Calculations of Long Range Potential Wells for Cs_2 Molecules below the Cs (*n*s, $n \geq 8$) + Cs (6s) Asymptotes[†]

Bradford Normand, Warren T. Zemke,[‡] Robin Côté, Marin Pichler,[§] and William C. Stwalley*,[||]

Department of Physics, University of Connecticut, Storrs, Connecticut 06269-3046

Received: February 26, 2002; In Final Form: May 16, 2002

The weakly bound long range potential curves between a highly excited Cs* (*n*s, $8 \leq n \leq 20$) atom and a ground state Cs atom are calculated using simple but reasonably accurate models for dispersion and exchange interactions. Such curves will help in the design of experiments to observe corresponding spectra.

I. Introduction

Recently, weakly bound long range levels have been observed near highly excited asymptotes of the $^{39}K_2$ molecule using optical−optical double resonance photoassociative spectroscopy of ultracold atoms.[1,2] Similar experiments are underway in our group on the Cs_2 molecule. For this reason, we have carried out theoretical calculations to estimate the long range potential energy curves which give rise to these weakly bound long-range levels for the case of Cs_2 to help in experiment selection. Later, we hope to extend these results to other alkali pairs.

Our theoretical calculations include two terms, an estimate of long-range dispersion using the approach of Proctor and Stwalley[3,4] and an estimate of long-range exchange using the approach of Smirnov and Chibisov.[5] For ground state atoms, these two terms are found to agree well with experimentally determined potentials for Li_2,[6] Na_2,[7] K_2[8,9] and NaK[10] (see also refs 11 and 12).

Our model calculation uses the equation

$$V(R) = -V_{EX}(R) + V_{DISP}(R) \tag{1}$$

to estimate the potential of the weakly bound van der Waals wells at the Cs* (*n*s) + Cs (6s) asymptotes. Note that both V_{EX} and V_{DISP} are negative, so the first term is repulsive and the second attractive, corresponding to the antisymmetrical (triplet) state (see section III). Details of the calculations of the dispersion and exchange terms are given in sections II and III, respectively. The results are presented in section IV with a discussion of the scaling with principal quantum number *n* and the prospects for observation in future experiments.

Note that a similar calculation[13] was previously carried out for the K* (6s) + K (4s) asymptote of K_2, which agreed well with observations,[1] e.g., well depth ∼10% shallower than observed. However, that work and the details of the calculation have not been published and the work is apparently not continuing. Recently, $V_{DISP}(R)$ was calculated for Rb* (*n*p) + Rb* (*n*p), and the existence of long-range potential wells was predicted.[14]

II. Long-Range Dispersion

The long-range interaction between two different neutral S-state atoms is well-known to be expressible by the asymptotic expansion:

$$V_{DISP} = -C_6R^{-6} - C_8R^{-8} - C_{10}R^{-10} - ... \tag{2}$$

Proctor and Stwalley[3,4] developed simple expressions for these C_n coefficients when the excitation frequencies of one atom are significantly less than the excitation frequencies of the second atom, i.e., when the first atom has a much greater polarizability than the second atom. For example, the alkali atoms have much lower frequencies and higher polarizabilities than the inert gas atoms. In particular, these expressions include analytical results for multipole oscillator strength sums for a more polarizable hydrogen-like atom, here the excited Cs* (*n*s) atom with $n \geq 8$. We have not considered $n = 7$ because more accurate results are available for $n = 7$ and 8.[15] The specific approximations involved for each C_n term are summarized in ref 4, i.e., those terms proportional to the ground-state Cs polarizability.[16] We believe these calculations should be accurate to less than 10% for $n = 8$ and significantly better for higher *n*. In agreement with this estimate, the C_6, C_8, and C_{10} values in atomic units calculated based on ref 4 are $2.42 \times 10^5 \equiv 2.42$ (5), 2.76 (8), and 3.45 (11) compared to the values of 2.34 (5), 3.04 (8), and 3.76 (11) in ref 15. Our values of C_n for $8 \leq n \leq 20$ are given in Table 1. Note that C_6, C_8, and C_{10} scale approximately as $(n^*)^4$, $(n^*)^8$, and $(n^*)^{12}$ respectively, where $n^* = [2(E_\infty - E_n)]^{-1/2}$, as shown in eqs 12a−c of ref 4.

