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RESEARCH ARTICLE

Dissociation of homonuclear diatomic halogens via multireference coupled cluster calculations

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We have computed the potential energy surfaces (PESs) of F_2 , Cl_2 , Br_2 , and I_2 using the size-extensive state specific multireference coupled cluster (SS-MRCC) method. The MR character of the system considered here at large distances and the presence of low-lying intruder states are known to be the major causes of incorrect or inaccurate predictions of the PES. The SS-MRCC theory is tailored to treat degeneracies of varying extent while bypassing the intruder problem. The quality of the computed PES has been gauged by computing spectroscopic constants. The calculated properties show a good agreement with available experimental data and the errors in the calculated molecular properties compare favourably with the most elaborate current-generation calculations of the literature. The accuracy of the computed PES of F_2 is such that it has been proved to calculate the vibrational spectrum of the 22 levels with a minimum and maximum absolute deviation of 2 and 57 cm^{-1} , respectively, from the experimental values. The highly satisfactory performance of the SS-MRCC method, vis-a-vis the other sophisticated methods, in describing the vibrational levels is noticeable for one of the more difficult systems such as F_2 clearly indicates that the present method is reliable in studying the vibrational energy levels.

Keywords: energy surface; spectroscopic constants; vibrational levels; coupled cluster; multireference; halogen molecules

1. Introduction

The homonuclear diatomic halogen molecules (such as Cl_2 , Br_2 , and I_2) and their corresponding heteronuclear hydrogen halides attract special attention owing to their pivotal role in atmospheric chemistry as potential sources of intermediates that trigger the depletion and subsequent destruction of the ozone layer. The knowledge of the true electronic structure of diatomic halogen molecules is also crucial and relevant for shedding light on the true reaction mechanisms of these intermediates in the ozone layer. Quantitatively accurate energy calculations on potential energy surfaces (PESs) of ground-state X_2 ($X = F, Cl, Br, \text{ and } I$) systems as recognised in the literature clearly point towards several difficulties, and it is well recognised that along the dissociating reaction path of X_2 , the zeroth-order reference function changes multiconfigurationaly. Moreover, they are the prototype systems for a variety of spectroscopic and reaction dynamics studies. Despite the tremendous methodological developments, finding ways to correctly and reliably describe PESs for bond breaking is still an important issue in the realm of electronic structure theory. The task for computational chemists is to explore the PESs with methods that are efficient and accurate enough to describe the phenomena of interest [1].

In spite of phenomenal success of single-reference coupled cluster (SRCC) (a number of pedagogical reviews

on the SRCC methodologies being available in Ref. [2]) methods for closed-shell and some high-spin open-shell molecules around the equilibrium region, there are a large number of problems (e.g., computation of the energy surface) for which the underlying assumption that the wavefunction is dominated by one reference determinant or configuration breaks down (degenerate situation or multireference case (MR)) and the effectiveness of the method goes down. Although a number of methods have been proposed and implemented to treat such situations within the SR framework [3–8], they have been shown to provide good results for moderate quasi-degenerate situation cases. The SR-based methods for treating quasi-degeneracy have an inherent limitation that they are obliged to treat the non-dynamical correlation attendant upon the quasi-degeneracy via higher body cluster operators. The challenge of quantitatively accurate PES calculations arises from the fact that, away from equilibrium geometries, even zeroth-order descriptions typically call for MR wavefunctions. Genuine multireference coupled cluster (MRCC) approaches, which allow multiple configurations to be treated as reference configurations in a democratic manner, have also been developed and implemented. From among the numerous MRCC schemes, state-specific (SS) or single root (sr) MRCC schemes (which target only one state at a time) [9–15] derived from the Jeziorski–Monkhorst (JM)

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wavefunction ansatz have recently emerged as viable generalisations of SRCC theory for the study of MR situations mentioned above. Although the limitation to a single state may be considered a drawback of the SS/sr methods, the advantage is that they tend to be less sensitive to the intruder state problem [16] (which is connected to the existence of multiple solutions of the underlying CC equations which are the innate features of the highly nonlinear form of the Bloch equations [17]). The numerical instability of the state-universal MRCC (SU-MRCC) [18–20] is one of the main drivers for the development of the SS methods. Another interesting development in the SSMR formalism is the block correlated method of Li and co-workers [21] which has also been fairly extensively explored. Like the MRexpT [12] method, this is also non-extensive for the valence electrons. In Refs. [22,23], different versions of both SU and SS were critically reviewed and further prospects of using the MRCC ansatz in electronic structure theory were briefly addressed. One would hope that after more than a few decades of tremendous development, one should nowadays be capable of performing routine MRCC calculations for atomic or molecular systems with arbitrary complexity and generality. Unfortunately, this is not the case. We believe that in the near future MRCC calculations would be routinely used for their precision on more complex systems with arbitrary multidimensional reference spaces.

