

Supplementary Information : Intermolecular potential of singlet O_4H^+ ion

F. George D Xavier^a

^aDepartment of Chemistry, University of Coimbra, Coimbra, 3004-525, Portugal

ARTICLE HISTORY

Compiled July 17, 2026

This is the model discussed in Figure 4 of the manuscript fitting half of the data set and the model will reproduce the other half. The fit is accurate with root mean square deviation of 7 cm^{-1} . This model has the property of permutational invariance and suitable to the data used in this work.

$$\begin{aligned}
 y &= \sum_i^{i=5} a_i \left[\tanh(\beta_i r_1^2) \right] \left[\text{sech}(\mu_i r_1^2) \right] \\
 V &= \left[\sum_i^{i=13} A_i y^i \right] + \underbrace{\left[\frac{1}{2} \times 0.15513 \left(1 - \tanh \left[h_1 (r_1 + c_0) \right] \right) + \frac{1}{2} \times 0.15513 \left(1 + \tanh \left[h_1 (r_1 - c_0) \right] \right) \right]}_{\text{an additive term accounting for correct electronic correlation on either sides of the curve}}
 \end{aligned}
 \left. \vphantom{\sum_i^{i=5}} \right\} \begin{array}{l} \text{preserving} \\ \text{permutational} \\ \text{symmetry} \end{array}$$

$a_1 = 2.2000114914759292$	$A_1 = 1080.6982727487982$
$a_2 = 1.6315073989093054$	$A_2 = -364.01212381235996$
$a_3 = 5.387559056206077$	$A_3 = 87.45010747391402$
$a_4 = 5.3875594116006$	$A_4 = -29.417939329510403$
$a_5 = 3.0238934609183765$	$A_5 = -17.79928111498431$
$\mu_1 = 0.9184685459297239$	$A_6 = 75.5623848846403$
$\mu_2 = 1.1472459457992235$	$A_7 = 22.438053502201925$
$\mu_3 = 0.13411231741720428$	$A_8 = -49.620099263141306$
$\mu_4 = -0.13411225149248798$	$A_9 = -29.175033692270805$
$\mu_5 = 0.9465254162729005$	$A_{10} = 34.86123910998284$
$\beta_1 = 0.7687044383305801$	$A_{11} = 57.590664926753256$
$\beta_2 = 0.9523532790731593$	$A_{12} = 8.964405839198703$

$\beta_3 = 0.7420941189859277$	$A_{13} = 2.0962686444561505$
$\beta_4 = -1.1525575267697563$	$h_1 = 2.3263007722991818$
$\beta_5 = -0.34175493690581515$	$c_0 = 2.7816471316977087$

The level calculation yields a total of 39 vibrational states for the singlet spin state and shows double degeneracies at some levels. It exists only for few levels and vanish then quickly. It predicts a dissociation energy fo the two product fragmentation which is close to 34070 cm^{-1} . In solving Schrödinger equation, a proton mass in atomic units was used in the mass factor assuming the amplitude of proton only contributes to the overall molecular vibration in this mode (second mode shown in Figure 2 of the main manuscript) and other atoms at rest. The values are tabulated here and shown in Figure 6 in the manuscript. The degenerate levels are underlined.

