High-quality interatomic potential for Li+ · He

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Abstract

CCSD(T)/aug-cc-pVQZ and CCSD(T)/aug-cc-pV5Z methods have been employed to obtain accurate interatomic potentials for Li+ · He, from which spectroscopic parameters are derived. A potential is presented using the larger basis set consisting of 91 points ($R \geqslant 1.3$ Å). An accurate value for the long-range D_4 parameter could be obtained from the potential, but it was not possible to extract higher D_n terms. Since accurate values for D_n ($n = 4$, 6, 7 and 8) could be derived from literature data, these parameters were fixed (and damped), allowing the short-range potential to be fitted accurately to a Born–Mayer potential. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction and background

The M+ · Rg complexes, where M is an alkali metal and Rg is an inert gas, are prototypes of a closed-shell, singly-charged cation interacting with a closed-shell atom. As such, they have been studied by a variety of experimental and theoretical methods, with such studies yielding information on the short- and long-range portions of the potential energy curve (see, for example, [1,2], and references cited therein). The interaction potentials of these species are important for calculating the transport properties of the cations in a bath of the inert gas, which is of consequence in understanding the mobility of ions in plasma discharges and the far reaches of the Earth's atmosphere.

The purpose of the present study is to calculate an accurate potential for the smallest such complex, Li+ · He, at the CCSD(T) level of theory employing basis sets of quadruple- and quintuple-ζ quality. The most accurate curve available to date for this system does not employ a 'standard', readily available theoretical method, and hence comparison of like systems is difficult. In addition, the number of points that have been presented in previous work is not large, and a more-complete curve would increase the accuracy of any fitted potential. Finally, we wished to investigate the accuracy to which both short- and long-range intermolecular parameters could be extracted from the curve.

2. Theoretical methods

The interatomic potential for this closed-shell $^1\Sigma^+$ species was computed at the CCSD(T) level of

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theory. Both the aug-cc-pVQZ and aug-cc-pV5Z basis sets were employed, with all electrons being correlated; spherical harmonics were employed. (For Li^+, the cc-pVXZ basis sets were employed, and extended by one diffuse function of each type in an even-tempered fashion.) Originally 43 energies were calculated ($R = 1.3$–25 Å) using both basis sets with basis set superposition error (BSSE) being accounted for in a point-by-point manner by employing the full counterpoise correction of Boys and Bernardi [3]. Thereafter the aug-cc-pV5Z set was increased to 91 energies at intermolecular separations from 1.3–40.0 Å – this set was used for all subsequent analyses. All energy calculations were performed employing MOLPRO [4].

From this interatomic potential, the calculated equilibrium interatomic separation, the dissociation energy and rovibrational energy levels were derived using LeRoy's LEVEL program [5].

3. Comparison of the potential with previous results

Unless stated otherwise, atomic units are employed hereafter.

3.1. Equilibrium separation and dissociation energy

Using the set of 43 energies, R_e was calculated to be 1.904 Å and 1.897 Å using the aug-cc-pVQZ and aug-cc-pV5Z basis sets, respectively. These values compare favourably with the most accurate of previous calculations (a summary of values available up until 1994 has been given by Bililign et al. [6]). We note especially the more recent values of 1.95 Å obtained at the QCISD(T) level [6] using a 6-311G* basis set augmented with three p and three d functions on He and Li, respectively,

and the very recent calculation of 1.894 Å obtained using the extended group function model [7] – this is probably the most accurate calculation to date. It is clear that an extended basis set is required to obtain an accurate bond length in this species. Prior to these studies, the most reliable potentials were the CEPA and CEPA2 potentials of Hariharan and Staemmler [8], and Senff and Burton [9] who obtained R_e values of 1.892 and 1.894 Å, respectively. Our results, together with those of the best of the previous calculations, establish $R_e(Li^+ \cdot He) = 1.896 \pm 0.002$ Å.

The calculated dissociation energies, D_e from the present work are 637.6 and 649.2 cm^{-1} using the aug-cc-pVQZ and aug-cc-pV5Z basis sets, respectively. These values compare to previous values of 546 cm^{-1} ([6]), 653 cm^{-1} ([7]), 649 cm^{-1} ([8]) and 653 cm^{-1} ([9]). Our values, together with the best previous ones establish $D_e(Li^+ \cdot He) = 652 \pm 5$ cm^{-1}.