In the present paper, we focus on the application of the rigorously size-extensive [8] SS-MRCC theory of Mahapatra *et al.* [11] to the ground states of X_2 ($X = \text{F, Cl, Br, and I}$) molecular systems, although a number of investigations via this method (see Refs. [24–29] for representative recent studies) have confirmed the superiority of the method over the other related approaches for the treatment of problems involving a strong static correlation in conjunction with a dynamic one. In this work, we also focus on the calculation of the spectroscopic constants (obtained from a fourth to sixth order Dunham fit [30] polynomial of the computed PESs, which gave consistent results) such as equilibrium bond length R_e (Å), vibrational frequency ω_e (cm^{-1}), anharmonicity constant $\omega_e x_e$ (cm^{-1}), and dissociation energy D_e (kcal mol^{-1}) which are all very important spectroscopic parameters. Here, we have calculated dissociation energy with respect to the lowest point on the PES and equilibrium bond distance corresponding to the lowest point on the PES rather with respect to the lowest vibrational level, since this is an important intrinsic property of the theoretical potentials. The difference between these two quantities is the zero-point energy. It is also important to note that the theoretical equilibrium distances are the locations of the minima of the theoretically computed dissociation surfaces. Investigation of the equilibrium bond length and harmonic frequency would help us to assess the performance of the SS-MRCCSD method around equilibrium geometry, whereas an estimation of anharmonicity constant

and dissociation energy would describe the efficacy of the method far from the equilibrium region.

2. Results and discussions: Bond breaking ground state energy surfaces in Halogen dimers

The procedure we used involved running an initial restricted Hartree–Fock (RHF) calculation followed by SS-MRCC analysis with various singles–doubles (SD) truncation of cluster operators. In our computation, the reference or model space is spanned by two closed-shell configurations, involving two active electrons and two active orbitals that belong to different symmetry species of the spatial symmetry group of the system [CAS(2,2)], a condition that defines them uniquely. From a conceptual point of view, the single bonding in X_2 is basically a chemical reaction that involves one bonding orbital and the corresponding higher lying antibonding orbital. CAS(2,2) is thus the smallest active space that allows for a qualitatively correct treatment of the single-bond breaking since, in the dissociation region, both bonding and antibonding orbitals become quasi-degenerate non-bonding orbitals. The main essence of the development of MR-based theory is to employ as small an active or reference space as possible. It should be noted that the basis sets, correlation consistent polarised valence quadruple-zeta (cc-pVXZ) atomic basis functions developed by Dunning [31] (taken from the Computational Chemistry Environment Basis Set Database [32]), used in the present study are optimised to recover the correlation energy of the valence electrons and thus are less effective in accessing the core–valence correlation effects. Correlation consistent basis sets, cc-pVnZ, of Dunning [31] provide a hierarchy of basis sets with accuracy (i.e., completeness) systematically increasing with n . We emphasise that the manifest *theoretical calculational error*, associated with any *ab initio* result, is essentially an algebraic sum of the errors stemming out from every electronic structure method that has been put to practice and that due to the issues originating from the basis-set convergences. In the case that these two sources of error enjoy opposite signs, there might be an occasional cancellation of the errors for some specific basis sets (n). This is often envisaged to occur in perturbative techniques. As observed in various previous studies, the basis-set errors vary in a systematic manner with increasing n for the correlation consistent basis.

In our program, the one- and two-electron integrals are all calculated with the GAMESS program [33]. Our MRCC codes have been interfaced with the GAMESS package. In our pseudo-potentials (PP) calculation, we used the consistent-correlated cc-pVXZ-PP basis sets of Peterson *et al.* [34] that can be obtained from the Extensible Computational Chemistry Environment Basis Set Database [32]. These basis sets are small-core energy-consistent PPs. For the first-, second-, and third-row post- d elements, only the [Ne], [Ar]3 d^{10} , and [Kr]4 $d^{10}4f^{14}$ cores are replaced by PPs,

respectively. Dolg [35] has investigated the accuracy of large-core PPs for systems containing the post-*d* elements bromine and iodine and observed that large-core PPs lead to an overestimate of the correlation energy of the valence electrons by around 10% and to a discrepancy of approximately 2 mH in energy differences. Although an appropriate choice of PP can provide correct scalar and spin-orbit (SO) relativistic effects, the accompanying basis sets can also be much smaller in comparison to all-electron basis sets due to the omission of the low-lying core electrons. While PPs take care of the most important relativistic effects, they do not usually implicitly incorporate electron correlation.

