Potential energy surface of the $1^2 A'$ Li$_2$+Li doublet ground state

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The lowest doublet electronic state for the lithium trimer ($1^2 A'$) is calculated for use in three-body scattering calculations using the valence electron FCI method with atomic cores represented using an effective core potential. It is shown that an accurate description of core-valence correlation is necessary for accurate calculations of molecular bond lengths, frequencies and dissociation energies. Interpolation between $1^2 A'$ \textit{ab initio} surface data points in a sparse grid is done using the global interpolant moving least squares method with a smooth radial data cutoff function included in the fitting weights and bivariate polynomials as a basis set. The Jahn-Teller splitting of the $1^2 E'$ surface into the $1^2 A_1$ and $1^2 B_2$ states is investigated using a combination of both CASSCF and FCI levels of theory. Additionally, preliminary calculations of the $1^2 A''$ surface are also presented using second order spin restricted open-shell Möller-Plesset perturbation theory.

Introduction

With the success of ultracold molecular formation among the alkali metals over the past decade via photoassociation \cite{Esry2008} and more recently with Feshbach resonances \cite{Jaksch2012}, the dynamics of molecules in ultracold traps have become an important topic to many physicists. Alkali dimers have been formed in many different homonuclear and heteronuclear configurations, for both singlet and triplet ground electronic states. Furthermore, recent experiments using K$\text{Rb}$ \cite{Buchmann2007} and theoretical proposals for Li$\text{Na}$ \cite{Deiglmayr2009} have shown the possibility of efficiently forming ultracold ground vibrational state diatoms. While both ground and excited singlet and triplet states of alkali diatomics have been studied extensively both experimentally and theoretically, alkali trimers have generally been ignored by both theorists and experimentalists alike. In the last few years there has been an increase of interest in few-body physics with continued success in the cooling and trapping of atoms.

In these few-body systems, experimental interest in three body effects range from loss rate predictions to probing few-body quantum effects such as Efimov states (Esry and co-workers \cite{Esry2003} and Grimm and co-workers \cite{Grimm2013} for example) due to the strong non-additive effects seen in alkali systems. To date, \textit{ab initio} calculations for the sodium trimer have been done by several groups \cite{Collin2008a,Collin2008b} as well as the potassium trimer \cite{Collin2008a,Collin2008b,Collin2008c}. In the case of lithium, the quartet ground state $1^4 A'$ surface has been well studied \cite{Kleppitsch2001,Kleppitsch2002,Kleppitsch2003,Kleppitsch2004} whereas the doublet system has been effectively ignored. The Jahn-Teller effect and conical intersections between the $1^2 E'$, $2^2 E'$ and $1^2 A'$ surfaces have been studied \cite{Buchmann2012,Buchmann2013}, as well as the vibrational \cite{Buchmann2011}, rovibrational \cite{Buchmann2011b} and hyperfine \cite{Buchmann2012a} structures of the lithium trimer. However, to the best of our knowledge the entire ground or excited state surfaces for the doublet lithium trimer have not been completely studied.

The structure of this paper is as follows, we first discuss the inclusion of core polarization potentials to accurately describe the effects of core valence correlation while using an effective core potential (ECP). The steps taken to optimize the basis set so as to provide accurate benchmark Li$_2$ spectroscopic values are then described in detail. Following this we show how accurate calculations of the potential energy surface (PES) were done with a low density of \textit{ab initio} points through the use of the global interpolant moving least squares (IMLS) fitting procedure. Finally we describe the calculations we have done on both the $1^2 A'$ and $1^2 A''$ surfaces of the lithium trimer and future goals for the use of these surfaces. In this work, all calculations have been done using the MOLPRO 2008.1 quantum chemistry package \cite{MOLPRO} unless otherwise stated.

