

01 Jul 2019

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Recommended Citation

L. Biolsi and M. Biolsi, "The Ideal and Real Gas Heat Capacity of Cesium Atoms at High Temperatures," *International Journal of Thermophysics*, vol. 40, no. 7, article no. 69, Springer, Jul 2019.

The definitive version is available at <https://doi.org/10.1007/s10765-019-2527-z>

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The Ideal and Real Gas Heat Capacity of Cesium Atoms at High Temperatures

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Received: 22 June 2018 / Accepted: 11 June 2019 / Published online: 1 July 2019
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Abstract

The ideal gas heat capacity, C_p , of cesium atoms is calculated to high temperatures using statistical mechanics. There are a large number of electronic states in the state sum that determines the partition function: 174 known levels for cesium atoms below the first ionization potential. Thus, at high temperatures, C_p becomes very large unless the number of contributing states is constrained. Two arguments are used to do this. First, at high temperatures, the increased size of the atoms constrains the sum (Bethe method). Second, the existence of interacting charged species at higher temperatures, which lowers the ionization potential, constrains the sum (ionization potential lowering method). If atoms constitute a real gas obeying the virial equation of state, the lowest non-ideal contribution to C_p depends on the second derivative of the second virial coefficient, $B''(T)$, which depends on the interaction potential energy curves between two atoms. When two ground-state (2S) cesium atoms interact, they follow either of two potential energy curves. When a 2S cesium atom interacts with a cesium atom in the first electronically excited (2P) state, they follow any of eight potential energy curves. The values of $B''(T)$ for the ten states are determined, then averaged, and used to calculate the lowest order non-ideal contribution to C_p .

Keywords Cesium atoms · Ideal gas at high temperatures · Non-ideal gas · Virial coefficients

Selected papers of the 20th symposium on thermophysical properties.

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1 Introduction

The normal boiling point of cesium metal is 963 K [1], and the first ionization potential (IP) is 3.89 391 eV [2], corresponding to thermal energy, kT , of 45 187 K where k is Boltzmann's constant and T is temperature. Thus, there are some cesium atoms in the gas phase over the temperature range from about 1000 K to 50 000 K.

The heat capacity, C_p^0 , of cesium atoms behaving as an ideal gas is given as a function of temperature to 6000 K in the NIST-JANAF Thermochemical Tables [3]. One purpose of this paper is to extend the calculations to higher temperatures. However, as T increases and more excited electronic states contribute to C_p^0 , the sum over excited states must be constrained or the values of C_p^0 become much too large [4–6].

In addition, if it is assumed that cesium atoms constitute a non-ideal gas obeying the virial equation of state, the lowest order non-ideal gas correction to C_p^0 is given by a term that depends on [7] the second derivative of the second virial coefficient, $B''(T)$, which is calculated here for each of the ten lowest lying electronic states of Cs_2 .

2 Ideal Gas Heat Capacity

The heat capacity of a mole of atoms is [5]

$$C_p^0 = 20.786 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + C_{p,el}^0 \quad (1)$$

where the first term is the translational contribution and $C_{p,el}^0$ is the electronic contribution [8];

$$C_{p,el}^0 = \frac{RT}{q_{el}} \left[T \frac{\partial^2 q_{el}}{\partial T^2} - \frac{T}{q_{el}} \left(\frac{\partial q_{el}}{\partial T} \right)^2 + 2 \frac{\partial q_{el}}{\partial T} \right] \quad (2)$$

and R is the gas constant. The electronic partition function, q_{el} , is

$$q_{el} = \sum_i g_i e^{-E_i/kT} \quad (3)$$

where the sum over i is the sum over the electronic states, E_i , of an atom and g_i is the degeneracy of state i .

The ground state of a cesium atom is [2] $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$. The Atomic Spectra Database (ASD) table [2] lists 173 other known electronic states of cesium atoms with energies less than those of the first IP, each corresponding to the excitation only of the single $6s$ electron. Results are given to $n = 25$ where n is the value of the principal quantum number (labeling the energy level). However, this list of states is incomplete. For cesium, the degeneracy, g_n , of an energy level, E_n , is [4]:

$$g_n = 2n^2 \quad (4)$$

For instance, for $n = 25$, $g_n = 1250$. However, the ASD table [2] lists the energies of only the $25s$, $25p$, $25d$, $25f$, and $25g$ states with a total degeneracy of 40. Thus, the energies of 1210 states are missing. There is a similar problem for all other energy levels.

