

## Potential of the $A^1\Sigma_u^+$ state of $\text{He}_2$

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The potential of the lowest excited singlet state of  $\text{He}_2$  is calculated. The best function includes 209 configurations constructed from 10  $\sigma$  basis orbitals. Excellent agreement with experimental quantities depending on the shape of the potential near the minimum (equilibrium interatomic separation, vibrational and rotational constants for the lower vibration levels) is obtained. The dissociation energy is  $18\,600\text{ cm}^{-1}$ , compared to the experimental  $19\,910 \pm 50\text{ cm}^{-1}$ . Agreement is not as good for the highest vibrational levels.

### 1. INTRODUCTION

The lowest excited singlet of the  $\text{He}_2$  molecule, the  $A^1\Sigma_u^+$  state, plays an important role in spectroscopic studies of helium gas. A broad emission band extending from 600 to 1000 Å was discovered by Hopfield [1] and ascribed to the  $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  transition. This band is now commonly used as a light source in that region [2, 3]. Using an uncondensed discharge, Tanaka and Yoshino found 14 emission bands [4], and later added a 15th [5]. They assigned the individual bands to transitions from the discrete vibrational levels of the upper state to the repulsive ground state. Smith [6], on the other hand, argued that the initial states responsible for the emission were quasi-bound, with energies above separated atoms but trapped by a maximum in the potential, and the bands resulted from the nodal structure of the wavefunction. The insensitivity of the relative intensities of the bands to He pressure [6] supports this argument. Using his spectroscopic data, Smith obtained a dissociation energy  $D_e = 2.55 \pm 0.17\text{ eV}$  and a potential maximum of  $0.03 \pm 0.03\text{ eV}$  at  $3.0 \pm 0.3\text{ Å}$ .

Two other sources of information pertaining to the  $A^1\Sigma_u^+$  state are available. Tanaka and Yoshino [5] measured the absorption spectrum of the  $X \rightarrow A$  transition. They obtained six bands, assigned to transitions to the six highest vibrational levels of the  $A$  state, with diffuse rotational structure. They propose a dissociation energy of 2.02 eV and a potential hump of 0.059 eV. Ginter [7] investigated the  $C^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$  emission and characterized the four lowest vibrational levels of the  $A$  state. Recently, Smith and Chow [8] analysed all available data to deduce an empirical potential. Their preferred values are  $2.345 \pm 0.015\text{ eV}$  for the dissociation energy and  $0.05 \pm 0.1\text{ eV}$  for the potential maximum. Sando and Dalgarno [9] and Sando [10] obtained another empirical potential by varying it to reproduce the observed emission and absorption 600 Å band spectra. Their potential supports one more vibrational level than Smith and Chow's (the number of levels is not known) and yields a dissociation energy of 2.50 eV and a potential maximum of 0.05 eV. Ginter and Battino [11], using the previously determined dissociation energy of the  $\text{He}_2^+$  ground state [12], suggested  $D_e = 2.33 \pm 0.02\text{ eV}$  for the  $A$  state. Liu [13] has recently redetermined the  $\text{He}_2^+$  dissociation energy; his values for the

	$R_e$ (bohrs)	$\omega_e$ ( $\text{cm}^{-1}$ )	$\omega_e^{\text{ste}}$ ( $\text{cm}^{-1}$ )	$\omega_e^{\text{ye}}$ ( $\text{cm}^{-1}$ )	$D_e$ ( $\text{cm}^{-1}$ )	Potential maximum Height ( $\text{cm}^{-1}$ )	Position (bohrs)
<i>Ab initio</i> potentials:							
Browne [15]	2.08	1878	37	-0.4	15 780	1400	4.99
Allison <i>et al.</i> [16]	(2)				14 600	670	5.86
Scott <i>et al.</i> [17]	2.11	1704	47	0.8	13 860	1230	5.18
Present work, CI 124	2.01	1824	36	-0.2	15 700	1200	5.1
Present work, CI 209	1.966	1874	42	0.7	18 600	700	5.3
Empirical potentials:							
Smith and Chow [8]	1.98	1865	37	0.2	18 920 $\pm$ 120	400 $\pm$ 80	5.7
Sando and Dalgarno [9, 10]	1.965	1820	33	-0.2	20 170	400	5.9
Experiment	1.965 [7]	1861.3 [7]	35.0 [7]		19 910 $\pm$ 50 [13]†	650 $\pm$ 150 [13]	

† See discussion in text.