v	Energy(cm^{-1})					
	C_{2h}			C_{2v}		
	$L = 0$	$L = 1$	$L = 2$	$L = 0$	$L = 1$	$L = 2$
0	1208.66	6024.0	8412.03	1314.91	2105.0	3180.27
1	3621.29	6024.0	8412.03	3921.89	5198.01	6457.65
2	6019.09	10730.7	13033.1	6484.49	8420.2	9801.47
3	8390.20	10730.7	13033.1	8978.06	11697.2	13153.4
4	10720.7	13438.8	13507.1	11401.6	15011.0	16502.3
5	12994.7	13438.8	13507.1	13783.5	18284.4	19778.6
6	<u>13404.6</u>	15208.7	15980.0	16101.1	18518.4	22034.8
7	<u>13404.6</u>	15208.7	15980.0	18331.0	21500.0	22969.3
8	15192.5	15908.9	17344.6	20478.9	24346.0	26010.3
9	<u>15873.2</u>	15908.9	17344.6	22527.7	24594.3	26922.5
10	<u>15873.3</u>	18229.5	18309.5	24462.5	27531.0	28877.2
11	<u>17283.0</u>	18229.5	18309.5	26266.4	28392.4	29721.1
12	<u>18191.1</u>	19228.4	20349.6	27894.5	30163.5	30895.5
13	<u>18195.7</u>	19228.4	20349.6	29224.2.	30293.1	31558.7
14	19200.1	20366.0	21091.4	30151.1	31252.6	31802.6
15	<u>20214.3</u>	20366.0	21091.4	30958.9	32168.0	32699.1
16	<u>20326.5</u>	21968.5	22498.4	31632.4	32865.8	33511.5
17	20999.2	21968.5	22498.4	3220.4	33031.1	34045.0
18	21928.3	23127.8	24019.2	32959.8	33789.6	34149.1
19	22400.1	23127.8	24019.2	33560.7	34338.1	34556.9
20	23101.9	24671.5	25496.6	34067.6	34619.6	34632.9
21	23934.6	24671.5	25496.6	34451.5	34639.9 ¹	34647.1 ¹
22	24647.1	26274.4	27112.4	34621.8	34641.7 ¹	34658.4 ¹
23	25431.7	26274.4	27112.4			
24	26253.3	27895.9	28758.9			
25	27054.3	27895.9	28758.9			
26	27878.0	29545.5	30393.2			
27	28707.8	29545.5	30393.2			
28	29529.6	31163.5	31959.6			
29	30348.2	31163.5	31959.6			
30	31149.3	32649.5	33286.7			
31	31919.3	32649.5	33286.7			
32	32636.8	33661.9	33836.5			
33	33251.1	33661.9	33836.5			
34	33651.9	33932.7	34021.7			
35	33813.1	33932.7	34021.7			
36	33926.1	34046.9	34047.0 ¹			
37	34007.2	34047.0 ¹	34047.1 ¹			
38	34044.7	34047.0 ¹	34047.2 ¹			
39	34049.8 ¹	34047.1 ¹	34047.3 ¹			

This model given below fits the ground state potential energy curve shown in Figure 8. The unknowns are listed via fitting the data. The model is used to compute the levels contained in the well of the curve (see Figure 9) and one must solve Schrödinger equation using the model to find out the corresponding Eigen levels. The excited state

¹not converged

curve in Figure 8 of the manuscript is fitted with the same type of model but with seventh degree polynomial instead of five. The unknowns are listed below.

$$y = a_1 \operatorname{sech}[\mu_1(x - x_0)] + a_2 \operatorname{sech}[\mu_2(x - x_0)] + a_3 \operatorname{sech}[\mu_3(x - x_0)] + a_4 \operatorname{sech}[\mu_4(x - x_0)] \\ + a_5 \operatorname{sech}[\mu_5(x - x_0)]$$

$$V = \frac{1}{x^q} (A_1 y + A_2 y^2 + A_3 y^3 + A_4 y^4 + A_5 y^5)$$

$$x_0 = 5.171338129515436$$

$$q = 8.472879002654446$$

$$a_1 = 2.4845069834930444$$

$$a_2 = -3.118014073364913$$

$$a_3 = -2.953586292150412$$

$$a_4 = -2.9535862921626816$$

$$a_5 = -2.953586292268485$$

$$A_1 = -2094.1068496606326$$

$$A_2 = -825.1752626771683$$

$$A_3 = -16.90959883272914$$

$$A_4 = 24.615448163348074$$

$$A_5 = 2.340522767790384$$

$$\mu_1 = 0.5105199043155496$$

$$\mu_2 = -0.3595900512159141$$

$$\mu_3 = -0.3596811809724695$$

$$\mu_4 = -0.3596811809811012$$

$$\mu_5 = -0.3596811809819504$$

$$y = a_1 \operatorname{sech}[\mu_1(x - x_0)] + a_2 \operatorname{sech}[\mu_2(x - x_0)] + a_3 \operatorname{sech}[\mu_3(x - x_0)] + a_4 \operatorname{sech}[\mu_4(x - x_0)] \\ + a_5 \operatorname{sech}[\mu_5(x - x_0)]$$

$$V = \frac{1}{x^q} (A_1 y + A_2 y^2 + A_3 y^3 + A_4 y^4 + A_5 y^5 + A_6 y^6 + A_7 y^7)$$