The missing states should be accounted for in the calculation of C_p^0 . This is done by using the “FILL” procedure; i.e., the missing states are assumed to have the energy of the highest observed state for that value of n [4], a procedure that has been used in a number of high-temperature monatomic gas calculations, e.g., [4–6, 9–11]. For sodium, all “inner” ground-state energy levels (except the valence level) are filled, and for potassium, with only one “inner” energy level (e.g., the 3d) other than the valence level unfilled, the “FILL” procedure should be quite accurate. However, for cesium, the ground-state “inner” $n = 4$ and $n = 5$ energy levels are both unfilled (e.g., the 4f, 5d, 5f, and 5g). Thus, the “FILL” procedure for cesium may be somewhat less accurate than for sodium and potassium.

When the “FILL” procedure is used to calculate $C_{p,el}^0$ as a function of temperature, the results are unreasonably large at intermediate temperatures; e.g., $C_{p,el}^0$ is predicted to be $144.744 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 5000 K which is most unlikely. This large result occurs because energy levels to $n = 25$ are included in the calculation. The sum over states (or energy levels) must be constrained.

3 Constraining the Sum Over Energy Levels

This very large value of $C_{p,el}^0$ at 5000 K is expected [4–6] as a large number of energy states/levels are included in the summation in Eq. 3. To avoid this, the sum over states or energy levels in q_{el} , i.e., Eq. 3, must be constrained so that the values of $C_{p,el}^0(T)$ are reduced; e.g., a “cutoff” procedure for states is required [4].

One method for doing this was suggested by Bethe [12]. As n increases, the size of an atom increases and it can be shown, e.g., [5, 13], that the maximum value of n , n_{max} , contributing to q_{el} is

$$n_{max} = 2.4561T^{1/6} \quad (5)$$

at 1 bar pressure. This approach has been used in a number of calculations, e.g., [4–6, 11, 13–17]. The results for $C_{p,el}^0$ as a function of T obtained for cesium atoms using the Bethe method are given in the third column of Table 1. The results in the second column are from the NIST-JANAF Thermochemical Tables [3]. Below 1200 K, $C_{p,el}^0$ is zero. The values of n_{max} as a function of T obtained using this method are given in the second column of Table 2.

The second method commonly used to constrain the sum over n depends on the fact that, as the energy associated with energy level n nears the IP, some atoms ionize and spectroscopic studies show that this has the effect of lowering the IP of the remaining neutral atoms [4–6, 13, 18–21] due to the stabilization of an ion that occurs because it is surrounded by other charged particles aligning themselves so that charged particles with the opposite sign dominate among nearest neighbors, providing a net attractive interaction. This is discussed in some detail in Refs. [6, 21]. It can be shown that for this method [13],

$$E_{n_{max}} = IP - kT \quad (6)$$

Table 1 Electronic contribution to the ideal gas heat capacity, $C_{p,el}^0$ ($J \cdot mol^{-1} \cdot K^{-1}$), of cesium atoms as a function of temperature

T(K)	JANAF	Bethe	IP – kT
1200	0.005	0.005	0.005
1500	0.055	0.055	0.055
2000	0.563	0.562	0.562
3000	5.296	5.321	5.142
4000	15.464	17.960	13.107
5000	24.962	44.416	21.912
6000	29.149	61.120	28.005
7000		56.448	25.425
8000		41.658	24.350
9000		27.223	22.041
10 000		17.863	18.602
20 000		1.091	5.809
30 000		0.271	2.731
40 000		0.107	1.429
50 000		0.052	0.876

Table 2 Maximum value of n , n_{max} , contributing to q_{el} as a function of temperature

T(K)	Bethe	IP – kT
1200	8	11
1500	8	10
2000	8	8
3000	9	7
4000	9	6 ^a
5000	10	6 ^a
6000	10	6 ^a
7000	10	6 ^a
8000	11	6 ^a
9000	11	6 ^a
10 000	11	6 ^a
20 000	12	6 ^a
30 000	13	6
40 000	14	6
50 000	15	6

^aAlso including contributions from some “high lying” $n = 5$ states above the $n = 6$ energy level

This is called the “IP–kT” method and has been used in a number of calculations, e.g., [4–6, 9–11, 21–23]. The results for $C_{p,el}^0$ as a function of T for cesium obtained using this method are given in the fourth column of Table 1, and the values of n_{max} as a function of T obtained using this method are given in the third column of Table 2.