As a direct comparison to experiment is not always possible, previous theoretical results should be taken into consideration when calibrating electronic structure models. To assess the comparative performances of electronic structure methods from a perfectly quantitative standpoint, one needs to use the same basis set, and the same set of orbitals should be used in all calculations to avoid, or at least attenuate to a considerable extent, the differences that originate from the theoretical artefacts while comparing the results. Here, we have assembled the results of different methods for different basis sets just for reference.

Among the various dihalogen molecules, as reported in the literature [24,25,36–46], bond breaking in F_2 is a rather challenging example due to anomalously strong correlation effects. It is already known that F_2 is unbound at the HF level. Hence, the F_2 molecule is a very challenging case for the RHF-based CC approaches (see Ref. [4]). In contrast to fluorine, chlorine and bromine molecules are bound at the HF level. Chlorine and bromine introduce a new level of complexity to our computational methods because they are so large. Chlorine and bromine have 17 and 35 electrons, respectively, and taking into consideration every electron for these atoms costs a great deal computationally. In systems containing heavy atoms, such as chlorine or bromine, relativistic effects and SO coupling cannot be neglected (in some cases even in the first-order perturbative treatment) to get correct results. In our calculations presented in this paper, the inner-shell electron correlation has been disregarded. Here, we like to mention that the dynamical correlation and higher angular momentum basis functions are recognised as important elements for the accurate computation of the ground state PESs of X_2 by electronic structure theorists.

In our present calculations, the $1s$ core orbitals of F in F_2 have been kept frozen, whereas the calculations for Cl_2 and Br_2 have been done with the exclusion of the He- and Ne-core correlation, respectively. In calculations of heavy-element systems, the frozen core approximation is often used to reduce the computational effort. It would be an interesting point to check the error due to this. For the ground-state F_2 and Cl_2 , we have also estimated the results at the complete-basis-set (CBS) limit. In the present work, we have used Equation (3) of Ref. [47] for extrapolation

(CBS limit) of the calculated spectroscopic constants. The resulting values are extrapolated to the CBS limit in an attempt to eliminate the basis-set truncation error. Quite akin to those *ab initio* methods which rely on the expansion of the molecular wavefunction in Slater determinants, the MRCC too suffers from poor convergence behaviour towards the basis-set limit. It has been observed that the error in energy scales as $(L + 1)^{-3}$, where L is the highest value of the angular momentum in the basis set. This effect jeopardises the achievement of results close to the CBS limit, unless suitable extrapolation techniques are administered.

2.1. Fluorine molecule (F_2)

We first focus on the ground state F_2 which is one of the weakest covalently bound species, and an accurate description of its ground state and associated properties has been a challenge to *ab initio* theory for very strong non-dynamical and dynamical correlation effects owing to the large number of lone pair–lone pair interactions and the near-degeneracy of the orbitals involved. The difficulty in treating the dissociation of the F_2 molecule is evident at the mean-field level of theory. At the unrestricted HF level, it is not even bound and for its very strong dynamical correlation effects, the full valence complete active space self-consistent field (CASSCF) method yields only half of the binding energy. There is also a very large error in the dissociation energy (with respect to the lowest point on the PES and the equilibrium bond distance corresponding to the lowest point on the potential energy curve) for CCSD with the RHF reference being notoriously bad. Based on the conclusion of Bytautas *et al.* [41–44] and Evangelista *et al.* [24,25], there should be a small error in the dissociation of F_2 when treated with CCSD(T) due to the very strong MR character of this problem that can be ameliorated by the addition of quadruples, pentuples, etc. Moreover, many-body perturbation theory and some of the CC methods also do not predict the asymptote of the PES correctly. As a result of this, numerous many-body theories have been applied to F_2 [24,25,36–40,45,46,48,49]. In a series of papers, Bytautas and co-workers [41–44] studied the *ab initio* energy surface for the dissociation of the F_2 molecule. In their most recent study [43], the long-range interactions along the dissociation surface were studied using calculations at the CASSCF and MR-CISD levels of theory in conjunction with the Davidson correction (MR-CISD+Q). Additional contributions due to SO coupling and scalar relativistic effects were also taken into account. The dissociation energy of F_2 has also been calculated to high accuracy with the relaxed active space based fixing tailored-CC with high-order cluster operator(s) at a small fraction of the cost of doing a full CCSD(T) calculation [46]. Very recently, Csontos *et al.* [50] have provided a reliable, well-established theoretical estimate for the dissociation energies and heats of formation. In this work, they have tried to resolve the discrepancies