The close agreement of the above results also establishes that the CCSD(T)/aug-cc-pV5Z level of theory is (as expected) very accurate, and consequently that a derived interatomic potential should be of high quality.

3.2. The interatomic potential and spectroscopy of $Li^+ \cdot He$

The calculated spectroscopic constants using the two sets of 43 points are given in Tables 1 and 2. As may be seen, the results are very similar, indicating that saturation of the basis set has occurred.

Table 3 contains the interatomic potential for $Li^+ \cdot He$ consisting of the set of 91 calculated energies using the aug-cc-pV5Z basis set. The energies are given in cm^{-1}, with respect to the

Table 1
Calculated rovibrational spectroscopic constants for $^7Li \cdot {}^4He$ at the CCSD(T)/aug-cc-pVQZ level of theory

v	$E(v,0) - E(0,0)$	B_v (cm^{-1})	$D_v \times 10^4$ (cm^{-1})	$-H_v \times 10^7$ (cm^{-1})
0	0	1.698	3.164	1.178
1	205.702	1.433	4.828	2.666
2	348.882	1.142	6.601	5.949
3	437.320	0.837	9.137	13.208

$E_{rot,v} = B_v J(J+1) - D_v J^2 (J+1)^2 + H_v J^3 (J+1)^3$.

Table 2
Calculated rovibrational spectroscopic constants for ^{7}Li · ^{4}He at the CCSD(T)/aug-cc-pV5Z level of theory

v	$E(v,0) - E(0,0)$	B_v (cm^{-1})	$D_v \times 10^4$ (cm^{-1})	$-H_v \times 10^7$ (cm^{-1})
0	0	1.713	3.681	1.160
1	208.579	1.446	4.807	2.604
2	354.236	1.155	6.556	5.817
3	444.144	0.850	9.041	12.642

Table 3
Calculated interatomic curve for Li$^+$ · He at the CCSD(T)/aug-cc-pV5Z level of theory

R (Å)	$V(R)$ (cm^{-1})	R (Å)	$V(R)$ (cm^{-1})	R (Å)	$V(R)$ (cm^{-1})
1.300	3950.760	4.000	−49.004	15.000	−0.234
1.325	3292.485	4.100	−44.236	17.000	−0.141
1.35	2717.234	4.250	−38.137	18.000	−0.112
1.375	2215.396	4.400	−33.069	20.000	−0.073
1.400	1778.438	4.700	−25.254	21.000	−0.059
1.425	1398.781	5.000	−19.638	22.000	−0.049
1.45	1069.701	5.200	−16.751	24.000	−0.034
1.475	785.227	5.400	−14.377	25.000	−0.029
1.500	540.062	5.600	−12.410	27.000	−0.021
1.525	329.505	5.800	−10.768	30.000	−0.013
1.55	149.389	6.000	−9.388	33.000	−0.008
1.575	−3.983	6.200	−8.222	35.000	−0.006
1.600	−133.887	6.300	−7.707	40.000	−0.003
1.625	−243.226	6.400	−7.231		
1.65	−334.569	6.600	−6.385		
1.675	−410.191	6.800	−5.659		
1.700	−472.106	7.000	−5.033		
1.800	−615.283	7.200	−4.491		
1.900	−649.134	7.400	−4.021		
2.000	−625.127	7.600	−3.611		
2.100	−573.546	7.800	−3.251		
2.200	−511.656	8.000	−2.936		
2.300	−448.908	8.200	−2.658		
2.400	−390.078	8.400	−2.412		
2.500	−337.245	8.600	−2.194		
2.600	−290.987	8.800	−2.000		
2.700	−251.101	9.000	−1.827		
2.800	−217.015	9.200	−1.672		
2.900	−188.026	9.400	−1.534		
3.000	−163.413	9.600	−1.409		
3.100	−142.529	9.800	−1.297		
3.200	−124.778	10.000	−1.196		
3.300	−109.653	10.500	−0.983		
3.400	−96.723	11.000	−0.815		
3.500	−85.632	11.500	−0.682		
3.600	−76.083	12.000	−0.575		
3.700	−67.830	12.500	−0.488		
3.800	−60.674	13.000	−0.416		
3.900	−54.445	14.000	−0.309		

Energy given relative to the dissociation limit: $D_e = -649.155$ cm^{-1}.

dissociation limit, although atomic units are employed in the figures, since the relevant equations have all been used in atomic units. The complete set of rovibrational levels were calculated employing LEVEL, and the results are given in Table 4; these results should prove useful in the analysis of future microwave and/or infrared spectra.