4 Cesium Atoms as a Real Gas

Assume that cesium atoms obey the virial equation of state, i.e., [24]

$$\frac{PV}{RT} = 1 + \frac{B(T)}{RT}P + \frac{C(T) - B(T)^2}{(RT)^2}P^2 + \dots \quad (7)$$

where P is pressure, V is volume, $B(T)$ is the second virial coefficient, and $C(T)$ is the third virial coefficient. The virial equation has been written as a power series in pressure since this form is convenient for calculating C_p . For a gas obeying the virial equation of state, C_p is given by [7, 25]

$$C_p = C_p^0(IG) - TP \frac{d^2 B(T)}{dT^2} - D(T)P^2 + \dots \quad (8)$$

where $C_p^0(IG)$ is the ideal gas result and $D(T)$ is a lengthy expression involving $B(T)$ and $C(T)$ [6, 7, 25]. Now $B(T)$ depends on two-body interactions between atoms but $C(T)$ depends on the interactions among three atoms [7]. There are rigorous results for many two-body interactions between cesium atoms in various electronic states but not for three-body interactions. Thus, this work considers only the contribution from the second term on the right in Eq. 8.

Classically, $B_{cl}(T)$ is given by [24]

$$B_{cl}(T) = 2\pi \int_0^\infty \left(1 - e^{-V(R)/kT}\right) R^2 dR \quad (9)$$

where R is the distance between two interacting atoms and $V(R)$ is the electronic interaction potential energy. Semiclassical corrections to $B_{cl}(T)$ are obtained by expanding in powers of Planck's constant [24]. The resulting expressions are lengthy and given elsewhere [24, 26]. The classical and first three semiclassical corrections to $B(T)$ and its derivatives are included in these calculations.

5 Electronic States of Cs_2 and $B(T)$

The potential energy, $V(R)$, of interaction between two cesium atoms depends on the electronic state associated with the atom–atom interaction, i.e., on the electronic state of Cs_2 . When two ground-state (2S) cesium atoms interact, they can interact along two potential energy curves: the ground $X^1\Sigma_g^+(1)$ and the excited $a^3\Sigma_u^+(1)$ states. When a ground-state atom interacts with an atom in the first excited (2P) electronic state, they can interact along eight potential energy curves: the $1^1\Sigma_{g,u}^+$, $3^3\Sigma_{g,u}^+$, $1^1\Pi_{g,u}$, and $3^3\Pi_{g,u}$ gerade/ungerade pairs of states [27]. Nine of the ten electronic states are bound. Only the $3^3\Sigma_u^+(2)$ state is repulsive [28]. The symbols (1) and (2) following term symbols are used to distinguish between states with the same term symbol.

One way to represent the bound states is with the Hulburt–Hirschfelder (HH) potential, V_{HH} [29, 30], which is a simple accurate general-purpose potential for representing

atom–atom and atom–ion bound-state interactions. More accurate potentials are available for specific interactions but they often require either significant curve fitting or the use of empirical parameters, or both. However, the HH potential is easy to use when the experimental spectroscopic constants for a given electronic state are known and do not require any curve fitting; see Eq. 10. It is probably the simplest potential available for accurately representing bound-state interactions between two atoms and between an atom and a +1 ion.

The HH potential often gives excellent agreement with “experimental” Rydberg–Klein–Rees (RKR) [31–33] potentials for many atom–atom and atom–ion interactions [34–38]. Other methods used to obtain “experimental” potential energy curves for diatomic species include the inverse perturbation analysis (IPA) method, e.g., [39–41], and the direct potential fitting (DPF) method, e.g., [42–45]. The HH potential often represents the “experimental” potentials as accurately, or nearly as accurately, as more complicated potentials.

The HH potential has the reduced form [29, 30]

$$V_{HH}^*(R^*) = e^{-2Ax} - 2e^{-Ax} + Bx^3(1 + Gx)e^{-2Ax} \quad (10)$$

where

$$\begin{aligned} V_{HH}^* &= \frac{V_{HH}}{D_e} & x &= \frac{R^*}{d} - 1 & R^* &= \frac{R}{\sigma} & d &= \frac{R_e}{\sigma} \\ c &= 1 + a_1 \sqrt{\frac{D_e}{a_0}} & b &= 2 - \frac{\frac{7}{12} - D_e a_2 / a_0}{c} \\ a_0 &= \frac{\omega_e^2}{4B_e} & a_1 &= -1 - \frac{\alpha_e \omega_e}{6B_e^2} & a_2 &= \frac{5}{4} a_1^2 - \frac{2\omega_e \chi_e}{3B_e} \\ A &= \frac{\omega_e}{2\sqrt{B_e D_e}} & B &= cA^3 & G &= bA \end{aligned}$$