Computational Details

Core-Valence Correlation

To accurately describe dissociation energies, equilibrium geometries and vibrational frequencies in alkali-metal clusters, it is necessary to account for the electronic core-valence (CV) correlation energy \cite{Cvitas2005}. For all electron calculations this is possible for the lighter alkali atoms (Li through K) by using the explicitly correlated basis of Iron, Oren and Martin (IOM) \cite{Iron2005}. This approach has recently been done by Cvitaš \textit{et al} \cite{Cvitas2014} for the spin aligned $1^4 A'$ Li$_3$ surface using spin restricted coupled cluster calculations with single, double and iterative triple excitations (RCCSD(T)). To account for CV correlation in heavier atoms, where all electron calculations are prohibitively expensive, it is necessary to use a core polarization potential (CPP). This is also necessary for valence electron full configuration interaction (FCI) calculations where an ECP (a physically equivalent representation to the frozen core approximation which has no CV correlation) is substituted...
for the atomic electrons. This method has been used with great success for calculating both lithium dimer potential curves [25] and trimer potential surfaces of potassium [12].

The theoretical description of the CPP is a straightforward addition to that of the ECP model of atomic cores. In the Born-Oppenheimer approximation the non-relativistic molecular Hamiltonian can be separated into kinetic and interaction operators $T$ and $V$ respectively. Approximating the core of each nuclei with an $l$ dependent pseudopotential and including the polarization effects at the nuclei gives for the interaction operator

$$ V = \sum_k (V^k + V_{cpp}^k) + \sum_{j>i} \frac{1}{r_{ij}} + V_{cc}, $$

where

$$ V^k = \sum_i \frac{Q_k}{r_{ik}} + \sum_{il} B_{il}^{k} \exp(-\beta_{il}^k r_{il}^2) P_{l}^{k} $$

is the core pseudopotential,

$$ P_{l}^{k} = \sum_m [klm_i] (klm_i) $$

is the projection operator onto the subspace of angular momentum $l$ on core $k$ and $V_{cc}$ is the core-core coulomb interaction. Here the polarization potential, $V_{cpp}^k$, for a given core $k$, is expressed in terms of a static polarizability and external field at the nuclei position by

$$ V_{cpp}^k = -\frac{1}{2} \alpha_k \mathbf{F}_k \cdot \mathbf{F}_k. $$

where the electric field $\mathbf{F}_k$ at core $k$ arising from the coulomb interaction with the electrons at $\mathbf{r}_{ki}$ and other cores at $\mathbf{R}_{kj}$ is

$$ \mathbf{F}_k = \sum_i \frac{\mathbf{r}_{ki}}{r_{ki}^3} C(r_{ki}) - \sum_j \frac{Z \mathbf{R}_{kj}}{R_{kj}^3}. $$

The value of the static polarizability for Li$^+$ is $\alpha_k = 0.1915 a_0^{-3}$ [26] and the cutoff function $C(r_{ki})$ defined by Fuentealba et al [26] is given as

$$ C(r_{ki}) = (1 - e^{-\delta_k r_{ki}}), $$

with the cutoff parameter chosen to be $\delta_k = 0.8316 a_0^{-2}$. This form of the cutoff parameter was first presented by Müller et al [27] and produces good agreement for ground and low excited states, however it does show diminished results for Rydberg states [27]. Our calculations using this core polarization potential to describe the core valence correlation energy were done using the MOLPRO 2008.1 [22] implementation of the Fuentealba et al [26] CPP.

### Basis Set

Atomic and molecular polarizabilities are important factors for long range interatomic and molecular interactions. In ultracold systems this is a dominant contribution to the scattering length in addition to the location of the inner wall. To accurately describe both of these quantities in the lithium trimer, we require that the basis set be flexible enough to describe atomic polarization at long range while accurately representing the inner wall. Very accurate polarizability calculations require an accurate description of electron correlation and a large basis set containing diffuse functions such as the Sadlej basis sets [31, 32], but this is computationally impractical to implement for large all electron systems. Accurate polarizability calculations can be achieved using an ECP with a small but well chosen basis set as demonstrated by Labello, Ferreira and Kurutz (LFK) [33, 34]. Their basis set augments the Stevens, Basch and Krauss (SBK) ECP basis [28] with an additional $p$ function and four extra $d$ functions optimized following the Sadlej [31, 32] method.