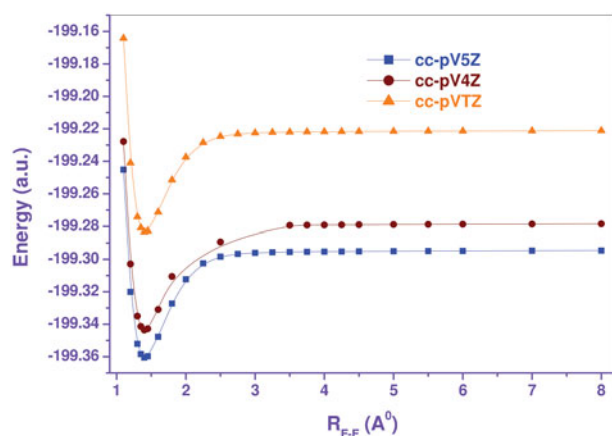


Figure 1. (Colour online) Comparison of $X^1\Sigma^+$ F_2 PESs generated with SS-MRCCSD calculations using cc-pVXZ basis sets.

between the most recently published experimental results for both the thermochemical quantities. In their extensive investigation on the dissociation of F_2 , the reference orbitals for the correlated MR methods have been taken from all-electron CASSCF calculations [i.e. CASSCF (18,10)] and the core orbitals have also been correlated. The computation of the dissociation energy surface of F_2 in the ground state has also been a popular benchmark testing even for current-generation *ab initio* methods because the MR character of the system at large internuclear separations and the presence of low-lying intruder states are known to be the major causes of difficulties for theoretical calculations. To make our conclusions more sound, we have run the calculations for large basis sets which enable a comparison with the experimental data. We have used Dunning's cc-pVXZ bases [31,32] with $X = D, T$ and QZ . The $1s$ core orbitals of F were kept frozen in all calculations. The results obtained by our present calculations for the ground state F_2 are summarised in Figure 1. The dependence of the correlation energy contributions on the basis sets is also evident from Figure 1. As shown in the figure, for the SS-MRCCSD computation, there are no unphysical barriers in the dissociation curves such as those encountered with various theories in the long-range potential of F_2 [39,41–44]). The SS-MRCCSD/cc-pVXZ surfaces closely follow the surfaces/curves obtained via *state-of-the-art* recent calculations [41–46]. From the work of Purwanto *et al.* [40], it has been observed that the DFT local spin–density approximation and generalised gradient approximation of Perdew–Burke–Erzerhof provide very high dissociation energies in comparison to the experimental data. Although the shape of the B3LYP PES is not correct in the intermediate region, the hybrid B3LYP dissociation energy is closer to the experimental value. They have also found that in the case of F_2 with the cc-pVXZ basis, the RCCSD(T) method breaks down in the dissociation limit. On the other hand, the PES provided by UCCSD(T) is correct in the dissocia-

tion limit, but the shape of the surface near the equilibrium distance is distorted in nature, which invites a significant error in the intermediate geometries. In that paper, they have shown that with a single determinant $|\phi^{UHF}\rangle$, the auxiliary-field quantum Monte Carlo (AF-QMC) PES of the difficult F_2 molecule is qualitatively incorrect in the intermediate dissociation region [40]. Recent work of Pittner and co-workers [49] reports PESs and spectroscopic constants for the F_2 molecule in its ground state by exploiting explicitly correlated (F12) Mukherjee's MRCC (coined here as Mk-MRCCSD(T)F12) method. These results are also useful for comparisons presented in this work.

It is worth mentioning here that the existence of a barrier along the dissociation surface of F_2 has been confirmed by various workers [43,50] at various levels of *ab initio* methods. However, we have not found any trace of the barrier along the dissociation surface of F_2 . No barrier has also been observed in the previous works [25,36–40,45,46,48].