and σ is the effective rigid sphere diameter, i.e., the smallest value of R at which $V_{HH}(R)$ goes to zero. Also, D_e is the electronic dissociation energy, ω_e is the fundamental vibrational frequency, $\omega_e \chi_e$ is the anharmonicity constant, B_e is the rotational constant, α_e is the vibration–rotation coupling constant, and R_e is the equilibrium internuclear separation. These constants are known experimentally for the ground and excited electronic states of many diatomic species. For such states, a (usually) quite accurate potential is obtained by simply plugging these constants into the formula for V_{HH} .

For cesium, these six constants are known for seven states: the $X^1\Sigma_g^+(1)$ [46] with D_e from Refs. [42, 47], $a^3\Sigma_u^+(1)$ [48], $b^3\Pi_u$ [49], $A^1\Sigma_u^+$ [50], $^3\Sigma_g^+$ [51], $^1\Sigma_g^+(2)$ [52], and $B^1\Pi_u$ [53] with D_e from Ref. [54] states. The values of A , B , G , R_e , and σ obtained from these spectroscopic constants and used in Eq. 10 are given in Table 3.

The bound-state potential energy curves for the $^1\Pi_g$ and $^3\Pi_g$ states are represented by the Morse potential:

$$V_M(R) = D_e \left[1 - e^{-A'(R-R_e)} \right]^2 \quad (11)$$

Table 3 Parameters for the HH potential, Eq. 10, obtained from spectroscopic constants

Par.	$X^1 \Sigma_g^+(1)$	$a^3 \Sigma_u^+(1)$	$b^3 \Pi_u$	$A^1 \Sigma_u^+$	$^3 \Sigma_g^+$	$^1 \Sigma_g^+(2)$	$B^1 \Pi_u$
A	3.2094	4.3086	2.2587	2.6291	2.8246	2.5952	3.4241
B	11.0863	- 29.0159	2.4433	21.4158	1.3017	10.8315	18.9615
G	1.7833	0.043 613	2.4599	12.9657	2.0729	3.8974	2.0582
$R_e(\text{\AA})$	4.64 793	6.2354	4.46 711	5.292	5.5425	5.8318	4.86
$\sigma(\text{\AA})$	3.50 281	5.3479	3.13 012	4.287	4.1632	4.2884	3.66

A, B, and G are unitless

where

$$A' = \sqrt{\frac{2m}{D_e}} \pi c \omega_e$$

and m is the mass of the molecule and c is the speed of light. For the $^1 \Pi_g$ state, the values $D_e = 0.18\ 206\ \text{eV}$, $A' = 2.7216\ \text{\AA}^{-1}$, and $R_e = 5.6973\ \text{\AA}$ are from spectroscopic information in Ref. [52], and for the $^3 \Pi_g$ state, the values $D_e = 0.03\ \text{eV}$, $A' = 7.56\ 394\ \text{\AA}^{-1}$, and $R_e = 5.435\ \text{\AA}$ are obtained from Ref. [28].

The $^3 \Sigma_u^+(2)$ state is purely repulsive and is represented by the exponential repulsive potential:

$$V_{ER}(R) = A'' e^{-B'R} \tag{12}$$

The constants A'' and B' are obtained by making a fit to the theoretical potential energy curve for this state in Table I.(E) of Ref. [28]. The results are $A'' = 0.945\ 681\ \text{eV}$ and $B' = 0.253\ 278\ \text{\AA}^{-1}$.

Calculations of $B''(T)$ have been carried out for each of the ten states. Again, the classical value and the first three semiclassical corrections have been determined. The results must be degeneracy averaged [55]:

$$\left(\frac{d^2 B(T)}{dT^2}\right)_{DA} = \frac{\sum_j \frac{d^2 B_j(T)}{dT^2} g_j(Cs_2) e^{-E_j(Cs_2)/kT}}{(\sum_i g_i(Cs) e^{-E_i(Cs)/kT})^2} \tag{13}$$

where j labels the electronic states of Cs_2 . The final result for the lowest order non-ideal contribution to the heat capacity of a virial gas is [7]:

$$C_p(NI) = -TP \left(\frac{d^2 B(T)}{dT^2}\right)_{DA} \tag{14}$$

Results for $C_p(NI)$ at 1 bar are given in Table 4.