3.3. Fitting the interatomic parameters

The interatomic potential between a closed-shell metal cation and a rare gas atom is generally expressed as the sum of a repulsion potential and the attractive dispersion and induction terms. The repulsion term is often taken, for simplicity, as a Born–Mayer potential

$$V_{\text{rep}}(R) = A e^{-bR} \tag{1}$$

with the attractive induction and dispersion terms being expressed as a sum:

$$V_{\text{disp,ind}}(R) = -\sum f_n(R) \frac{D_n}{R^r}, \tag{2}$$

where the f_n are damping factors, to account for the charge overlap that occurs as the atoms approach closely. The form of the damping factors

has been discussed in detail by Tang and Toennies [10–12] and Stone [13]. We employ the Tang–Toennies damping factors [12] herein:

$$f_n(R) = 1 - \exp(-bR) \sum_{k=0}^{n} \frac{[bR]^k}{k!}, \tag{3}$$

where b is generally taken as being the same exponent b obtained from a fit of the repulsive region of the curve to a Born–Mayer potential. It may be seen that $f_n(R) \to 1$ as $R \to \infty$, and that the Born–Mayer potential $\to 0$ as $R \to \infty$, and so at long range the interatomic (attractive) potential may be expressed as the leading term of Eq. (2):

$$V_{\text{very long range}}(R) = -D_4/R^4. \tag{4}$$

Consequently, a plot of the interaction energy versus $-1/R^4$ should produce a linear plot for sufficiently long R, with the slope equalling D_4; such a plot is shown in Fig. 1 and yields $D_4 = 0.693$ for the CCSD(T)/aug-cc-pV5Z data. (The range of R employed here was $R = 10$–40 Å, and the fit was forced through the origin.)

The D_n are related to the polarizabilities and dispersion coefficients in the following way (see Maroulis and Thakkar [14,15] for a discussion of the dispersion terms):

Table 4
The calculated bound rovibrational energy levels of Li$^+$–He (in cm^{-1}); CCSD(T)/aug-cc-pV5Z level of theory

^{7}Li$^+$–^{4}He

J	$v = 0$	$v = 1$	$v = 2$	$v = 3$	$v = 4$	$v = 5$	$v = 6$	$v = 7$
0	−519.975	−311.396	−165.739	−75.323	−27.55	−7.191	−0.925	−0.007
1	−516.551	−308.506	−163.431	−73.627	−26.446	−6.59	−0.699	
2	−509.712	−302.737	−158.831	−70.258	−24.266	−5.427	−0.299	
3	−499.476	−294.113	−151.971	−65.259	−21.074	−3.784		
4	−485.869	−282.669	−142.901	−58.702	−16.965	−1.803		
5	−468.929	−268.454	−131.687	−50.683	−12.087			
6	−448.701	−251.529	−118.421	−41.338	−6.65			
7	−425.241	−231.973	−103.214	−30.845	−0.993			
8	−398.616	−209.878	−86.211	−19.446				
9	−368.907	−185.359	−67.592	−7.491				
10	−336.206	−158.552	−47.592					
11	−300.618	−129.622	−26.52					
12	−262.269	−98.77	−4.819					
13	−221.302	−66.248						
14	−177.883	−32.382						
15	−132.212							
16	−84.524							
17	−35.115							

Energies are given with respect to the dissociation limit ($D_e = -649.155$ cm^{-1}).
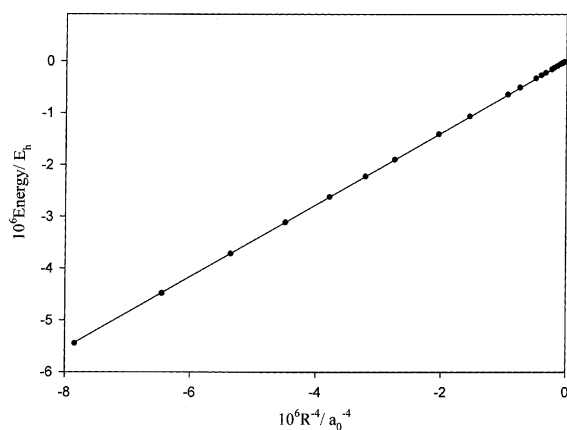
Fig. 1. Graph of energy $= -D_4 R^{-4}$ ($R = 10–40$ Å).

