
$f_1^{(2)}$ / cm^{-1}		−4060(538)	−4050(52)
$f_{11}^{(0)}$ / cm^{-1}	42910	42943.3(57)	42892(67)
$f_{11}^{(1)}$ / cm^{-1}	222	−2262(281)	−2330(107)
$f_{11}^{(2)}$ / cm^{-1}		−4318(300)	−4338(70)
$f_{13}^{(0)}$ / cm^{-1}	−1016	−1070(17)	−1030(11)
$f_{13}^{(1)}$ / cm^{-1}		4694(252)	c
$f_{111}^{(0)}$ / cm^{-1}		693(253)	c
$f_{111}^{(1)}$ / cm^{-1}		3769(658)	c
$f_{113}^{(0)}$ / cm^{-1}		−1262(78)	c
$f_{113}^{(1)}$ / cm^{-1}		9961(757)	c
$f_{1111}^{(0)}$ / cm^{-1}		2222(214)	c
$f_{1113}^{(0)}$ / cm^{-1}		−202(114)	c
Weighted RMS / cm^{-1}		0.05	0.01
Weighted RMS (Band Origins) / cm^{-1}		0.09	0.08

[a] Ref. [31]

[b] Ref. [3]

[c] Fixed at Jensen's value

TABLE II

Observed and Computed Rotational Energy Levels of Water, in cm^{-1}, with $J = 10$ for the Vibrational Ground State[a]

Level	Jensen[b]	Obs-Calc	This Work	Obs-Calc
$10_{0,10}$	1114.3669	0.165	1114.5752	−0.043
$10_{1,10}$	1114.3840	0.166	1114.5928	−0.043
$10_{1,9}$	1292.8694	0.149	1293.0596	−0.041
$10_{2,9}$	1293.4641	0.170	1293.6738	−0.040
$10_{2,8}$	1438.0359	−0.067	1438.0298	−0.061
$10_{3,8}$	1445.9680	0.160	1446.1675	−0.039
$10_{3,7}$	1538.5979	0.448	1538.2505	−0.100
$10_{4,7}$	1581.0188	0.317	1581.3560	−0.020
$10_{4,6}$	1616.6970	0.241	1616.5342	−0.081
$10_{5,6}$	1717.9143	0.805	1718.6753	0.053
$10_{5,5}$	1724.0750	0.631	1724.6821	0.024
$10_{6,5}$	1873.4045	1.569	1874.8154	0.158
$10_{6,4}$	1873.9128	1.060	1875.3071	0.155
$10_{7,4}$	2051.8552	2.514	2054.0273	0.318
$10_{7,3}$	2051.8796	2.491	2054.0513	0.318
$10_{8,3}$	2250.7507	3.532	2253.7568	0.527
$10_{8,2}$	2250.7517	3.532	2253.7573	0.527
$10_{9,2}$	2466.5583	4.697	2470.4644	0.791
$10_{9,1}$	2466.5583	4.697	2470.4644	0.791
$10_{10,1}$	2695.9045	5.985	2700.7729	1.116
$10_{10,0}$	2695.9045	5.985	2700.7729	1.116

[a] Observed energy levels taken from Ref. [24]

[b] Potential of Ref. [3]

Each computation of energy levels constituted one step in the nonlinear least squares. Eigenvectors obtained from the variational solutions were used to compute derivatives of the energy levels with respect to the parameters in the potential using the Hellmann–Feynman theorem:

$$\frac{\partial E_{J,n}}{\partial c_\alpha} = \left\langle J, n \left| \frac{\partial \mathscr{H}}{\partial c_\alpha} \right| J, n \right\rangle . \tag{1}$$

A numerical check on this procedure, actually performed for H_3^+ and its isotopomers, found it to be accurate to at least four figures. The derivatives and the computed energy levels were used together in the Levenberg–Marquardt method for nonlinear least squares (*22, 23*). The experimental data used in the fit included all measured band origins below 20 000 cm^{-1} as well as rotationally excited states with $J < 9$ below 10 000 cm^{-1}. The experimental data were weighted according to the reported uncertainties and were taken from a number of published sources (*24–30*). The calculations were performed on a Cray YMP and required 4 megabytes of memory and approximately 2 cpu hours per cycle in the least-squares refinement.