Table 1. Properties of the  $A^1\Sigma_u^+$  state of  $\text{He}_2$ .

$A^1\Sigma_u^+$  state of  $He_2$ ,  $D_e = 2.469 \pm 0.006$  eV, and a potential maximum of  $0.080 \pm 0.018$  eV, seem more reliable than earlier estimates and are therefore quoted in table 1 as 'experimental' values.

Several *ab initio* calculations have been carried out [14–17]. All of them predict a bound  $A$  state with a maximum in the potential, but numerical results vary widely (see table 1). The most extensive calculations, those of Scott *et al.* [17], do not agree very well with the experimental  $R_e$ ,  $D_e$  and  $\omega_e$  values. All previous potentials were obtained using generalized valence-bond functions. In the present paper we describe a potential for the  $A^1\Sigma_u^+$  state of  $He_2$  calculated with many-configuration functions constructed from molecular orbitals.

## 2. THE $^1\Sigma_u^+$ POTENTIAL

Any *ab initio* calculation seeking to obtain a reasonably accurate molecular potential must involve a wavefunction with a considerable number of configurations. When dealing with closed-shell systems, it is a great help to use the Hartree–Fock function as a first configuration. The bulk of the energy reduction is then contributed by the doubly-excited configurations, with singly-, triply- and higher-excited configurations being much less important. The situation is somewhat different for open shells. In particular, Brillouin's theorem does not apply and single excitation may contribute significantly. The contribution of high excitations is still small in this scheme, and it is therefore advantageous to use Hartree–Fock orbitals. The choice of orbitals loses its significance as the limit of complete CI (all possible configurations included) is approached.

A difficult problem in computations of the type reported here is the choice of basis orbitals. Machine time and core memory available on the Tel-Aviv University CDC3400 computer severely limited the size of the basis set we could use and did not allow extensive exponent optimization. Several basis sets, taken from previous calculations for the lowest  $^1\Sigma_u^+$  and  $^3\Sigma_u^+$  states of  $He_2$ , were tried instead, and energies obtained from wavefunctions including SCF plus singlet and double excitations were compared at several internuclear separations. The basis set finally chosen was taken from Poshusta and Matsen [18] and consists of five basis orbitals on each atom (see table 2). The molecular orbitals were obtained by solving the SCF equations for the lowest  $^3\Sigma_u^+$  state. Unlike the singlet state, the triplet is amenable to calculation by the straightforward one-open-shell method of Roothaan [19]. As an extensive CI calculation was to be carried out later, we did not think it worthwhile to solve the more difficult equations for the singlet. Convergence difficulties were encountered for  $R_{He-He} > 3.3$  bohr, and SCF orbitals for  $R = 3.3$  bohr (table 2) were used. Again, the error introduced by this procedure is expected to be small, as we were not far from the complete CI limit. As a check, two calculations of CI energy at 3.3 bohr were carried out, with SCF orbitals obtained at 2.1 and 3.3 bohr. Calculated CI energies differed by only  $3 \times 10^{-5}$  hartree.

The five  $\sigma_g$  and five  $\sigma_u$  SCF orbitals give rise to 400 configurations of  $^1\Sigma_u^+$  symmetry. We started with the 116 configurations including no more than two excited orbitals, then added all others in groups, and retained the configurations with highest coefficients. The same procedure was repeated at several interatomic separations, and it was found that the same 209 configurations had to be included. The functions obtained this way will be referred to as CI 209 functions.