$$D_4 = \alpha_1/2, \tag{5}$$
$$D_6 = \alpha_2/2 + C_6, \tag{6}$$
$$D_7 = -B/2,$$
$$D_8 = \alpha_3/2 + \gamma/24 + C_8, \tag{7}$$

where α_1 is the static dipolar polarizability, α_2 the static quadrupolar polarizability, and α_3 is the static octupolar polarizabilty; B and γ are the dipole–dipole–quadrupole and second dipole hyperpolarizabilities, respectively. The D_4 value derived from the graph in Fig. 1 gives $\alpha_1 = 1.386$ for He, which is very close to the 'exact' value of 1.383192 [16–18] (our value is also in excellent agreement with the ab initio values obtained by Rice et al. [19] and the results of perturbation theory from Thakkar [20]). The small difference is probably due to the combined effects of the other terms at long R, the damping factor, and the small inaccuracies remaining in the ab initio treatment.

A fit of the medium–long range portion of the potential energy curve is not as easy as might be expected – a point made in our previous work on $Na^+ \cdot Rg$ (Rg = He, Ne, Ar) [21]. The reason is that the fit is quite sensitive to the range of R which is included. Many attempts were made in the present work to extract a value for D_6, first by fitting various ranges of the potential, and by employing variants of the equations (multiplying through by R^4 and R^6); but it appears that, for $Li^+ \cdot$ He at least, there is no region where D_6 is

dominant enough to ignore the repulsive potential, the damping factors and the higher order terms.

Eq. (6) shows that there are two contributions to D_6: α_2 and C_6. The quadrupolar polarizability of He, α_2, has been calculated by a number of workers, with Thakkar [20] having a summary. There appears to be a close agreement between all values, supporting the statement [22] that the accuracy of α_2 is of the order of a few percent, with $\alpha_2 = 2.4451$, the most recent value appearing to be that of Bishop and Pipin [17]. In addition, there appears to be a reliable C_6 value of 0.298 obtained from combination rules [12], which agrees well with previous data cited in [12] (although values of C_6 as high as 0.34 have been reported). In addition, relatively reliable values for α_3, γ, B and C_8 seem to be available. We therefore decided to calculate D_4, D_6 and D_8 from these values and to fix them; the data employed are summarized in Table 5. Calculation of the long-range region using these parameters, and comparison with the calculated curve showed the agreement was very good (see below). We then least-squares fitted the portion of the potential energy curve between 1.3 and 6 Å to the sum of the repulsive (Eq. (1)) and attractive terms (Eq. (2), first terms) including the damping factors (we note that fitting the whole curve between 1.3 and 40 Å, as expected, had no observable effect on the fitted short-range parameters).

Slight difference in the values of A and b were apparent, depending on the lowest R value included in the least-squares fit. Including the points

Table 5
Literature values for interatomic potential parameters employed to calculated D_n ($n = 4–8$)

Parameter	Value (a.u.)
α_1	1.383192[a]
α_2	2.4451[a]
α_3	10.6204[a]
γ	43.104[a]
B	−7.3267[a]
C_6	0.298[b]
C_8	1.98[b]

[a] From [17].
[b] Selected from values presented in [12].

1.3–1.38 Å slightly favoured the repulsive region i.e. the curve was a better fit in that region than around the minimum, whereas fitting the points from 1.5 Å onwards was clearly favouring the attractive region of the potential. As a compromise, we took the range 1.4–40 Å, which led to $A = 20.8682$; $b = 2.554$. Fig. 2 displays the ab initio points calculated in the present work and the best fitted curve. Also shown are calculated curves obtained with the same D_4, D_6, D_7 and D_8 terms as used herein, but A and b values as reported by Ahlrichs et al. [12] and Fowler and Hutson [23]. These two previously reported sets of Born–Mayer parameters do not appear to describe the region $<4a_0$ as well as those derived herein, which is perhaps unsurprising, since Fowler and Hutson only employed the SCF method, and Ahlrichs et al. only used the first order SCF energy. No account was taken of correlation energy in the short-range region, and nor was BSSE allowed for – both may be expected to have an effect when the atoms are close together where the electrons are in close proximity, and the orbitals on each centre overlap.