3. THE POTENTIAL

The functional form chosen for the potential used in this work is the MORBID form from Jensen (*18*). Here, the potential is expanded in terms of Jacobi and Morse variables as

TABLE III

Observed and Computed Rotational Energy Levels of Water, in cm^{-1}, with $J = 10$ for the (0, 1, 0) Vibrational State[a]

Level	Jensen[b]	Obs-Calc	This Work	Obs-Calc
$10_{0,10}$	2704.5837	0.513	2705.1494	−0.052
$10_{1,10}$	2704.6233	0.517	2705.1899	−0.050
$10_{1,9}$	2902.6047	0.541	2903.1787	−0.033
$10_{2,9}$	2903.8552	0.572	2904.4565	−0.028
$10_{2,8}$	3058.0730	0.296	3058.4678	−0.069
$10_{3,8}$	3072.1204	0.607	3072.7524	−0.026
$10_{3,7}$	3162.1863	0.073	3162.3696	−0.110
$10_{4,7}$	3223.7273	0.820	3224.5351	0.010
$10_{4,6}$	3253.3283	0.410	3253.7968	−0.059
$10_{5,6}$	3381.9548	1.311	3383.1660	0.099
$10_{5,5}$	3386.1868	1.213	3387.3174	0.083
$10_{6,5}$	3562.6956	2.009	3564.4604	0.245
$10_{6,4}$	3563.0042	2.000	3564.7612	0.242
$10_{7,4}$	3767.8870	2.824	3770.2720	0.440
$10_{7,3}$	3767.9006	2.824	3770.2846	0.458
$10_{8,3}$	3993.7668	3.741	3996.811	0.697
$10_{8,2}$	3993.7668	3.741	3996.8120	0.697
$10_{9,2}$	4236.1689	4.773	4239.9067	1.040
$10_{9,1}$	4236.1689	4.773	4239.9067	1.040
$10_{10,1}$	4491.2519	5.912	4495.7085	1.485
$10_{10,0}$	4491.2519	5.942	4495.7085	1.485

[a] Observed energy levels taken from Ref. [24]

[b] Potential of Ref. [3]

$$V(\Delta r_{12}, \Delta r_{13}, \rho) = V_0(\rho) + \sum_j F_j(\rho) y_j + \sum_{i \leq j} F_{jk}(\rho) y_j y_k + \sum_{i \leq j \leq k} F_{jkl}(\rho) y_j y_k y_l + \cdots, \qquad (2)$$

where Δr_{12} and Δr_{13} represent displacements from the equilibrium OH bond lengths, and ρ is the bond angle supplement. The Morse coordinates y_j are defined as

$$y_j = 1 - \exp(-a\Delta r_{j2}). \qquad (3)$$

Here a is an adjustable parameter in the model. According to the notation of Jensen, $F_{jk\ldots}(\rho)$ are defined as

$$F_j(\rho) = \sum_{i=1}^{4} f_j^{(i)}(\cos\rho_e - \cos\rho)^i \qquad (4)$$

and

$$F_{jk\ldots}(\rho) = f_{jk\ldots}^{(0)} + \sum_{i=1}^{N} f_{jk\ldots}^{(i)}(\cos\rho_e - \cos\rho)^i. \qquad (5)$$

The potential was augmented with a term to account for unphysical behavior as the bond angle approaches 0° (*33*) and is given by

TABLE IV

Observed and Computed Rotational Energy Levels of Water, in cm^{-1}, with $J = 10$ for the (0, 2, 0) Vibrational State[a]

Level	Jensen[b]	Obs-Calc	This Work	Obs-Calc
$10_{0,10}$	4260.8643	−0.513	4261.1104	−0.759
$10_{1,10}$	4260.9863	−0.519	4261.2337	−0.767
$10_{1,9}$	4480.8066	−0.414	4481.1045	−0.712
$10_{2,9}$	4483.5674	−0.358	4483.9048	−0.677
$10_{2,8}$	4644.9567	−0.740	4645.1186	−0.901
$10_{3,8}$	4669.9893	−0.266	4670.4078	−0.672
$10_{3,7}$	4753.6338	−0.890	4753.7253	−0.992
$10_{4,7}$	4842.0137	0.107	4842.6361	−0.505
$10_{4,6}$	4864.6543	0.073	4865.0789	−0.707
$10_{5,6}$	5026.2920	0.782	5027.2723	−0.198
$10_{5,5}$	5028.8993	0.911	5030.0358	−0.225
$10_{6,5}$	5236.6668	1.720	5238.0497	0.336
$10_{6,4}$	5236.0195	1.773	5237.3677	0.053
$10_{7,4}$	5471.1224	2.681	5472.9792	0.824
$10_{7,3}$	5471.1280	2.684	5472.9844	0.818
$10_{8,3}$	5725.0379	2.987	5727.3729	0.652
$10_{8,2}$	5725.0394	2.986	5727.3745	0.651
$10_{9,2}$	5992.2187	2.158	5995.1204	−0.743
$10_{9,1}$	5992.2187	2.158	5995.1204	−0.743
$10_{10,1}$	6312.9843	5.384	6317.4114	0.957
$10_{10,0}$	6312.9843	5.384	6317.4114	0.957