Using the SBK pseudopotential, we further optimized the uncontracted LFK basis (see Table I for the exponents) with and without the CPP for the Li$_2$ X$^1\Sigma_g^+$ ground state. This was done using three scale factors $\lambda(\lambda = s, p, d)$ optimized at the FCI level to give the best calculated value of the dissociation energy. As a benchmark, the CVQZ and CV5Z IOM basis [24] at the CCSD(T) level correlating all electrons (no frozen core) gives an error in the calculated dissociation energy of 46.087 cm$^{-1}$ and 27.902 cm$^{-1}$ respectively, while at the valence FCI level the unscaled LFK basis the error is 1.25 cm$^{-1}$. Optimizing the uncontracted LFK basis with and without the CPP gives an error in the calculated dissociation energy of 4.469 cm$^{-1}$ and 10.040 cm$^{-1}$ respectively. Using a small basis set as in the SBK ECP, the error in the calculated dissociation energy is 0.300 cm$^{-1}$.

### Table I: Uncontracted basis set exponents for the lithium Stevens, Basch and Krauss [28] pseudopotential basis used in this work. The $s$, $p$ and $d$ orbital exponents are each scaled to give an optimal dissociation energy for Li$_2$ as discussed in the text.

| Orbital Type | SBK | LFK | Scaled LFK |
|--------------|-----|-----|------------|
| $s$          | 0.6177000 | 0.6177000 | 0.52504500 |
|              | 0.1434000 | 0.1434000 | 0.12189000 |
|              | 0.0504800 | 0.0504800 | 0.04290800 |
|              | 0.0192300 | 0.0192300 | 0.01634550 |
| $p$          | 0.6177000 | 0.6177000 | 0.00690155 |
|              | 0.1434000 | 0.1434000 | 0.64858500 |
|              | 0.0504800 | 0.0504800 | 0.15057000 |
|              | 0.0192300 | 0.0192300 | 0.05300400 |
| $d$          | 0.1346266 | 0.13799227 | 0.0065729 |
|              | 0.0546860 | 0.05605315 | 0.02019150 |
|              | 0.0180355 | 0.01848639 | 0.01346266 |
|              | 0.0076882 | 0.00788041 | 0.0180355 |
ing the $\beta_{\lambda}$ coefficients to give the best dissociation energy, we obtain a difference of 0.077 cm\(^{-1}\) using the scaled exponents listed in Table 1, corresponding to the scale factors $\beta_s = 0.85$, $\beta_p = 1.05$ and $\beta_d = 1.025$. In Figure 1 and Table I, the results from the different basis functions and methods can be seen compared to the Rydberg-Klein-Rees (RKR) curve adjusted to reproduce the ultracold scattering results 35. We chose to use this scaled, uncontracted LFK basis with the SBK ECP and Fuentealba CPP in calculating the potential energy surface of the lithium trimer at the FCI level of theory.

Surface Representation

Calculations of ab initio points at the FCI level are very computationally intensive, even for three electrons with the compact basis just described, so to accurately describe an entire potential energy surface with a low density of ab initio points we implemented the global IMLS fitting method 36. In this method the potential energy at an arbitrary point $Z$ in the $(x, y)$ plane is approximated by the use of a linearly independent basis $b_j(Z)(j = 1, \ldots, n)$ and expansion coefficients $a_j(Z)(j = 1, \ldots, n)$ so that the interpolated energy is given by

$$V_{\text{int}}(Z) = \sum_j a_j(Z)b_j(Z).$$

(7)

The expansion coefficients $a_j(Z)$ are found by minimizing the error function

$$E(V_{\text{int}}) = \sum_{j=1}^{N_d} w_j(Z) \left( \sum_{i=1}^{n} a_i(Z)b_i(Z) - f_j(\ell_j) \right)^2$$

(8)

of the interpolated energy $V_{\text{int}}$ and the ab initio energy $f_j(\ell_j)(i = 1, \ldots, N_d)$ at coordinates $\ell_j$ where $N_d$ is the number of ab initio data points.