We also attempted to determine the Born–Mayer b parameter separately from the b parameter in the Tang–Toennies damping functions, but it was clear from the statistical tests that the latter was not very well determined from this fit. Our conclusion is that only one b parameter should be considered – the normal procedure. Note that the Tang–Toennies factors are not the only such factors available, but appear to perform adequately; in addition, it is worth emphasising that they do not have the correct behaviour as $R \to 0$, since they completely damp out the dispersive and inductive energies, whereas in fact these should tend towards the correlation energy of the united atom (see [13]).

In Fig. 3, we show the cumulative effect of adding in the various portions of the potential. What is immediately apparent here, is that the repulsive potential has a significant effect until ca $8a_0$, while the D_n ($n \geqslant 6$) terms contribute significantly until ca $6a_0$. This gives some indication as to why it was not possible to extract D_6 from this potential: there is no region in which D_6 dominates the potential enough to be determined independently of other parameters. It is clear that the extraction of D_n parameters and the Born–Mayer potential parameters from an ab initio potential energy curve is not a trivial exercise (except for D_4), and may not always be possible; however, it is fair to say that data required to describe the attractive region of the potentials are becoming available via both experimental and theoretical
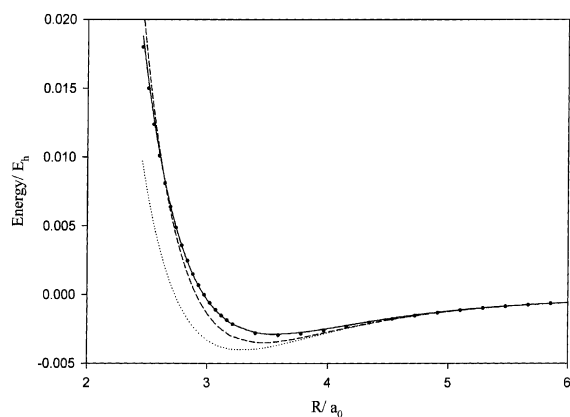

Fig. 2. Graph showing the calculated CCSD(T)/aug-cc-pV5Z energies as a function of R. The points are the results of the ab initio calculations. The solid line is the fitted potential fixing D_n ($n = 4$–8) as explained in the text, and fitting the Born–Mayer parameters, A and b; the dashed line employs the same D_n, but uses A and b from [23]; the dotted line employed A and b from [12].
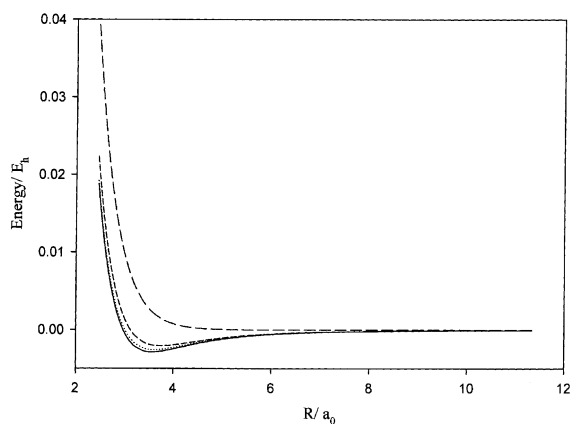

Fig. 3. Graph showing the effect of the various contributions to the interaction energy. Solid line: potential curve from present work. Long dashed line: repulsion (Ae^{-bR}) only. Short dashed line: $Ae^{-bR} - f_4 D_4 R^{-4}$. Dotted line: $Ae^{-bR} - f_4 D_4 R^{-4} - f_6 D_6 R^{-6}$.

routes, and so it is possible to determine the repulsive region in the light of the other data.