Table 4 Non-ideal contribution to the heat capacity of cesium atoms, $C_{p,NI}(J \cdot mol^{-1} \cdot K^{-1})$, as a function of temperature at 1 bar

T(K)	$C_{p,NI}$	T(K)	$C_{p,NI}$
1000	16.120	4500	0.024
1500	1.178	5000	0.017
2000	0.288	6000	0.009
2500	0.122	7000	0.004
3000	0.070	8000	0.002
3500	0.046	9000	0.002
4000	0.033	10 000	0.000

6 Discussion

The Bethe and IP – kT methods for constraining the sum over atomic states are both used to keep the “ideal gas” heat capacity of atoms from becoming unacceptably large. Both methods are ad hoc and neither is really satisfactory but they appear to be the best methods available for this purpose. The IP – kT method reduces the value of $C_{p,el}^0$ more than the Bethe method as shown in Table 1. The same result is found for other atoms when the two approaches are compared, e.g., Refs. [4–6].

This is expected since Table 2 shows that the number of electronic energy levels, n , contributing to $C_{p,el}^0$ becomes less for the IP – kT method as T increases while n becomes larger for the Bethe method as T increases. It seems reasonable to expect that n would increase as T increases but, as shown in the fourth column of Table 1, the values of $C_{p,el}^0$ are quite large, probably unreasonably large, when the Bethe method is used but significantly smaller when the IP – kT method is used.

The IP – kT results appear to be more in line with what one would expect the values of $C_{p,el}^0$ to be for atoms although experimental information to use for testing the methods is lacking. The IP – kT method is used to generate the JANAF Thermochemical Tables [3] for all atoms at higher temperatures and is probably the present method of choice for calculating $C_{p,el}^0$ for atoms at higher temperatures.

Somewhat surprisingly, although the “ideal gas” results for $C_{p,el}^0$ are obtained using rather unsatisfactory methods, the expressions for the non-ideal contributions to C_p^0 for a virial gas are rigorous. Thus, the accuracy of the results in Table 4 depends on two things in addition to the fact that only the lowest order contribution is calculated: the accuracy of the semiclassical approach for calculating $B(T)$ and the accuracy of the electronic potential energy curves used to calculate $B(T)$.

The result in Table 4 at 1000 K is clearly much too large to be correct, and the result at 1500 K may also be too large. Similar results were found for sodium [5] and potassium [6]. The primary reason for this is probably that the semiclassical expansion for $B(T)$ fails at lower temperatures and a full quantum mechanical calculation of $B(T)$, involving the evaluation of phase shifts [24], is required.

The only other source of error in the calculation of $C_p(NI)$ is the error in the potentials used for the ten electronic states. Errors in representing the potential energy curve for the ground $X^1 \Sigma_g^+(1)$ state will be considered in some detail since it makes the primary contribution to $B(T)$ at many temperatures.

Table 5 Ratio of the HH to the DPF [42] potential energy, $V(\text{HH})/V(\text{DPF})$, for various values of the vibrational quantum number, v , for the ground $X^1\Sigma_g^+$ state of Cs_2 for $R < R_e$

v	$V(\text{HH})/V(\text{DPF})$	v	$V(\text{HH})/V(\text{DPF})$
0	1.000	68	1.020
4	1.001	72	1.021
8	1.002	76	1.022
12	1.003	80	1.023
16	1.004	84	1.024
20	1.006	88	1.024
24	1.007	92	1.025
28	1.008	96	1.026
32	1.010	100	1.026
36	1.011	104	1.026
40	1.012	108	1.027
44	1.014	112	1.027
48	1.015	116	1.028
52	1.016	120	1.029
56	1.017	124	1.028
60	1.018	128	1.028
64	1.019	132	1.028
		136	1.028

For this state, there are a number of determinations of the spectroscopic constants needed in the HH potential and a number of determinations of RKR, IPA, and DPF potentials. We have examined a variety of combinations of spectroscopic constants and “experimental” potentials. In all cases, the HH potential accurately represents the experimental potential. To illustrate this, the spectroscopic constants in Ref. [46], with D_e from Refs. [42, 47], are used to calculate the HH potential which is then compared with the RKR-like results obtained from the DPF potential, $V(\text{DPF})$, given in Appendix C of Ref. [42]. Comparisons are shown in Tables 5 and 6 as the ratio $V(\text{HH})/V(\text{DPF})$. Since there are lists of two R values for each of 137 values of the vibrational quantum number, v , in the appendix [42], for simplicity only results for every fourth value of v are given in Tables 5 and 6. Table 5 is for $R < R_e$ and Table 6 is for $R > R_e$. The agreement is very good over the entire range of R values which cover 99.3 % of D_e , i.e., essentially the entire attractive region of the potential.