Basis function†	$\phi_1$ ‡	$\phi_2$	$\phi_3$	$\phi_4$	$\phi_5$	$\phi_6$	$\phi_7$	$\phi_8$	$\phi_9$	$\phi_{10}$
1s <sub>A</sub> (1.42)	0.78827	-0.00450	0.80469	0.84300	11.82015	16.47481	-2.75875	3.27057	-19.47173	-23.62683
1s <sub>A</sub> (1.9979)	0.06242	0.71751	-0.85734	0.44620	-7.37065	-10.05099	1.64347	-2.04688	9.97475	12.39449
2s <sub>A</sub> (1.8488)	-0.25902	0.00643	-0.39290	0.34768	-4.72790	-6.55108	1.13824	-1.18504	10.38315	12.05278
2s <sub>A</sub> (0.5637)	0.11184	-0.00604	0.49553	1.82666	-0.62381	-1.46767	0.11458	-0.11013	0.35445	0.88646
2p <sub>σA</sub> (2.462)	0.01105	0.00134	0.00450	-0.00925	0.04081	-0.04672	0.68113	0.76301	0.00403	-0.07964

† Exponent given in parentheses.

‡ Expansion coefficients for basis functions on atom B may be found by symmetry.  $\phi_i$  has *g* character for odd *i*, *u* character for even *i*.

Table 2. SCF orbitals,  $R = 3.3$  bohr.

No.	Orbitals				Coef.	No.	Orbitals				Coef.
1	1	1	2	3	0.87219	69	9	9	6	1	0.00002
2	1	1	2	5	-0.30706	70	9	9	6	3	0.00019
3	1	1	2	7	-0.00499	71	9	9	8	3	0.00007
4	1	1	2	9	-0.02199	72	9	9	10	1	0.00018
5	1	1	4	3	0.01987	73	9	9	10	3	0.00021
6	1	1	6	3	0.05914	74	10	10	1	4	-0.00173
7	1	1	8	3	0.00235	75	10	10	1	6	-0.00012
8	1	1	10	3	0.01808	76	10	10	5	2	0.00205
9	3	3	2	1	0.28429	77	7	7	6	1	-0.00010
10	1	1	4	5	-0.01967	78	7	7	8	3	0.00021
11	1	1	4	7	0.00060	79	7	7	6	3	-0.00026
12	1	1	4	9	-0.00292	80	8	8	1	4	-0.00356
13	1	1	6	5	-0.00339	81	5	5	2	7	-0.00102
14	1	1	6	7	-0.00229	82	5	5	4	1	-0.00383
15	1	1	6	9	0.00445	83	5	5	4	3	0.00146
16	1	1	8	5	0.00134	84	5	5	6	1	0.00097
17	1	1	8	7	0.01096	85	5	5	10	3	0.00054
18	1	1	8	9	0.00092	86	6	6	1	4	-0.00221
19	1	1	10	5	0.00135	87	6	6	5	2	0.00213
20	1	1	10	7	-0.00121	88	2	2	5	4	0.00614
21	1	1	10	9	0.00623	89	2	2	5	6	0.01554
22	2	2	1	4	0.20139	90	2	2	5	10	0.00605
23	2	2	1	6	-0.01987	91	3	3	4	5	-0.00447
24	2	2	1	8	-0.00114	92	3	3	6	5	-0.00680
25	2	2	1	10	-0.01098	93	3	3	6	9	-0.00346
26	2	2	3	4	-0.07964	94	3	3	8	7	-0.00909
27	2	2	3	6	-0.05182	95	3	3	10	5	-0.00395
28	2	2	3	8	-0.00712	96	3	3	10	7	0.00067
29	2	2	3	10	-0.01593	97	3	3	10	9	-0.00435
30	3	3	2	5	0.03395	98	8	8	5	2	0.00394
31	3	3	2	7	0.00246	99	9	9	2	5	0.00230
32	3	3	2	9	0.01137	100	7	7	2	5	0.00575
33	3	3	4	1	0.00306	101	7	7	4	1	-0.00395
34	3	3	6	1	0.01350	102	5	5	2	9	-0.00211
35	3	3	8	1	0.00047	103	5	5	6	3	0.00113
36	3	3	10	1	0.00254	104	1	5	7	6	0.00070
37	4	4	1	2	-0.00094	105					0.00234
38	4	4	3	2	-0.00159	106	1	5	7	8	-0.00288
39	5	5	2	1	-0.03596	107					-0.00633
40	5	5	2	3	-0.01714	108	1	9	5	10	-0.00162
41	6	6	1	2	-0.00432	109					0.00277
42	6	6	3	2	-0.00777	110	3	5	7	8	-0.00006
43	7	7	2	1	-0.00697	111					0.00017
44	7	7	2	3	-0.01817	112	3	5	9	10	-0.00025
45	8	8	3	2	-0.01268	113					0.00020
46	8	8	1	2	-0.00539	114	2	4	6	5	0.00014
47	9	9	2	1	-0.00424	115					0.00561
48	9	9	2	3	-0.00758	116	1	5	7	4	0.00124
49	10	10	1	2	-0.00344	117					0.00110
50	10	10	3	2	-0.00658	118	1	7	5	10	0.00010
51	2	2	5	8	0.00231	119					-0.00054
52	2	2	7	4	0.00064	120	1	5	9	4	0.00231
53	2	2	7	6	-0.00040	121					-0.00091
54	2	2	7	8	0.00046	122	1	9	5	6	-0.00091
55	2	2	7	10	-0.00002	123					0.00207
56	2	2	9	4	-0.00077	124	1	9	5	8	-0.00009
57	2	2	9	6	0.00123	125					0.00033
58	2	2	9	8	0.00019	126	3	5	7	6	0.00011
59	2	2	9	10	0.00087	127					-0.00006
60	3	3	4	7	0.00151	128	3	5	9	6	-0.00049
61	3	3	4	9	-0.00180	129					0.00030
62	3	3	6	7	0.00312	130	3	7	9	8	-0.00032
63	3	3	8	5	-0.00248	131					0.00042
64	3	3	8	9	-0.00053	132	2	6	4	7	-0.00016
65	8	8	1	6	-0.00009	133					0.00185
66	8	8	9	2	0.00017	134	2	6	4	9	0.00096
67	9	9	4	1	-0.00188	135					-0.00282
68	9	9	4	3	0.00062						