4. Conclusions

We have presented high-quality spectroscopic parameters for the cationic complex, $Li^+ \cdot He$, obtained from interatomic potentials obtained employing the CCSD(T)/aug-cc-pVQZ and CCSD(T)/aug-cc-pV5Z basis sets. The results indicate that convergence in the basis set is close, and that the reported parameters at the highest level of theory ought to be reliable. A comprehensive interatomic curve is presented at the CCSD(T)/aug-cc-pV5Z level of theory, and from it Born–Mayer parameters were obtained, assuming literature values for the parameters describing the attractive potential: an overall potential is herein presented that describes the interaction between $Li^+ \cdot He$ from short-range to very long-range. It would, in principle, be possible to generate a full-CI potential, but this would be very expensive. We note that the close agreement between the R_e and D_e values from the present work, and those from previous high-level studies, indicates that little benefit would result from the effort.

We conclude that in the present case, it is not possible to decompose the interatomic potential unambiguously into the separate repulsive, inductive and dispersive terms, and that caution should be employed if such a decomposition is attempted. It is always possible to obtain good statistical fits (in that the fitted errors are small); however, the meaningfulness of the derived coefficients may be questionable on occasions (as indicated by the high dependence of the parameters). We note that recently Breckenridge and co-workers [24,25] have analyzed the extent of the various contributions to the interaction energies for some small $M^+ \cdot Rg$ complexes.

Acknowledgements

References

[1] A.D. Koutselos, E.A. Mason, L.A. Viehland, J. Chem. Phys. 93 (1990) 7125.
[2] H.R. Skullerud, T.H. Løvaas, K. Tsurugida, J. Phys. B 32 (1999) 4509.
[3] S.F. Boys, F. Bernardi, Mol. Phys. 19 (2970) 533.
[4] Molpro is a package of ab initio programs written by H.-J. Werner, P.J. Knowles, with contributions from J. Almlöf et al. With the CCSD treatment being described in: C. Hampel, K. Peterson, H.J. Werner, Chem. Phys. Lett. 190 (1992) 1.
[5] R.J. LeRoy, Level 7.2 – A computer program for solving the radial Schrödinger equation for bound and quasibound levels, and calculating various expectation values and matrix elements, University of Waterloo Chemical Physics Research Program Report CP-555R, 2000.
[6] S. Bililign, M. Gutowski, J. Simons, W.H. Breckenridge, J. Chem. Phys. 100 (1994) 8212.
[7] M.T. Elford, I. Røeggen, H.R. Skullerud, J. Phys. B 32 (1999) 1873.
[8] P.C. Hariharan, V. Staemmler, Chem. Phys. 15 (1976) 409.
[9] U.E. Senff, P.G. Burton, Mol. Phys. 58 (1986) 637.
[10] K.T. Tang, J.P. Toennies, J. Chem. Phys. 80 (1984) 3726.
[11] K.T. Tang, J.P. Toennies, Z. Phys. D 1 (1986) 91.
[12] R. Ahlrichs, H.J. Böhm, S. Brode, K.T. Tang, J.P. Toennies, J. Chem. Phys. 88 (1988) 6290.
[13] A.J. Stone, The Theory of Intermolecular Forces, Oxford University Press, Oxford, 1996.
[14] G. Maroulis, A.J. Thakkar, J. Chem. Phys. 89 (1988) 7320.
[15] G. Maroulis, A.J. Thakkar, Chem. Phys. Lett. 156 (1989) 87.
[16] T.M. Miller, B. Bederson, Adv. At. Mol. Phys. 13 (1977) 1.
[17] D.M. Bishop, J. Pipin, Chem. Phys. Lett. 236 (1995) 15.
[18] Z.-C. Yan, J.F. Babb, A. Dalgarno, G.W.F. Drake, Phys. Rev. A 54 (1996) 2824.
[19] J.E. Rice, P.R. Taylor, T.J. Lee, J. Almlöf, J. Chem. Phys. 94 (1991) 4972.
[20] A.J. Thakkar, J. Chem. Phys. 75 (1981) 4496.

[21] P. Soldán, E.P.F. Lee, T.G. Wright, Mol. Phys. 97 (1999) 139.

[22] K.T. Tang, J.M. Norbeck, P.R. Certain, J. Chem. Phys. 64 (1976) 3063.

[23] P.W. Fowler, J.M. Hutson, Phys. Rev. B 33 (1986) 3724.

[24] K.L. Burns, D. Bellert, A.W.-K. Leung, W.H. Breckenridge, J. Chem. Phys. 114 (2001) 2996.

[25] K.L. Burns, D. Bellert, A.W.-K. Leung, W.H. Breckenridge, J. Chem. Phys. 114 (2001) 7877.