However, the dispersion interactions between an excited cesium atom and a ground state cesium atom must be slightly modified to take into account the possibility of exchange of excitation between the otherwise identical cesium atoms. In terms of the notation of Marinescu and Dalgarno,[15] we must use degeneracy-adapted basis functions $\Psi_{\beta}^{(0)} = 1/(2)^{1/2} [\varphi_{n_g n_e} + \beta\varphi_{n_e n_g}]$ for atoms in states $\{nlm\} = \{n_g 00\}$ and $\{n_e 00\}$ where the coefficient $\beta = \pm 1$ is determined by the state

[†] Part of the special issue "Donald Setser Festschrift".

* To whom correspondence should be addressed.

[‡] Permanent address: Department of Chemistry, Wartburg College, Waverly, IA 50677.

[§] Present address: Department of Physics, Rice University, Houston, TX 77251.

[||] Also Department of Chemistry and Institute of Materials Science.

10.1021/jp020518k CCC: $22.00
Published on Web 07/04/2002

TABLE 1: Long Range Dispersion Coefficients C_6, C_8, and C_{10} (in Atomic Units) for Excited Cs* (*ns*) Atoms Interacting with Ground State Cs (6s) Atoms for $8 \leq n \leq 20$

n	C_6	C_8	C_{10}	n	C_6	C_8	C_{10}
8	2.42 (5)[a]	2.76 (8)	3.45 (11)	15	1.45 (7)	9.93 (11)	6.66 (16)
9	5.98 (5)	1.73 (9)	5.19 (12)	16	2.05 (7)	1.99 (12)	1.89 (17)
10	1.25 (6)	7.59 (9)	4.66 (13)	17	2.83 (7)	3.79 (12)	4.94 (17)
11	2.34 (6)	2.62 (10)	2.95 (14)	18	3.81 (7)	6.86 (12)	1.20 (18)
12	4.00 (6)	7.65 (10)	1.45 (15)	19	5.03 (7)	1.19 (13)	2.75 (18)
13	6.45 (6)	1.98 (11)	6.01 (15)	20	6.51 (7)	2.00 (13)	5.96 (18)
14	9.86 (6)	4.62 (11)	2.13 (16)				

[a] 2.42 (5) = 2.42×10^5.

TABLE 2: Hund's Case a (c) States Arising at Cs (*ns*) + Cs (6s) Asymptotes (n = 7)

symmetry			parameter	
a	c	parity p	spin σ[a]	β[15]
$^1\Sigma_g^+$	(0_g^+)	+1	+1	+1
$^1\Sigma_u^+$	(0_u^+)	−1	+1	−1
$^3\Sigma_g^+$	$(0_g^-, 1_g)$	+1	−1	−1
$^3\Sigma_u^+$	$(0_u^-, 1_u)$	−1	−1	+1

[a] $\sigma = +1$ for singlet and $\sigma = -1$ for triplet spin states.

symmetries as shown in Table 2. In our case, the ground state is $n_g = 6$ and the excited state is $n_e \geq 8$.

Using such basis functions, one finds the dispersion coefficients

$$C_6^{\beta} = C_6 + \beta C_6' \tag{3}$$

where

$$C_6 = \sum_{nm} \frac{(nl|r|n_g0)^2(ml|r|n_e0)^2}{E_{nl} + E_{ml} - E_{n_e0} - E_{n_g0}} \tag{4}$$

and

$$C_6' = \sum_{nm} \frac{(n_g0|r|nl)(nl|r|n_e0)(n_g0|r|ml)(ml|r|n_e0)}{E_{nl} + E_{ml} - E_{n_e0} - E_{n_g0}} \tag{5}$$

Here, $(nl|r|n'l')$ represents a radial matrix element.[15]

Similarly

$$C_8^{\beta} = C_8 + \beta C_8' \tag{6}$$

and

$$C_{10}^{\beta} = C_{10} + \beta C_{10}' \tag{7}$$

as detailed in ref 15.