[a] Observed energy levels taken from Ref. [32]
[b] Potential of Ref. [3]

$$V_{\mathrm{HH}} = \sum_{i=1}^{2} C_i \exp[-\alpha_i (r_{\mathrm{HH}} - d_{\mathrm{HH}})] \tag{6}$$

with definitions consistent with those given by Choi and Light (*33*).

4. RESULTS AND DISCUSSION

For the initial four steps in the iterative refinement of the potential, only a small subset of the parameters determined in Jensen's work was varied, including ρ_e, r_e, a, $f_0^{(2)}$, $f_0^{(3)}$, $f_1^{(1)}$, $f_{11}^{(0)}$, $f_{11}^{(1)}$, and $f_{13}^{(0)}$. Significant decreases in χ^2 were noted to occur in the first few steps. Once it was found that all of the adjusted parameters could be statistically determined from the data set, an additional five parameters were adjusted. Much smaller reductions in the weighted square error were observed for the second set of refinements. The results of the final parameter adjustments, along with the estimated uncertainties in these parameters, are listed in Table I. The weighted RMS deviation given in this table represents the sum of the squares of the residuals in the data set divided by each of their respected uncertainties as

$$\sigma_{\mathrm{Fit}} = \frac{1}{N - M} \sum_{i=1}^{N} (E_i^{\mathrm{obs}} - E_i^{\mathrm{calc}})^2 / \sigma_i , \tag{7}$$

where N is the number of experimental data points and M is the number of freely adjusted parameters in the fit. The coefficients in the H-H contribution to the potential

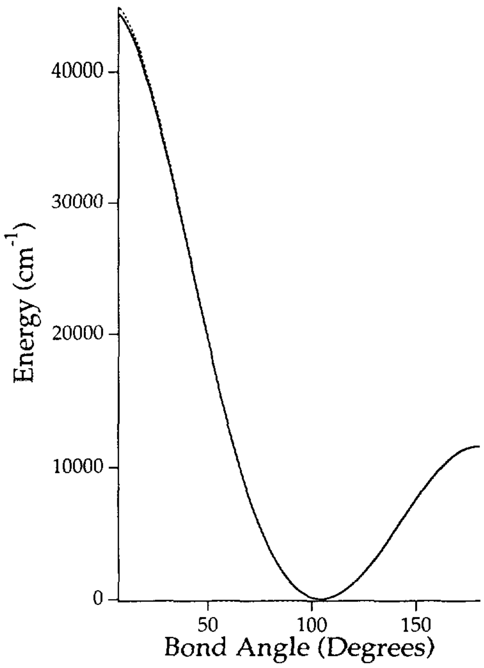

FIG. 1. Comparison of the potential from this work (solid line) and that due to Jensen (*3*) (dashed line) as a function of bond angle. The curves represent the minimum energy for each bond angle.

were held fixed at the values given previously (*33*). For brevity, we include only a few examples to demonstrate the relative accuracy of the current results compared to those of the previous potential; results for $J = 10$ for the lowest three vibrational states are given in Tables II–IV. A complete list of the observed and calculated data used in the least squares may be obtained from one of the authors.

Obvious improvements are noted for the current potential in the following ways. Rotational states in the ground and first vibrational levels are more accurately reproduced than in any of the previously reported potentials. Due to the weighting scheme, the accuracy of the results here for the first triad is in many cases not as good as that from Jensen's potential. For some levels the discrepancy between theory and experiment exceeds 1 cm^{-1}, when the measurement accuracy is two to three orders of magnitude smaller than this. These difficulties could perhaps be removed if the weighting scheme was altered in order to factor more significantly data with larger experimental uncertainty. Another possibility could be that the accurate determination of high-J levels together with the useful prediction of higher vibrational bands requires more terms accounting for the variation of the potential with bond angle supplement. Figure 1 shows a plot of the potential deduced in the current work alongside that due to Jensen, with the bond angle. The contributions from the H–H repulsion term have been omitted for clarity. On the scale of the plot, there is only a very small difference between the current work and Jensen's; however, a plot of the difference in the two potentials shown in Fig. 2 shows the difference to be large enough to cause significant shifts in spectroscopic energy levels.