Expressing the solution to the normal equations $\partial E(V_{\text{int}})/\partial a_j = 0$ in matrix form we obtain the linear equation for the expansion coefficients

$$BW(Z)B^T a(Z) = BW(Z)f,$$

(9)

where $W(Z)$ is the diagonal matrix of weights $w_i(Z)$ and $B$ is the matrix

$$B = \begin{pmatrix} b_1(\ell_1) & b_1(\ell_2) & \cdots & b_1(\ell_{N_d}) \\ b_2(\ell_1) & \cdots & \cdots & b_2(\ell_{N_d}) \\ \vdots & \cdots & \cdots & \vdots \\ b_{N_d}(\ell_1) & b_{N_d}(\ell_2) & \cdots & b_{N_d}(\ell_{N_d}) \end{pmatrix}.$$ 

(10)

The linear system in Eq. 9 is routinely ill conditioned and so is solved by singular value decomposition.

The weights $w_i(Z)$ dictate the effective range at which a given ab initio point will contribute to the global fit and the effective contribution to the fit. We use Guo et al’s 37 form of the weight function, which introduces a cutoff function $S(\chi)$ to the unnormalized weight function $v_i(\|Z - \ell_i\|)$ so as to smoothly go to zero at a given cutoff radius $R_{\text{cut}}$. The cutoff function is given 37 by

$$S(\chi) = \begin{cases} (1 - \chi^m)^4 & \text{if } 0 \leq \chi \leq 1, \\
0 & \text{if } \chi > 1, \end{cases}$$

(11)

with $m = 10$ and the unnormalized weight function is

$$v_i(Z) = \frac{\exp[-\|Z - \ell_i\|^2/\zeta^2]}{\left(\|Z - \ell_i\|/\zeta\right)^4 + \epsilon}$$

(12)

| Method/Basis                  | $r_e$ [Å] | $\omega_e$ [cm\(^{-1}\)] | $D_0$ [cm\(^{-1}\)] | $D_e$ [cm\(^{-1}\)] |
|------------------------------|-----------|----------------------------|----------------------|----------------------|
| Expt.\(^a\)                 | 2.673     | 351.43                     | 8434.58              | 8516.36\(^b\)        |
| Recommended\(^c\)           | 2.667     | 352.98                     | 8340.12              | 8516.43              |
| FCI/SBK scaled LFK          | 2.693     | 346.54                     | 8198.85              | 8371.83              |
| FCI/SBK+CPP LFK             | 2.663     | 353.89                     | 8338.45              | 8515.10              |
| FCI/SBK LFK                 | 2.687     | 347.19                     | 8197.18              | 8371.04              |
| RCCSD(T)/CVQZ\(^d\)         | 2.676     | 353.05                     | 8294.15              | 8470.27              |
| RCCSD(T)/CV5Z\(^a\)         | 2.674     | 353.08                     | 8311.70              | 8488.46              |

\(^a\) Taken from Herzberg 29
\(^b\) Extracted from the scattering RKR data 30
\(^c\) FCI/SBK+CPP with scaled LFK using $\beta_s = 0.85$, $\beta_p = 1.05$ and $\beta_d = 1.025$
\(^d\) CVnZ is the n-zeta core valence correlation consistent basis set from IOM 23.
FIG. 1: Benchmark singlet Li$_2$ potential energy curves using both the core-valence correlation consistent basis sets of Iron, Oren and Martin [24] and core polarization potential Stevens, Basch and Krauss pseudopotential [28] with an extended and scaled ECP basis set calculated at the RCCSD(T) and full configuration interaction level of theory respectively. The scattering RKR curve is the inner wall shifted version of Côté et al [30] such that the potential predicts the correct scattering lengths and Feschbach resonances.