However, the ratios C_6'/C_6, C_8'/C_8, and C_{10}'/C_{10} are most significant when discussing the pair of atoms Cs(6s) and Cs*(*ns*) where $n - 6 = 1$; for example, when the quantum number $n = 7$, the three ratios equal 0.34, 0.18, and 0.11, respectively.[15] When $n = 8$ (i.e., $n - 6 = 2$), the three ratios equal −0.019, 0.030, and −0.001, respectively,[15] and when $n \geq 9$, the ratios are negligible. Therefore, in what follows, all C_n' terms are neglected in eqs 3, 6, and 7 because we believe they are smaller than the uncertainties in the C_n values.

III. Long-Range Exchange

The long-range interaction between two different neutral S-state atoms A and B has been estimated by Smirnov and Chibisov:[5]

$$V_{EX}(R) = -\frac{1}{2}J(\alpha,\beta,R)R^{[(2/\alpha)+(2/\beta)-(1/(\alpha+\beta))-1]}e^{-(\alpha+\beta)R} \tag{8}$$

where $\alpha = (n_A^*)^{-1}$, $\beta = (n_B^*)^{-1}$, and

$$J(\alpha,\beta,R) = A^2B^2 2^{[-2-(2/(\alpha+\beta))]}\Gamma\left(\frac{1}{\alpha+\beta}\right)\left(\frac{2}{\alpha+\beta}\right)^{[2+(1/(\alpha+\beta))]} \times \{\gamma(\alpha,\beta)f(\alpha,\beta,R) + \gamma(\beta,\alpha)f(\beta,\alpha,R)\} \tag{9}$$

where the asymptotic radial atomic wave function for atom A is

$$\varphi_A(r) = Ar^{(1/\alpha)-1}e^{-\alpha r} \tag{10}$$

(and likewise for atom B),

$$\gamma(\alpha,\beta) = \left(\frac{\alpha+\beta}{2\beta}\right)^{[(2/\alpha)-(2/(\alpha+\beta))]} \tag{11}$$

and

$$f(\alpha,\beta,R) = \int_0^1 dy\, e^{[\{(y-1)/\beta\} + R(\beta-\alpha)y]}(1-y)^{[(2/\beta)-(1/(\alpha+\beta))]} (1+y)^{[(2/\alpha)-(2/\beta)+(1/(\alpha+\beta))]}\left[1 + \left(\frac{\beta-\alpha}{\beta+\alpha}\right)y\right]^{[-2-(1/(\alpha+\beta))]} \tag{12}$$

When $\alpha = \beta$, the function $J(\alpha,\beta,R)$ becomes independent of R. The values of A and B are obtained using the approach of Bardsley et al.[17]. The calculation of V_{EX} was checked by comparison with the results of Côté et al.[18]

With regard to the states in Table 2, eq 1 applies to the antisymmetric (triplet) states, whereas an attractive term $+V_{EX}$ corresponds to the symmetric (singlet) states, which we do not consider here because the potential wells are not restricted to large internuclear distances. The weakly bound long range states are thus $^3\Sigma_g^+$ and $^3\Sigma_u^+$, which correspond to 0_g^- and 1_g and 0_u^- and 1_u states, respectively, in the limit of very large R.

IV. Results and Discussion

The estimates of V_{EX} and V_{DISP} discussed above allow for ready calculation of the long-range potential wells for a wide range of n. Our results are shown for n = 8, 12, 16, and 20 in Figure 1. Note the narrowing of the potential well as n increases.

We also note here that $V(R)$ given by eq 1 goes to $-\infty$ as $R \rightarrow 0$ because the dispersion term has not been damped. However, there is a large maximum (for each n) at positive potential energy between the long-range well and the collapse to $V(0) = -\infty$ at short distance. The results reported here rely only on the potential well outside this maximum.