Table 3 (Continued)

No.	Orbitals				Coef.	No.	Orbitals				Coef.
136	2	8	4	7	0.00226	173					-0.00751
137					-0.00495	174	1	7	5	2	0.00233
138	2	4	10	5	0.00031	175					-0.00388
139					0.00277	176	1	9	5	2	0.01280
140	4	6	8	1	-0.00095	177					-0.00311
141					0.00031	178	1	9	7	2	0.00002
142	4	6	10	1	0.00185	179					-0.00038
143					0.00005	180	3	7	5	2	0.00386
144	1	3	5	2	0.01164	181					0.00131
145					0.00669	182	3	9	5	2	0.01108
146	1	7	3	2	-0.00539	183					0.00310
147					0.00438	184	3	9	7	2	-0.00049
148	1	9	3	2	-0.01377	185					-0.00029
149					0.00568	186	2	6	4	1	0.00216
150	1	5	3	4	0.00747	187					0.03629
151					-0.01299	188	2	4	6	3	0.00517
152	1	5	3	6	0.00191	189					0.01320
153					-0.01829	190	2	4	8	1	0.00121
154	1	5	3	8	0.00073	191					-0.00241
155					-0.00552	192	2	8	4	3	-0.00194
156	1	5	3	10	0.00166	193					-0.00151
157					-0.00947	194	2	4	10	1	0.00144
158	1	7	3	4	-0.00071	195					-0.01087
159					0.00359	196	2	4	10	3	0.00275
160	1	7	3	6	-0.00156	197					0.00458
161					0.00633	198	2	6	8	1	-0.00071
162	1	7	3	8	0.00657	199					0.00082
163					-0.01618	200	2	6	8	3	-0.00341
164	1	7	3	10	-0.00041	201					0.00018
165					0.00105	202	2	6	10	1	0.00380
166	1	9	3	4	0.00296	203					-0.00136
167					-0.00389	204	2	6	10	3	0.00660
168	1	9	3	6	0.00189	205					0.00043
169					-0.00692	206	2	10	8	1	0.00015
170	1	9	3	8	-0.00022	207					0.00005
171					-0.00120	208	2	8	10	3	0.00052
172	1	9	3	10	0.00352	209					-0.00010

Table 3. CI coefficients,  $R=3.3$  bohr. Orbitals shown in table 2.