Essentially, the same good agreement is obtained using other combinations of spectroscopic constants and experimental potentials. It is reasonable to conclude that the HH potential represents the ground electronic $X^1\Sigma_g^+$ state of Cs_2 very accurately.

For the first excited $a^3\Sigma_u^+(1)$ state, an “experimental” potential is not available [48]. An attempt to calculate an RKR potential led to bending of the inner wall of the potential well [48]. However, the vibrational potential energy data were used to construct a MLR (Morse long range) potential for this state [48]. A comparison of the HH and MLR potential for this state gives an error of no more than 0.77 % from 5.3 Å to 15.0 Å ($R_e = 6.23\,540$ Å). The R value of 5.3 Å is on the repulsive wall where the HH potential, based on the bound-state spectroscopic constants, would not

Table 6 Ratio of the HH to the DPF [42] potential energy, $V(\text{HH})/V(\text{DPF})$, for various values of the vibrational quantum number, v , for the ground $X^1\Sigma_g^+$ state of CS_2 for $R > R_e$

v	$V(\text{HH})/V(\text{DPF})$	v	$V(\text{HH})/V(\text{DPF})$
0	1.001	68	0.989
4	0.999	72	0.989
8	0.998	76	0.990
12	0.997	80	0.991
16	0.996	84	0.991
20	0.995	88	0.992
24	0.994	92	0.993
28	0.993	96	0.994
32	0.993	100	0.995
36	0.992	104	0.997
40	0.991	108	0.998
44	0.990	112	0.998
48	0.990	116	0.999
52	0.989	120	0.999
56	0.989	124	0.999
60	0.989	128	0.999
64	0.989	132	0.998
		136	0.998

necessarily be expected to be very accurate so this good agreement is satisfying. Even at $R = 5.0 \text{ \AA}$, where the HH potential is 125 % of D_e , the disagreement between the two potentials is only 4.8 %. At smaller R values, the HH potential rises more steeply than the MLR potential.

For $R > 15.0 \text{ \AA}$, agreement between the two potentials is almost perfect. In this region, the dispersion coefficients primarily determine the (small) values of the potential and the HH potential does not include terms representing dispersion coefficients. Thus, the good agreement is, again, satisfying. The HH potential appears to represent this state very accurately.

The MLR potential for the $a^3\Sigma_u^+(1)$ state was redone by Sovkov et al. [47]: call it MLR1. The HH potential is in agreement with the MLR1 potential in the attractive well region but the agreement is not as good as for the MLR potential. The disagreement is more significant along the repulsive wall with the MLR1 potential rising more steeply than the HH potential. Again, however, the good agreement in the attractive well region indicates that the HH potential is representing this state quite accurately.

For the $b^3\Pi_u$ state, RKR values are given in Table VI of Ref. [49] for 51 values of v . Table 7 gives the ratio $V(\text{HH})/V(\text{RKR})$ for every third value of v . The ratio in the second column is for $R < R_e$, and the ratio in the third column is for $R > R_e$. Although the agreement is not terrible, it is much worse than is usually obtained when comparing the HH and “experimental” potentials. For all 102 ratios, the average error is 14.8 % and the median error is 15.4 %.

Relatively poor agreement between the HH and RKR potential for an electronic state is often a sign that the state has some unusual property. In this case, the $b^3\Pi_u$

Table 7 Ratio of the HH to the RKR [49] potential energy, $V(\text{HH})/V(\text{RKR})$, for various values of the vibrational quantum number, v , for the $b^3\Pi_u$ state of Cs_2

v	$V(\text{HH})/V(\text{RKR})$	$V(\text{HH})/V(\text{RKR})$
0	1.023	0.976
3	1.059	0.936
6	1.079	0.912
9	1.093	0.894
12	1.106	0.878
15	1.116	0.864
18	1.125	0.851
21	1.133	0.839
24	1.139	0.828
27	1.147	0.819
30	1.153	0.809
33	1.159	0.800
36	1.164	0.792
39	1.169	0.784
42	1.173	0.777
45	1.178	0.770
48	1.182	0.763
50	1.184	0.759

state couples very strongly through spin–orbit interaction with the next higher lying state, the $A^1\Sigma_u^+$ state, which crosses the $b^3\Pi_u$ state. These two crossing states are well illustrated in Fig. 7 of Ref. [56] and Fig. 2.13 of Ref. [57]. The spin–orbit coupling means these states are non-adiabatic. The spin–orbit coupling does not split the ground-state 2S atom but splits the interacting excited state 2P atom into two states: a $^2P_{1/2}$ state (the lower state) and a $^2P_{3/2}$ state.