As the improvements in the current potential were almost entirely due to influences from the data in the two lowest vibrational states, it is interesting to see how the band

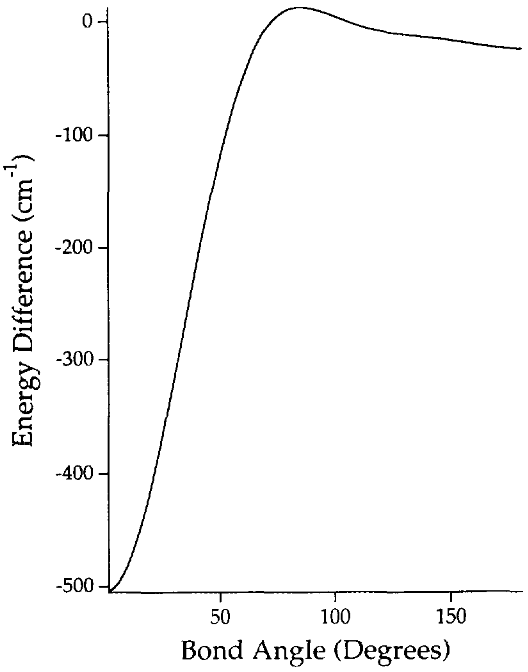

FIG. 2. The difference between the potential from this work and that of Jensen (*3*). Other details are as for Fig. 1.

origins of the system behave. Tables V and VI compare band origins computed with Jensen's potential and the present one. It should be noted that our calculation of the band origins with Jensen's potential are not the same as those quoted by Jensen (*3*) but agree with other more accurate determinations for this potential (*19*, *33*, *34*). Vibrational assignments to normal modes were made for the computed band origins by evaluating the expectation values of the Radau coordinates R, r, and $x = \cos(\theta)$. Our assignments have changed somewhat from those given previously (*19*), and are in agreement with those of Choi and Light (*33*). The current adjustments to the potential did not cause any vibrational levels to cross.

Tables V and VI show large changes in the computed values of some of the band origins at higher energies. These changes are largest for states with a number of quanta in the bending mode. During the course of the work it was determined that there were a number of misassignments in the available data sets. Due to the low relative weight of this data, it was assumed that these errors did not have a large influence on the final results. Using Jensen's potential, the observed band origins presented in Tables V and VI are reproduced with an unweighted standard deviation of 3.4 cm^{-1} compared to 3.0 cm^{-1} obtained with our new potential. More significantly, our new potential removes the systematic error, noted previously (*19*), which causes results obtained with Jensen's potential to consistently overestimate the higher band origins.

In subsequent investigations, it will be interesting to include the available microwave data for water in its ground and excited vibrational states. These data are of much higher measurement accuracy than the infrared energy levels used here and will provide a very stringent test of the potential.

TABLE V

Observed and (Observed − Calculated) Band Origins, in cm^{-1}, for Symmetric Vibrational States of Water