A slight complication arises from configurations consisting of four different orbitals. If we define

$$(ijkl) = \mathcal{A} \phi_i \phi_j \phi_k \phi_l (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)/2 \quad (1)$$

then  $(ijkl)$ ,  $(ikjl)$  and  $(ilkj)$  represent different functions, only two of which are independent. It is convenient to use two orthonormal combinations of these three functions, thereby avoiding off-diagonal elements in the overlap matrix. We choose arbitrarily the pair

$$\left. \begin{aligned} (ijkl)_1 &= (ijkl) + (ikjl), \\ (ijkl)_2 &= [(ijkl) - (ikjl)]/\sqrt{3}. \end{aligned} \right\} \quad (2)$$

The CI expansion coefficients for  $R=3.3$  bohr are listed in table 3. The two entries for each configuration constructed of four different orbitals refer to the functions of equation (2). It should be noted that such configurations were always included in pairs, even if only one member of the pair contributed significantly to the total function.

Another potential was calculated using all  $124 \sum_u^+$  configurations obtainable from a basis set consisting of three  $\sigma$  orbitals (1s with exponents 1.42 and 1.9979, 2s with 0.5637) and two  $\pi$  orbitals ( $2p_{\pm 1}$ , exponent 2.482) on each helium atom.

R (bohr)	CI 124	CI 209
1.0	—	-4.707286
1.5	-5.038173	-5.061564
1.8	-5.088369	-5.106313
1.9	—	-5.110009
1.966	—	-5.110573
2.0	—	-5.110397
2.1	-5.094202	-5.108414
2.2	—	-5.104776
2.3	—	-5.100043
2.4	-5.082387	-5.094621
2.5	—	-5.088835
2.7	-5.065585	-5.077065
3.0	-5.049677	-5.060863
3.3	-5.037080	-5.047820
3.6	-5.028312	-5.038247
3.9	-5.022865	-5.031725
4.2	-5.019854	-5.027592
4.5	-5.018443	-5.025174
4.8	-5.018011	-5.023910
5.1	-5.018145	-5.023388
5.4	-5.018583	-5.023319
5.7	-5.019164	—
6.0	-5.019788	-5.023843
7.0	-5.021610	—
8.0	-5.022728	-5.025982
10.0	—	-5.026605
12.0	-5.023681	-5.026631
15.0	—	-5.026537

Table 4. Calculated potentials (hartree).

Energy values of this CI 124 function together with the CI 209 function described above are presented in table 4, and figure 1 shows *ab initio* potentials for the  $A^1\Sigma_u^+$  state. Comparison with experiment (table 1) indicates that the CI 209 potential is quite accurate in the minimum region (compare values of  $R_e$ ,  $\omega_e$ ). It should also be noted that CI 209 is lower in this region than any previously calculated *ab initio* function. The CI 209 dissociation energy is 7 per cent lower than Liu's value [13]. The inferior results yielded by the CI 124 potential imply that  $\sigma$  orbitals are more important than  $\pi$  orbitals in small basis sets of the type used here. The same conclusion may be drawn from the 32-basis-function calculations of Scott *et al.* [17], where the most important configurations include  $\sigma$  orbitals only. When larger basis sets are used in more elaborate calculations,  $\pi$  orbitals will have to be included too.

Whereas our CI 209 potential seems to be fairly accurate near its minimum, it is less reliable for larger internuclear separations. This is most clearly demonstrated by the spacing of vibration levels, discussed in the next section. Figure 2 shows that the calculated potential resembles the empirical potential of Smith and Chow [8] much more closely than that of Sando [10]. The main deficiencies are too narrow a potential near the dissociation limit and too high a maximum. It should be noted that the disagreement between the two empirical potentials is not smaller than the difference between them and the calculated potential.