$$x_0 = 3.6685851418149915$$

$$q = 4.500806953749511$$

$$a_1 = -12.430685654808292$$

$$a_2 = 3.2215115604559053$$

$$a_3 = 3.223479049086567$$

$$a_4 = 3.2234789075384307$$

$$a_5 = 5.528715731049244$$

$$A_1 = 142.97194013697998$$

$$A_2 = -416.2609525491255$$

$$A_3 = 530.7431890553914$$

$$A_4 = -382.4679771476479$$

$$A_5 = 156.8692587013604$$

$$A_6 = -33.86683276715915$$

$$A_7 = 2.9799599610901057$$

$$\mu_1 = -2.4943021818420994$$

$$\mu_2 = -1.9152970464170012$$

$$\mu_3 = -1.9141087353544453$$

$$\mu_4 = -1.914104318896817$$

$$\mu_5 = 3.4635827435530664$$

v	Energy(cm^{-1})	v	Energy(cm^{-1})	v	Energy(cm^{-1})	v	Energy(cm^{-1})
0	370.57	21	14346.6			62	30825.6
1	1106.61	22	14931.4	42	24902.3	63	30970.1
2	1835.80	23	15508.5	43	25307.0	64	31092.3
3	2558.12	24	16077.9	44	25701.8	65	31188.2
4	3273.54	25	16639.3	45	26086.5	66	31249.4
5	3982.03	26	17192.9	46	26461.0	67	31257.9
6	4683.57	27	17738.5	47	26825.0		
7	5378.11	28	18275.9	48	27178.4		
8	6065.64	29	18805.3	49	27520.9		
9	6746.11	30	19326.4	50	27852.3		
10	7419.48	31	19839.2	51	28172.3		
11	8085.73	32	20343.6	52	28480.6		
12	8744.81	33	20839.5	53	28777.0		
13	9396.68	34	21326.8	54	29060.9		
14	10041.3	35	21805.3	55	29332.2		
15	10678.6	36	22275.1	56	29590.2		
16	11308.6	37	22736.0	57	29834.5		
17	11931.2	38	23187.8	58	30064.5		
18	12546.3	39	23630.5	59	30279.6		
19	13154.0	40	24063.9	60	30478.8		
20	13754.1	41	24487.9	61	30661.3		

This table contains the data for the levels for the first normal mode along the direction represented by arrows shown in Figure 2 in the manuscript. The levels are shown in Figure 9 of main manuscript as horizontal lines between left and right classical turning points with $v_{max} = 67$. The levels are obtained by solving Schrödinger equation using the corresponding model with the mass of an oxygen atom in atomic units in the inverse mass factor. The results stand for zero orbital momentum and similarly for non zero momentum, the levels exist but not given here. Inclusion of level data with zero and non zero momentum in the Dunham fit produce spectroscopic properties (short version) listed in Table 3 in the main manuscript.

The full set of spectroscopic properties of two electronic states calculated by fitting the level data with Dunham expansion upto fourth order. $Y_{v,J}$ is the Dunham coefficient to be known from fit and the index, v, J refer to rotation-vibration states. This table is the long and complete version of Table 3 given in main manuscript.

properties	X^1A_g	b^1B_u
$Y_{0,1}$	0.386141	9.31888
$Y_{0,2}$	-0.00128827	-1.97361
$Y_{0,3}$	-0.000124905	0.15542
$Y_{0,4}$	0.0000132576	-0.00388592
$Y_{1,0}$	742.827	635.766
$Y_{1,1}$	-0.0349604	-24.4252
$Y_{1,2}$	0.00471744	5.38511
$Y_{1,3}$	0.0000533031	-0.424068
$Y_{1,4}$	-0.0000206791	0.0106028
$Y_{2,0}$	3.38	-9.3
$Y_{2,1}$	0.01	18.8
$Y_{2,2}$	-0.00170471	-4.15187
$Y_{2,3}$	-0.0000181161	0.326947
$Y_{2,4}$	7.52277×10^{-6}	-0.00817451
$Y_{3,0}$	-0.033	2.6
$Y_{3,1}$	0.0028008	-5.46078
$Y_{3,2}$	-0.000349103	1.20402
$Y_{3,3}$	-3.97235×10^{-6}	-0.0948103
$Y_{3,4}$	1.53952×10^{-6}	0.00237047
$Y_{4,0}$	0.004	-0.55
$Y_{4,1}$	-0.0010217	0.530016
$Y_{4,2}$	0.000144789	-0.116858
$Y_{4,3}$	1.53823×10^{-6}	0.00920172
$Y_{4,4}$	-6.45276×10^{-7}	-0.00023006

The root mean square deviation of the model with respect to the ab initio data points is estimated to be 37 cm^{-1} . There is no permutational symmetry in the fitted points in this case and hence, model used differs from the one which has the permutational symmetry. Its form is relatively simple and with less computationally intensive.

$$y = \sum_i^{i=5} a_i \left[\tanh(\beta_i(r_1 - r_0)) \right] \left[\text{sech}(\mu_i(r_1 - r_0)) \right]$$

$$V = \left[\sum_i^{i=20} A_i y^i \right] + \overbrace{\left[\frac{1}{2} \times 0.1578 \left(1 - \tanh[h_1(r_1 + c_0)] \right) + \frac{1}{2} \times 0.2008 \left(1 + \tanh[h_2(r_1 - d_0)] \right) \right]}^{\text{extra additive fitting term to account for different electronic correlation on either sides of the curve}}$$