The values of well depth ϵ (in cm^{-1}), potential minimum separation R_m (in Bohr radii a_0 (atomic units)), and the quantity ϵR_m^2 (units of cm^{-1} a_o^2) are given in Table 3. It is clear that ϵ is rapidly decreasing with increasing n, whereas R_m is increasing modestly. We have calculated the number of bound vibrational levels in these shallow long-range wells for n = 8 and 9, finding 21 and 14 vibrational levels, respectively.

Based on the Bohr-Sommerfeld quantization condition,[19] the product ϵR_m^2 nearly completely determines the vibrational quantum number at dissociation, v_D, and hence the number of rotationless or s-wave bound states of our long-range potentials. For example, with a given value $(\epsilon R_m^2)_0$, the zero-point level is barely bound, and $v_D + {}^1/_2 \gtrsim {}^1/_2$. Similarly, for $\epsilon R_m^2 = 3(\epsilon R_m^2)_0$, $v_D + {}^1/_2 \gtrsim {}^3/_2$ and $v = 1$ is barely bound, and so on; with $\epsilon R_m^2 = N(\epsilon R_m^2)_0$, $v_D + {}^1/_2 \gtrsim N/2$ and $v = (N-1)/2$ is the

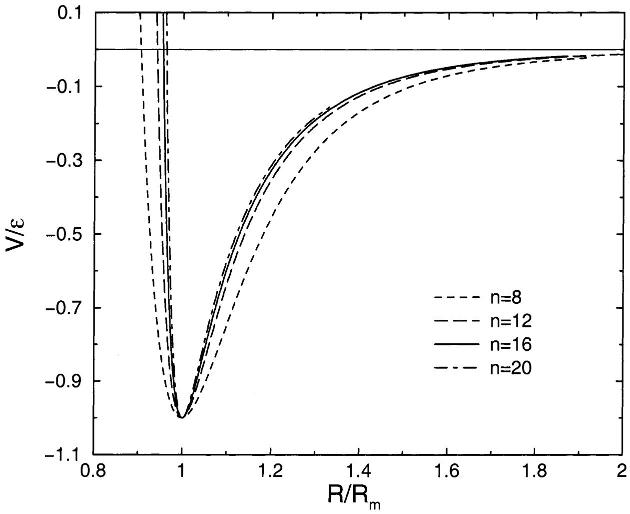

Figure 1. Potential energy curves (in units of the well depth ϵ and potential minimum R_m) for the near degenerate $^3\Sigma_g^+$ (O_g^-, 1_g) and $^3\Sigma_u^+$ (O_u^-, 1_u) states near the Cs* (ns) + Cs (6s) asymptotes for $n = 8$, 12, 16, and 20.

TABLE 3: Weakly Bound Long Range Potential Wells Corresponding to $^3\Sigma_g^+$ (O_g^-, 1_g) and $^3\Sigma_u^+$ (O_u^-, 1_u) States which Are Very Nearly Degenerate near the Cs* (*n*s) + Cs (6s) Asymptotes and Correspond to the Following Potential Well Depths, ϵ (in cm^{-1}), and Potential Minima, R_m (in a_0), and ϵR_m^2 (in cm^{-1} a_0^2)

n	ϵ (cm^{-1})	R_m (a_o)	ϵR_m^2 ($cm^{-1}a_0^2$)
8	5.21	46.9	11460.0
9	0.926	74.5	5139.5
10	0.227	108	2647.7
11	6.96 (−2)	147	1504.0
12	2.51 (−2)	192	925.3
13	1.02 (−2)	242	597.4
14	4.56 (−3)	299	407.7
15	2.14 (−3)	362	280.4
16	1.14 (−3)	428	208.8
17	6.31 (−4)	500	157.7
18	3.54 (−4)	579	118.7
19	2.09 (−4)	663	91.9
20	1.28 (−4)	752	72.4

highest level (i.e., barely bound). From the results of the potentials with $n = 8$ and 9, we obtain $(\epsilon R_m^2)_0 \approx 279$ and 190, respectively. From Table 3, we estimate that the $n = 16$ asymptotic states with $\epsilon R_m^2 \approx 209$ are probably the highest *n* states to support a zero-point level. For this reason, we have terminated our calculations at $n = 20$, with the higher *n* asymptotic states probably not supporting any bound levels.