FIG. 2: Molecule frame Jacobi coordinates are used to describe the lithium trimer geometry. Within this coordinate system the potential energy surface is calculated assuming that the lithium dimer bond $r_e$ is adiabatically relaxed as the colliding lithium atom approaches.

where $\epsilon = 10^{-10}$ removes the singularity at $\ell_i$. Then the normalized weight function is

$$w_i(Z) = \frac{S(||Z - \ell_i||^2/R_{\text{cut}})v_i(Z)}{\sum_{j} S(||Z - \ell_i||^2/R_{\text{cut}})v_j(Z)}$$ \hspace{1cm} \text{(13)}$$

where $R_{\text{cut}}$ is to be determined as to give the best fit. Finally the basis functions are chosen to be bivariate polynomials of order $n = 6$ such that

$$b(Z) = 1, Z_1, Z_2, Z_1^2, Z_2^2, Z_1 Z_2, \ldots, Z_1^{n-1} Z_2, Z_1 Z_2^{n-1}$$ \hspace{1cm} \text{(14)}$$

where the inverse coordinates $Z_i = 1/x_i$ are used in this work. With the choice of coordinates used here there is a coordinate singularity in $C_{2v}$ symmetry. To avoid this all coordinates $x_i$ are shifted by the same positive, arbitrary additive factor for the fit then transformed back upon completion. The scaling parameter $\zeta$ was chosen to be the average distance between the interpolant point $Z$ the $ab\text{ initio}$ points. With this definition the cutoff radius was defined in terms of $\zeta$ as $R_{\text{cut}} = 50.0 \cdot \zeta$. This interpolant method is used for the lithium trimer $1^2A'$ PES to obtain a global fit using a low number of $ab\text{ initio}$ points as references.

Results and Discussion

The $1^2A'$ surface of Li$_3$ was calculated at the full configuration interaction level using the scaled LFK basis set, the SBK pseudopotential [28] and core polarization potential described above, with the three valence electrons included in the FCI calculation. At the FCI level, there are 410670 configurations of $A'$ symmetry and 383292 configurations of $A''$ symmetry. All FCI calculations were performed with the Knowles-Handy determinant FCI program [38, 39] using the MOLPRO 2008.1 package [22].
FIG. 3: Near equilibrium geometry potential energy surface for the Li$_3$ $^1\!^2A'$ electronic state calculated using valence electron full configuration interaction theory. Equilibrium is found to be at bond lengths of $r_e = 3.218\,\text{Å}$ and $R_c = 2.238\,\text{Å}$ for $C_{2v}$ geometry configuration.

ometry was chosen so to best describe the diatomic-atomic collision process. As such we used the molecular frame Jacobi coordinates for a homonuclear system where we define a vector $r_e$ along the diatomic inter-nuclear axis and another vector $R_c$ from the diatomic center of mass to the colliding atom where the collision angle $\alpha$ is defined from the $C_{\infty v}$ axis (see Figure 2). With this coordinate system the most efficient grid of $ab\,\text{initio}$ points is an evenly spaced angular grid with the radial grid chosen to have the highest density of points at the minima. We calculated 26 with the collision angle varying between 90° and 45° on the $^1\!^2A'$ Li$_3$ surface by choosing $\alpha$ and $R_c$ then optimizing the dimer bond length to give the lowest energy configuration. The $^1\!^2A'$ state is found to have a triangular equilibrium geometry on the $^1\!^2A'$ surface with $r_e = 3.218\,\text{Å}$ and $R_c = 2.238\,\text{Å}$ for the Jacobi bond lengths with a dissociation energy of 4979.42 cm$^{-1}$. The interpolated surface near the equilibrium geometry is show in Figure 3.

We have investigated the lowest states of $^2A_1$, $^2B_1$ and $^2B_2$ symmetry and the first excited $^2A_1$ state in point group $C_{2v}$ using the complete active shell (CAS) method in conjunction with FCI. The same SBK and CPP representation of the core as in the FCI calculation of the $^1\!^2A'$ surface was used here with an active space of 12 orbitals ($5a_1, 2b_2, 4b_2, 1a_2$) for the energies of the $^1\!^2A_1$, $^1\!^2B_1$, $^1\!^2B_2$ and $^2\!^2A_1$ states as seen in Figure 4. Here $R_c$ is fixed and $r_e$ is optimized at the CAS level with tight convergence. This is followed by a FCI calculation to obtain the energy at this geometry, with typical errors in the CAS geometry optimization compared to that of the FCI geometries on the order of a mÅ. A conical intersection between the $^1\!^2A_1$ and $^1\!^2B_2$ surfaces is observed at $R_c = 2.51\,\text{Å}$ which is the result of Jahn-Teller splitting of the $^1\!^2E'$ $D_{3h}$ surface [17].