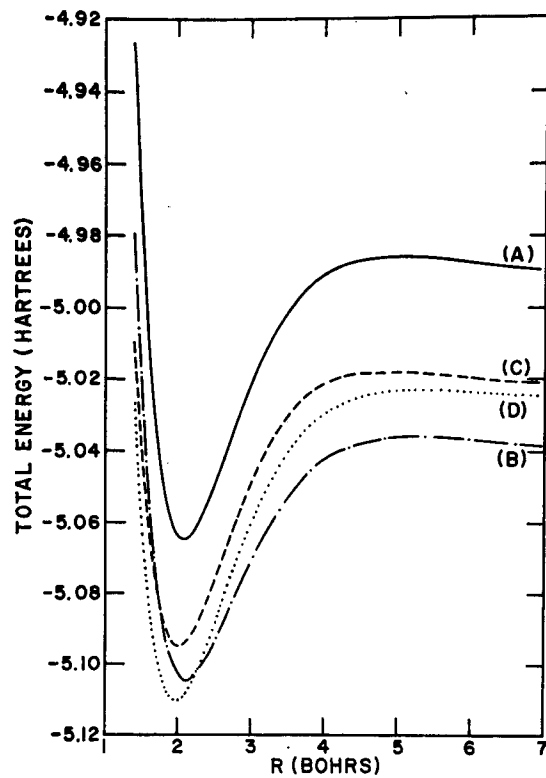


Figure 1. Calculated total energies of  $\text{He}_2$  ( $A^1\Sigma_u^+$ ). (A) Browne [15]; (B) Scott *et al.* [17]; (C) present work, CI 124; (D) present work, CI 209.

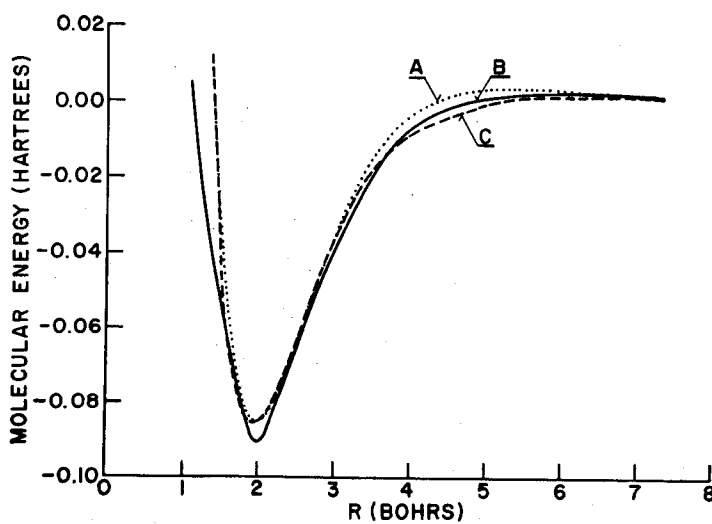


Figure 2. Comparison of CI 209 and empirical potentials. (A) CI 209; (B) Sando [10]; (C) Smith and Chow [8].



## 3. VIBRATION-ROTATION LEVELS

The differential equation of the two He nuclei moving in the  $^1\Sigma_u^+$  potentials described in the preceding section was solved, and vibration-rotation levels were obtained. Two methods were employed: (a) expanding the nuclear wavefunction in a harmonic oscillator basis set [20, 21], and (b) Cooley's numerical method for solving the eigenvalue equation [22]. The main advantage of method (a) is that wavefunctions are obtained in analytical form convenient for use in spectral calculations [23]. Convergence is slow however, especially for higher vibration levels, and up to 180 harmonic oscillator functions were needed to have all levels converged to a few wavenumbers. Eigenvalues were cross-checked by method (b).

Two quasi-bound (or resonance) vibration levels are accommodated by our potential. These levels, with positive energies (relative to separated atoms) but lying below the potential maximum, are responsible for the two absorption bands on the short wave-length side of the atomic line [5]. Eigenfunctions of resonance levels do not satisfy the boundary conditions of bound states; in particular, they do not vanish at infinity, but show instead oscillatory behaviour. It has nevertheless been shown [24] that bound basis sets may be used to expand functions of resonance states inside the potential well. We also solved the differential equation numerically (by Numerov's method) with oscillatory boundary conditions at large  $R$  and found that neglecting regions beyond the potential maximum had no effect on the resonance energy and function inside the well. Large  $R$  values are of no interest for  $X \rightarrow A$  transition calculations, as the atomic transition is forbidden.