We have also applied these potentials to calculate Franck−Condon factors from the well-known 0_g^- state[20] at the Cs* ($6p_{3/2}$) + Cs (6s) asymptote. We predict strong Franck−Condon factors (>0.1) going from high levels of the 0_g^- state at the $6p_{3/2}$ + 6s asymptote to the 0_u^- and 1_u states at the 8s + 6s and the 9s + 6s asymptotes. For example, to reach $v' = 0$ levels in the 0_u^- and 1_u states at 8s + 6s, one should excite $v'' = 48$, 49, 50, or 51, whereas for the 0_u^- and 1_u states at 9s + 6s, one should excite $v'' = 78$, 79, 80 or 81. Such predictions are invaluable in finding the previously unobserved weakly bound long range states.

Acknowledgment. Helpful discussions with Drs. M. Marinescu and H. Wang are gratefully acknowledged, as is support received from the National Science Foundation. We thank Professor Donald Setser for his many contributions and insights in Chemical Physics/Physical Chemistry.

References and Notes

(1) Wang, H.; Wang, X. T.; Gould, P. L.; Stwalley, W. C. *J. Chem. Phys.* **1997**, *106*, 7899.
(2) Stwalley, W. C.; Wang, H. *J. Mol. Spectrosc.* **1999**, *195*, 194.
(3) Proctor, T. R.; Stwalley, W. C. *J. Chem. Phys.* **1977**, *66*, 2063.
(4) Proctor, T. R.; Stwalley, W. C. *Mol. Phys.* **1979**, *37*, 1969.
(5) Smirnov, B. M.; Chibisov, M. I. *Sov. Phys. JETP* **1965**, *21*, 624.
(6) Zemke, W. T.; Stwalley, W. C. *J. Phys. Chem.* **1993**, *97*, 2053.
(7) Zemke, W. T.; Stwalley, W. C. *J. Chem. Phys.* **1994**, *100*, 2661.
(8) Zemke, W. T.; Tsai, C.-C.; Stwalley, W. C. *J. Chem. Phys.* **1994**, *101*, 10382.
(9) Zhao, G.; Zemke, W. T.; Kim, J. T.; Ji, B.; Wang, H.; Bahns, J. T.; Stwalley, W. C.; Li, L.; Lyyra, A. M.; Amiot, C. *J. Chem. Phys.* **1996**, *105*, 6192.
(10) Zemke, W. T.; Stwalley, W. C. *J. Chem. Phys.* **1999**, *111*, 4956.
(11) Zemke, W. T.; Stwalley, W. C. *J. Chem. Phys.* **1999**, *111*, 4962.
(12) Zemke, W. T.; Stwalley, W. C. *J. Chem. Phys.* **2001**, *114*, 10811.
(13) Marinescu, M. Private communication, 1997.
(14) Boisseau, C.; Simbotin, I.; Côté, R. *Phys. Rev. Lett.* **2002**, *88*, 133004.
(15) Marinescu, M.; Dalgarno, A. *Phys. Rev. A* **1995**, *52*, 311.
(16) Molof, R. W.; Schwartz, H. L.; Miller, T. M.; Bederson, B. *Phys. Rev. A* **1974**, *10*, 1131.
(17) Bardsley, J. N.; Holstein, T.; Junker, B. R.; Sinha, S. *Phys. Rev. A* **1975**, *11*, 1911.
(18) Côté, R.; Jamieson, M. J.; Yan, Z.-C.; Geum, N.; Jeung, G.-H.; Dalgarno, A. *Phys. Rev. Lett.* **2000**, *84*, 2806.
(19) Uang, Y. H.; Stwalley, W. C. *J. Chem. Phys.* **1982**, *76*, 5069.
(20) Fioretti, A.; Comparat, D.; Drag, C.; Amiot, C.; Dulieu, O.; Masnou-Seeuws, F.; Pillet, P. *Eur. Phys. J. D* **1999**, *5*, 389.