Preliminary calculations of the Li$_3$ $^1\!^2A''$ surface have been carried out using second order spin restricted open-shell Møller-Plesset perturbation (ROMP2) theory as implemented in Gaussian
FIG. 5: The Li$_{3}$ $1^2A''$ potential energy surface calculated at the second order spin restricted open-shell Møller-Plesset perturbation theory for collision angles 90° ($C_{2v}$) to 45°. The dissociation energy is 14156.5 cm$^{-1}$ with $R_C = 2.40\AA$ and $r_e = 2.77\AA$ in the $C_{2v}$ symmetry.

Conclusions

The electronic ground state $1^2A'$ surface of the lithium trimer has been calculated using valence electron FCI theory with the lithium cores represented using the SBK pseudopotential \[28\]. It was found to be necessary to systematically include core-valence correlation in the calculation for precise calculations of diatomic spectroscopic values. The basis set chosen is a $p$ and $d$ function augmentation of the SBK basis set \[28\] as given by Labello, Ferreria, and Kuntz \[33\] with the $s$, $p$, and $d$ functions optimized with the inclusion of a core polarization potential to predict the correct diatomic dissociation energy. With the recommended basis set of this work, the use of the core polarization potential to include core-valence effects lead to an improvement 26.4 mÅ in the bond length, 6.44 cm$^{-1}$ of the vibrational frequency and 144.605 cm$^{-1}$ dissociation energy of Li$_2$.

To interpolate between sparse \textit{ab initio} data points, the full interpolant moving least squares method was implemented using a scaled exponential weighting function with a smooth cutoff function as a constraint on the number of included data points. The surface was expanded using the inverse spatial coordinates with a 6 order bivariate polynomial. With this interpolation method the $1^2A'$ surface was calculated for collision angles 45° to 90° near the equilibrium Jacobi bond lengths of $r_e = 3.218\AA$ and $R_C = 2.238\AA$. A conical intersection is found between the $1^2A_1$ and $1^2B_2$ states in $C_{2v}$ symmetry near the equilibrium geometry of the $1^2A'$ surface. Because of the location of this intersection it is necessary to account for its existence in both chemical and ultracold physics. Also a preliminary surface for the excited state $1^2A''$ is presented at the ROMP2 level of theory. It is the authors intention to continue to study the long range interactions of the lithium trimer on the ground $1^2A'$ surface and to investigate both elastic collisions and photoassociation of the lithium diatom-atom pair for the formation of ultracold trimers.