$v$	CI 124	CI 209
0	-14 782	-17 502
1	-13 031	-15 710
2	-11 353	-13 997
3	-9 751	-12 355
4	-8 223	-10 784
5	-6 774	-9 288
6	-5 408	-7 872
7	-4 130	-6 539
8	-2 945	-5 290
9	-1 860	-4 129
10	-886	-3 061
11	-37	-2 091
12	666	-1 226
13	1 167	-477
14		143
15		604

Table 5. Calculated vibrational levels ( $\text{cm}^{-1}$ ).

Energies of vibration levels obtained with the two CI potentials are listed in table 5.  $\Delta G_{v+1/2}$  values from these and other *ab initio* potentials are compared in table 6 with results of Sando's empirical potential [10], constructed to reproduce the experimental values for the highest levels, and with experiment. Excellent agreement for the lower levels is given by the CI 209 potential. The number of vibrational levels is not known experimentally. It should be at least 15, the number of emission bands observed by Tanaka and Yoshino. The empirical potentials predict 17 [6, 8] or 18 [10] levels. If the highest level obtained with the

Browne [15]	Scott <i>et al.</i> [17]	CI 209	Sando [10]	Experiment [5, 7]
1802 (0)	1623 (0)	1792 (0)	1753 (0)	1791 (0)
1726 (1)	1496 (1)	1713 (1)	1685 (1)	1720 (1)
1644 (2)	1451 (2)	1642 (2)	1616 (2)	1648 (2)
1084 (7)	933 (7)	970 (10)	817 (12)	846
974 (8)	846 (8)	865 (11)	718 (13)	715
855 (9)	739 (9)	750 (12)	585 (14)	601
712 (10)	590 (10)	619 (13)	460 (15)	470
523 (11)	430 (11)	461 (14)	276 (16)	283

Table 6. Vibrational spacings  $\Delta G_{v+1/2}$  ( $\text{cm}^{-1}$ )†.

† Listed are values for the three lowest and five highest  $v$  numbers.  $v$  values are given in parentheses.

	Browne [15]	Scott <i>et al.</i> [17]	CI 209	Experiment [5, 7]
$B_0$	6.85	6.65	7.70	$7.671 \pm 0.001$
$B_1$	6.63	6.37	7.48	$7.446 \pm 0.001$
$B_2$	6.40	6.24	7.25	$7.218 \pm 0.001$
$B_3$	6.16	5.96	6.99	$6.985 \pm 0.002$
$B_4$	5.93	5.71	6.72	
$B_5$	5.69	5.44	6.46	
$B_6$	5.44	5.16	6.18	
$B_7$	5.17	4.88	5.91	
$B_8$	4.90	4.62	5.61	
$B_9$	4.61	4.35	5.31	
$B_{10}$	4.29	4.05	4.99	
$B_{11}$	3.92	3.64	4.64	$3.16-3.46\dagger$
$B_{12}$	3.43	3.08	4.26	$2.67-2.99\dagger$
$B_{13}$	2.73	2.60	3.83	$2.29-2.53\dagger$
$B_{14}$			3.31	$1.74-2.06\dagger$
$B_{15}$			2.65	$0.83\dagger$
$D_0 \times 10^4$	3.82	4.24	5.51	$5.43 \pm 0.02$
$D_1$	3.80	4.90	5.53	$5.40 \pm 0.03$
$D_2$	3.78	4.24	5.52	$5.41 \pm 0.03$
$D_3$	3.79	4.26	5.53	$5.40 \pm 0.06$
$B_e$	6.97	6.77	7.84	7.787
$\alpha_e$	0.233	0.238	0.244	0.228

† Vibrational quantum numbers not known.

Table 7. Rotational constants.

different potentials is matched with the highest experimental level (table 6), all *ab initio* potentials predict too large spacings. It is interesting to note that  $\Delta G_{v+1/2}$  values of the CI 209 potential are close to experimental values with  $v$  one unit lower. A tempting explanation of the discrepancy is to assume the existence of one higher resonance, possibly just above the potential maximum. However, no such resonance was discovered using our potential, and the disagreement of values is probably due to remaining deficiencies in our potential, discussed in the previous section.

Rotational constants are shown in table 7. Again agreement between CI 209 and the experiment is excellent for the lower vibration levels.  $B_v$  values for the higher levels are too high; this comparison is not relevant, as the calculated spectrum yields  $B$  values considerably lower than those given by the levels themselves [23].

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