(v_1, v_2, v_3)	Observed	Jensen [a]	This Work	(v_1, v_2, v_3)	Observed	Jensen [a]	This Work
0 1 0	1594.74635	0.406	0.017	1 2 2	13910.8	−1.0	2.9
0 2 0	3151.6301	−0.42	−0.58	4 0 0	14221.143	−2.5	−0.7
1 0 0	3657.05364	0.53	0.75	0 0 4	14536.9	−4.6	−0.1
0 3 0	4666.7931	−0.95	−0.35	2 5 0		14549.3	14542.0
1 1 0	5234.9851	0.64	0.83	1 8 0		14778.4	14766.4
0 4 0		6134.18	6132.49	0 5 2		14859.1	14849.2
1 2 0	6775.095	-0.01	0.76	3 3 0	15107	2.8	2.8
2 0 0	7201.54	−1.21	−0.41	0 11 0		15181.4	15165.2
0 0 2	7445.07	0.05	2.45	4 1 0	15344.5	−5.8	−1.2
0 5 0		7539.87	7536.64	1 3 2		15377.2	15371.6
1 3 0	8273.9773	0.64	2.5	2 1 2	15742.8	1.5	1.5
2 1 0	8761.5792	−1.39	−0.26	2 6 0		15809.4	15799.215
0 6 0		8863.29	8857.57	1 9 0		16023.8	16009.8
0 1 2	9000.1402	−2.10	0.7	0 1 4		16057.8	16052.0
1 4 0		9719.86	9716.53	0 6 2		16187.2	16174.8
0 7 0		10073.9	10065.7	3 4 0		16525.6	16518.0
2 2 0	10284.4	−1.5	0.6	0 12 0		16654.4	16635.6
0 2 2	10524.3	−1.4	2.3	1 4 2		16784.4	16776.9
3 0 0	10599.66	−3.2	−1.2	4 2 0	16825.2	−1.0	5.1
1 0 2	10868.86	−0.6	1.3	5 0 0	16898.4	−1.3	4.0
1 5 0		11082.4	11076.6	2 7 0		17054.8	17042.3
0 8 0		11234.5	11225.0	2 2 2	17227.7	1.4	6.0
2 3 0		11766.3	11762.9	1 10 0		17312.6	17295.1
0 3 2		12011.6	12006.4	0 7 2		17435.0	17419.2
3 1 0	12139.2	−5.4	−2.6	3 0 2	17458.2	1.2	0.1
1 6 0		12340.8	12332.1	0 2 4		17542.6	17535.2
1 1 2	12407.64	−0.9	1.7	1 0 4	17748.1	−6.6	−2.8
0 9 0		12504.2	12493.9	3 5 0		17878.0	17868.3
2 4 0		13195.9	13190.8	1 5 2		18119.8	18108.0
0 4 2		13453.7	13446.6	0 13 0		18172.1	18152.2
1 7 0		13604.9	13594.9	2 8 0		18257.5	18243.0
3 2 0	13642.2	−5.7	1.1	4 3 0		18272.2	18262.67
0 10 0		13793.5	13779.7	5 1 0	18393.0	11.5	−4.8
2 0 2	13828.3	−1.6	1.9				

[a] Modified potential of Ref. [3] (see the text).

As has been determined in a previous work (*11*), the effects of Born–Oppenheimer separation require that accurate potentials be calculated "effectively" for a given isotopic species, especially where the molecule contains hydrogen atoms. We feel that in the present case it may be permissible to perform a combined fit of spectroscopic data for the normal species, $H_2^{18}O$, and $H_2^{17}O$; however, the inclusion of data for deuterated species may lead to an overall degradation of the quality of the fit.

5. CONCLUSIONS

We present a new water potential determined by using spectroscopic data from a variety of sources. The use of rotational levels up to $J = 8$ in the fit gives a significant improvement in the representation of rotational excitation. This improved behavior extrapolates, for certain levels, over the entire range for which rotationally excited states are known experimentally. However, for high J, states with $K_a \sim J$ are poorly

TABLE VI

Observed and Calculated Band Origins for Antisymmetric Vibrational States of Water

(v_1, v_2, v_3)	Observed	Jensen [a]	This Work
0 0 1	3755.9	−0.1	1.5
0 1 1	5331.2	−0.9	0.5
0 2 1	6871.5	−2.0	0.05
1 0 1	7249.8	−1.2	0.5
0 3 1	8373.8	−1.9	1.0
1 1 1	8807.0	−2.7	−0.56
0 4 1	9833.6	0.9	5.56
1 2 1	10328.7	−3.8	−0.4
2 0 1	10613.4	−2.3	0.13
0 0 3	11032.4	−1.8	1.8
0 5 1		11235.3	11227.3
1 3 1	11813.2	−2.4	2.1
2 1 1	12151.3	−5.4	−2.9
0 1 3	12565.0	−2.2	−6.9
0 6 1		12571.5	12567.3
2 2 1	13652.7	−6.2	−1.7
0 7 1		13799.3	13785.0
3 0 1	13830.9	−1.3	2.3
0 2 3	14066.2	−9.9	−3.8
1 0 3	14318.8	−2.8	0.8
2 3 1	15119.0	−3.7	2.4
3 1 1	15347.9	−7.5	−2.7
1 1 3	15832.8	−6.5	−2.3
3 2 1	16821.6	−2.4	3.0
4 0 1	16898.8	−0.9	−4.2
1 2 3	17312.5	−8.0	1.6
2 0 3	17495.5	−1.7	−2.3
3 3 1	18265.8	4.7	−13.2
4 1 1	18393.3	−11.7	4.8
2 1 3	18990.0	−6.6	−1.1

[a] Potential of Ref. [3]

represented. These states are sensitive to bending portions of the potential which are poorly determined by the available band origins.

Future work will include the introduction of more parameters in the model. Extension of the experimental data to include higher J levels than those mentioned here should also be useful from the standpoint of helping to identify misassignments, which will become commonplace for more highly excited states. Also of interest should be the examination of the use of alternate forms for expressing the potential.

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