These two new atomic states lead to two new molecular states in the $\Omega_{g,u}^{(+/-)}$ notation: the $O_u^+(^2P_{1/2})$ and $O_u^+(^2P_{3/2})$ states; see Table III(b), columns 4 and 5, in Ref. [58]. These states do not cross, and they are also shown in the figures referred to above. The crossing of the original states occurs at about 5.8 \AA [57], within the attractive well region of each state. This probably has an effect on the quality of the RKR results.

The value used for D_e in the HH potential for the $b^3\Pi_u$ state, 7051 cm^{-1} [49], is larger than the value obtained by many others: e.g., 7029 cm^{-1} [59], 6775 cm^{-1} [60], 6404 cm^{-1} [61], and $7035.1427 \text{ cm}^{-1}$ [56]. As a test, the value of D_e from Ref. [56] was used in the HH potential instead of the value from Ref. [49]. However, the agreement with the RKR results is slightly worse in this case.

For the $A^1\Sigma_u^+$ state, RKR values are given in Table IV of Ref. [50] for ten values of v . For $R < R_e$, the largest error in the HH potential is 25.7% and the smallest error is 6.2%. For $R > R_e$, the largest error is 7.5% and the smallest error is 0.8%. The average error is 7.4% and the median error is 5.0%. Despite a fairly large error at several values of v , overall the HH potential is reasonably accurate. Since this state has a strong spin–orbit interaction with the $b^3\Pi_u$ state, this may have some effect on

Table 8 Percent contribution of each electronic state to the degeneracy-averaged value of $B''(T)$ as a function of temperature

State	% at 1500 K	% at 9000
$X^1 \Sigma_g^+(1)$	97.1	11.0
$a^3 \Sigma_u^+(1)$	1.9	2.2
$b^3 \Pi_u$	1.0	50.9
$A^1 \Sigma_u^+$	0.0	2.6
$3 \Sigma_g^+$	0.0	10.6
$1 \Sigma_g^+(2)$	0.0	1.0
$B^1 \Pi_u$	0.0	1.8
$1 \Pi_g$	0.0	3.2
$3 \Pi_g$	0.0	0.0
$3 \Sigma_u^+(2)$	0.0	16.8

the quality of the RKR potential energy curve as discussed above. The HH potential for this state predicts a local maximum [62] at approximately 9.5 Å.

RKR/IPA/DPF values are not available for the $3 \Sigma_g^+$ state.

For the $1 \Sigma_g^+(2)$ state, IPA values are given in Table X of Ref. [52] for 50 values of v . For $R < R_e$, the largest error in the HH potential is 21.0% and the smallest error is 0.01%. For $R > R_e$, the largest error is 3.2% and the smallest error is 0.04%. The average error is 4.8% and the median error is 2.4%. Despite fairly large errors at several values of v , overall the HH potential is quite accurate and correctly [52, 63, 64] predicts that this state has a local maximum.

For the $B^1 \Pi_u$ state, RKR values are given in Table 5 of Ref. [53] for 13 values of v . For $R < R_e$, the largest error is 5.1% and the smallest error is 1.6%. For $R > R_e$, the largest error is 4.9% and the smallest error is 1.3%. The average error is 2.1% and the median error is 1.9%. There is another set of RKR values in Table 4 of Ref. [54] for 21 values of v . For $R < R_e$, the largest error is 7.7% and the smallest error is 2.0%. For $R > R_e$, the largest error is 7.0% and the smallest error is 1.3%. The average error is 2.4% and the median error is 2.1%. The HH potential is quite accurate for this state and correctly [54] predicts that it has a local maximum.

For the $1 \Pi_g$ state, IPA values are given in Table XI of Ref. [52] for 36 values of v . For $R < R_e$, the largest error is 8.0% and the smallest error is 1.7%. For $R > R_e$, the largest error is 20.7% and the smallest error is 2.8%. The average error is 10.6% and the median error is 7.9%. The Morse potential is surprisingly accurate despite significant errors at a few values of v .