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References

[1] Jones, K. M.; Tiesinga, E.; Lett, P. D.; Julienne, P. S. Rev Mod Phys 2006, 78, 483.
[2] Kühler, T.; Góral, K.; Julienne, P. S. Rev Mod Phys 2006, 78, 1311.
[3] Ospelkaus, S.; Pe’er, A.; Ni, K.-K.; Zirbel, J. J.; NeyJenhuis, B.; Kotochigova, S.; Julienne, P. S.; Ye, J.; Jin, D. S. Nature Phys 2008, 4, 622.
[4] Ni, K.-K.; Ospelkaus, S.; de Miranda, M. H. G.; Pe’er, A.; NeyJenhuis, B.; Zirbel, J. J.; Kotochigova, S.; Julienne, P. S.; Jin, D. S.; Ye, J. Science 2008, 322, 1163861.
[5] Pellegrini, P.; Gacesa, M.; Côté, R. Phys Rev Lett 2008, 101, 053201.
[6] Esry, B.; Greene, C.; Burke, Jr., J. Phys Rev Lett 1999, 83, 1751.
[7] Kraemer, T.; Mark, M.; Waldburger, P.; Danzl, J. G.; Chin, C.; Engeser, B.; Lange, A. D.; Pilch, K.; Jaakkola, A.; Nägerl, H.-C.; Grimm, R. Nature 2006, 440, 315.
[8] Martins, J.; Car, R.; Buttet, J. J Chem Phys 1983, 78, 5646.
[9] Cocchini, F.; Upton, T.; Andreoni, W. J Chem Phys 1988, 88, 6068.
[10] Zhang, P.-H.; Li, J.-M. Phys Rev A 1983, 54, 665.
[11] Thompson, T.; Izmirlian, G.; Lemon, S.; Truhlar, D. J Chem Phys 1985, 82, 5597.
[12] Hauser, A.; Callegari, C.; Soldán, P.; Ernst, W. J Chem Phys 2008, 129, 044307.
[13] Colavecchia, F.; Burke Jr., J.; Stevens, W.; Salazar, M.; Parker, G.; Pack, R. J Chem Phys 2003, 118, 5484.
[14] Brue, D. A.; Li, X.; Parker, G. A. J Chem Phys 2005, 123, 091101.
[15] Cvitaš, M. T.; Soldán, P.; Hutson, J.; Honvault, P.; Launay, J.-M. J Chem Phys 2007, 127, 074302.
[16] Li, X.; Brue, D. A.; Parker, G. A. J Chem Phys 2008, 129, 124305.
[17] Gerber, W.; Schumacher, E. J Chem Phys 1978, 69, 1692.
[18] Sadygov, R. G.; Yarkony, D. R. J Chem Phys 1999, 110, 3639. And references therein.
[19] Keil, M.; Kramer, H.; Kudell, A.; Baig, M. A.; Zhu, J.; Demtröder, W.; Meyer, W. J Chem Phys 2000, 113, 7414.
[20] Meyer, W.; Keil, M.; Baig, M. A.; Zhu, J.; Demtröder, W. J Chem Phys 2001, 115, 2590.
[21] Kramer, H.; Keil, M.; Suarez, C. B.; Suarez, C. B.; Demtröder, W.; Meyer, W. J Chem Phys Lett 1999, 299, 212.
[22] Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Mitrushenko, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deeghan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampsel, C.; Hetzer, G.; Hrenar, T.; Knizia, G.; Köpl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pfüger, K.; Pitzer, R.; Reiter, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarrott, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. MOLPRO, version 2008.1, a package of ab initio programs.
[23] Martin, J. M. Chem Phys Lett 1995, 242, 343.
[24] Iron, M. A.; Oren, M.; Martin, J. M. Molecular Physics 2003, 101, 1345.
[25] Jasik, P.; Sienkiewicz, J. Chemical Physics 2006, 323, 563. And references therein.
[26] Fuentetabla, P.; Preuss, H.; Stoll, H.; Szentpály, L. V. Chem Phys Lett 1982, 89, 418.
[27] Müller, W.; Flesch, J.; Meyer, W. J Chem Phys 1984, 80, 3297.
[28] Stevens, W.; Basch, H.; Krauss, M. J Chem Phys 1984, 81, 6026.
[29] Herzberg, G. Molecular Spectra and Molecular Structure; vol. I. Spectra of Diatomic Molecules D. Van Nostrand Company, Inc.: Princeton, NJ, 1950.
[30] Côté, R.; Dalgarano, A.; Jamieson, M. Phys Rev A 1994.
[31] Sadlej, A. J Coll Czech Chem Commun 1988, 53, 1995.
[32] Sadlej, A. J Theor Chim Acta 1992, 79, 123.
[33] Labello, N.; Ferreira, A.; Kurtz, H. J Comp Chem 2005, 26, 1464.
[34] Labello, N.; Ferreira, A.; Kurtz, H. Int J Quantum Chemistry 2006, 106, 3140.
[35] Gacesa, M.; Pellegrini, P. Private communication.
[36] Lancaster, P.; Salkauskas, K. Curve and Surface Fitting; Academic Press, 1986.
[37] Guo, Y.; Tokmakov, I.; Thompson, D. L.; Wagner, A. F.; Minkoff, M. J Chem Phys 2007, 127, 214106.
[38] Knowles, P. J.; Handy, N. C. Chem Phys Letters 1984, 111, 315.
[39] Knowles, P. J.; Handy, N. C. Chem Phys Comp 1989, 54, 75.
[40] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision B.05. Gaussian, Inc., Wallingford, CT, 2004.