$A_1 = 0.026843633576263688$	$a_1 = 24.683346007292684$	$h_1 = 1.4035093988919418$
$A_2 = 0.013615887563453872$	$a_2 = -11.006176122989718$	$h_2 = 0.9051006624032045$
$A_3 = 0.15307476032783826$	$a_3 = 1.1650121485101277$	$c_0 = 0.7752103659248651$
$A_4 = 0.65385686694769$	$a_4 = 25.214314028355137$	$d_0 = 2.5376139972120964$
$A_5 = 0.6206987583064092$	$a_5 = 31.402349864775466$	$r_0 = 0.7106544674263038$
$A_6 = -9.934053561652608$	$\beta_1 = -0.34974887380007963$	
$A_7 = -13.409568040264201$	$\beta_2 = -0.8557955346800209$	
$A_8 = 108.6995265629116$	$\beta_3 = 0.7714533609757536$	
$A_9 = 83.52010790334467$	$\beta_4 = -0.7062483462405179$	
$A_{10} = -633.8610946259066$	$\beta_5 = 0.5819332114226816$	
$A_{11} = -256.2381834572584$	$\mu_1 = 0.4804152777654364$	
$A_{12} = 1994.8092806993543$	$\mu_2 = 0.8997053741472438$	
$A_{13} = 338.84133836731405$	$\mu_3 = 9.23783969355586$	
$A_{14} = -3193.5651170629476$	$\mu_4 = 0.7493005584619238$	
$A_{15} = -1.161474926778965$	$\mu_5 = 0.49862056574068964$	
$A_{16} = 2018.8243839500694$		
$A_{17} = -271.2748127056947$		
$A_{18} = 66.81743447753055$		
$A_{19} = -17.50904248367808$		
$A_{20} = 3.1983343459460887$		

$A_1 = 7.459004109520924 \times 10^{-7}$	$a_1 = 17.670460698786503$	$h1 = 1.6666994382173637$
$A_2 = 12.399957232984109$	$a_2 = 17.670202558372925$	$c0 = -2.5664571305736423$
$A_3 = -0.0003948122094381275$	$a_3 = 19.44085144677859$	
$A_4 = -2079.9858486279163$	$a_4 = 32.63981524910839$	
$A_5 = 0.050212352384742344.$	$a_5 = -33.16258696500684$	
$A_6 = 268134.2281903645$	$a_6 = 23.888031781737094$	
$A_7 = -1.2156553404863077$	$a_7 = -39.73845047186302$	
$A_8 = 1913.8894437400832$	$a_8 = 28.145682626415667$	
$A_9 = -1.0806677444889121$	$a_9 = 20.571277658445$	
$A_{10} = 2.9530854868439613$	$a_{10} = 26.420124822663364$	
$A_{11} = 1.6016402746558116$	$\beta_1 = 2.2810513296701873$	
$A_{12} = 1.3161660707476857$	$\beta_2 = 2.2809750072865347$	
	$\beta_3 = 2.2811584782153105$	
	$\beta_4 = -1.4894150203173853$	
	$\beta_5 = 1.4808091780488688$	
	$\beta_6 = 1.381930172904812$	
	$\beta_7 = 1.4813991231690264$	
	$\beta_8 = -0.8870349379228686$	
	$\beta_9 = 2.2812255636325998$	
	$\beta_{10} = -0.887257713276987$	
	$\mu_1 = 1.650296315446314$	
	$\mu_2 = 1.6503534656033862$	
	$\mu_3 = 1.6504874940662537$	
	$\mu_4 = 2.451954389251743$	
	$\mu_5 = 2.204923436981837$	
	$\mu_6 = -1.1265384058675234$	
	$\mu_7 = 2.2046759695560354$	
	$\mu_8 = 1.2573475481785106$	
	$\mu_9 = 1.6504646816883817$	
	$\mu_{10} = -1.255750222609803$	

v	Energy(cm^{-1})	v	Energy(cm^{-1})
0	1314.91	18	32959.8
1	3921.89	19	33560.7
2	6484.49	20	34067.6
3	8978.06	21	34451.5
4	11401.6	22	34621.8
5	13783.5		
6	<u>16101.1</u>		
7	<u>18331.0</u>		
8	20478.9		
9	<u>22527.7</u>		
10	<u>24462.5</u>		
11	26266.4		
12	27894.5		
13	<u>29224.2</u>		
14	30151.1		
15	<u>30958.9</u>		
16	<u>31632.4</u>		
17	32320.4		