There are no RKR/IPA/DPF results for the $3 \Pi_g$ state. The Morse results are compared with the theoretical calculations in Table I.(E) in Ref. [28]. Agreement is poor with an average error of 106.3% and a median error of 27.4%. The large difference between the average and median errors is due to a very large error at several small and large R values. Near R_e , errors are of the order of 10% to 15%. Better results could be obtained by fitting the Morse potential to the potential in Ref. [28] but the accuracy of that potential is unknown. As shown in Table 8, this state makes no contribution to $C_p(NI)$.

For the repulsive ${}^3\Sigma_u^+(2)$ state, the average error of the fitted exponential repulsive potential compared to the theoretical calculations in Table I.(E) of Ref. [28] is 10.5% and the median error is 12.1%. This agreement is reasonably good. Again, the accuracy of the theoretical results [28] is difficult to determine.

An exponential repulsive potential for this state is given in Eq. 4 of Ref. [65]. However, the values of V as a function of R range from about eight times to ninety-six times larger than the values obtained from the theoretical potential [28]. The potential in Ref. [65] was obtained by assuming that this repulsive state crosses the $C^1\Pi_u$ state, which dissociates to ${}^2S + {}^2D$ atoms, allowing the $C^1\Pi_u$ state to predissociate [65]. Thus, the theoretical potential [28] appears to have better justification. Figure 7 in Ref. [65] appears to show a shallow minimum and a local maximum for the ${}^3\Sigma_u^+(2)$ state. However, this is a consequence of spin-orbit coupling between the ${}^3\Sigma_u^+(2)$ and $C^1\Pi_u$ states as discussed previously for the $b^3\Pi_u$ and $A^1\Sigma_u^+$ states. Since spin-orbit coupling is not included in the theoretical calculations for the ${}^3\Sigma_u^+(2)$ state [28], this may be a significant source of error.

Table 8 shows the percent contribution of each electronic state of Cs_2 to the degeneracy-averaged value of $B''(T)$, given by Eq. 13, at two values of T . At 1500 K, the lowest value of T at which it is reasonably likely that quantum mechanical effects on $B''(T)$ have “washed out,” the overwhelmingly most important contribution comes from the ground $X^1\Sigma_g^+(1)$ state and it has been shown above that the HH potential gives very good agreement with the RKR/IPA/DPF “experimental” potentials for this state.

Most of the rest of the contribution at 1500 K comes from the first excited $a^3\Sigma_u^+(1)$ state. Since there are no RKR/IPA/DPF calculations for this state, it is necessary to rely on the MLR potential [48] as the standard. The HH potential is in very good agreement with the MLR potential. There is also a small contribution from the $b^3\Pi_u$ state for which agreement between the HH and RKR [49] potentials is not as good but the HH potential is still quite accurate. There is a rough rule of thumb that an error of a factor of two in the potential leads to an error of 20% to 40% in the calculation of transport properties [66]; i.e., the integrations over the potential required to calculate the transport properties “wash out” some of the error in the potential. It is reasonable to assume that something similar happens upon integrating over the potential to calculate $B''(T)$ and $C_p(NI)$. Thus, it can be concluded that at lower temperatures, but temperatures above which quantum mechanical effects are important, these calculations of $C_p(NI)$ are quite accurate.

At higher temperatures, the situation is different. At 9000 K, the highest temperature at which $C_p(NI)$ is $0.001 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ or greater, the $b^3\Pi_u$, ${}^3\Sigma_g^+$, and ${}^3\Sigma_u^+(2)$ states make more than 78% of the contribution to the degeneracy-averaged value of $B''(T)$. Again, the HH potential for the $b^3\Pi_u$ is reasonably accurate [49] but not as accurate as one might like. The accuracy of the ${}^3\Sigma_g^+$ potential cannot be determined since there are no RKR/IPA/DPF results for this state. The accuracy of the exponential repulsive potential for the ${}^3\Sigma_u^+(2)$ state is difficult to determine since the fit is to a theoretical potential [28] of unknown accuracy. Of course, if $C_p(NI)$ is nearly zero at 9000 K, then the accuracy of the representation of the states is unimportant. Table 4 shows that $C_p(NI)$ falls off rapidly with T , even at lower temperatures where the calculation

is quite reliable. Thus, errors in the potential at higher temperatures are probably not very important.

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