To judge the quality of the computed energy surfaces, in Table 1 we report the SS-MRCC R_e (Å), D_e (kcal mol $^{-1}$), ω_e (cm $^{-1}$), and $\omega_e x_e$ (cm $^{-1}$) of F_2 . Our spectroscopic constants have also been compared with the results of other theoretical estimates to illustrate the quality of our computation. The agreement of our CBS-extrapolated spectroscopic parameters at the SS-MRCCSD level with the Mk-MRCCSD(T) variants [24,49] is in general very good, which confirms that the singles–doubles approximation for the correlation treatment with RHF orbitals does not lead to a noticeable deterioration of the accuracy in comparison to the perturbative triples correction. Our results are also in good agreement with the spectroscopic constants of Purwanto *et al.* [40]. The spectroscopic constants of Purwanto *et al.* obtained by fitting the calculated AF-QMC PES (with a cc-pVQZ basis) to a three-term extended Morse curve are R_e (Å) = 1.411 and ω_e (cm $^{-1}$) = 912. Comparisons have also been provided with the results obtained via correlation energy extrapolation by intrinsic scaling (CEEIS) to approximate the FCI energy [43,44] to judge our results. The SS-MRCC results with different basis sets show how an increase in the size of basis sets affects the accuracy of the evaluation of the spectroscopic constants. Overall, our estimated spectroscopic constants for the F_2 system move towards the experimental measurements with the increasing size of the basis set. In general, the performance of our SS-MRCC method is converging in nature with the size of basis sets. The spectroscopic constants obtained with the SS-MRCC/CBS are also in good accordance with the values obtained by the current-generation calculations performed by various workers [24,25,36,41–44].

As seen in Table 1, the errors in the computed spectroscopic constants are usually large for several of the methods for the cc-pVDZ basis relative to that of the other bases. It is important to realise, however, that the poor performance of various methods for the cc-pVDZ basis is not due to its inability to describe charge transfer components

Table 1. Spectroscopic constants for the electronic ground state of the F₂ molecule.

Reference	Method	Basis	R_e (Å)	D_e (kcal mol ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	
Present	SS-MRCCSD	cc-pVDZ	1.4553	31.5	875.8	12.1	
		cc-pVTZ	1.4204	39.0	921.6	11.9	
		cc-pVQZ	1.4109	40.8	925.4	11.7	
		CBS	1.4056	41.75	926.3	11.57	
Ref. [37]	CCSD(T)	cc-pVQZ	1.413	36.7	921		
Ref. [38]	CCSD(T)	cc-pVCV6Z	1.409	36.0	955		
Ref. [25]	SRCCSD(T)	cc-pVDZ	1.4577	27.3	787	11.1	
		cc-pVTZ	1.4154	34.6	923	11.3	
		cc-pVQZ	1.4124	36.5	925	10.8	
		cc-pV5Z	1.4089	37.7	935	10.8	
		∞	1.4089	37.7	935	10.8	
		BW-MRCCSD	cc-pVDZ	1.4469	37.6	821	
			cc-pVTZ	1.4060	46.8	953	
			cc-pVQZ	1.4024	49.0	955	
			CBS	1.3988	50.8	963	
		Mk-MRCCSD	cc-pVQZ	1.4093	41.2	926	
CBS	1.4057		42.6	934			
Ref. [24]	Mk-MRCCSD(T)	CBS	1.4192	36.02	889		
Ref. [49]	Mk-MRCCSD(T)/HF orbitals	CBS	1.4171	34.5	887	11.1	
	Mk-MRCCSD(T)/CAS orbitals	CBS	1.4181	34.5	883	11.7	
Ref. [43]	CEEIS(3c)		1.4135	38.22	915.102	11.0420	
	CEEIS(3c)		1.4135	38.24	914.444	11.0206	
	El. sp. best PES				917.067	11.4369	
	El. sp. direct fit				917.104	11.4835	
Ref. [45]	Mk-MRCCSD-F12	cc-pVDZ	1.4256	49.12	913	9.1	
		cc-pVTZ	1.4081	43.12	930	11.0	
		cc-pVQZ	1.4060	41.74	935	10.9	
		cc-pV5Z	1.4070	41.28	932	10.8	
		cc-pVTZ-F12SP	1.4054	41.51	937	10.9	
		cc-pVQZ-F12SP	1.4076	41.04	932	10.7	
		cc-pV5Z	1.4197	35.05	890	11.3	
Ref. [49]	Mk-MRCCSD(T)-F12/HF orbitals	cc-pV5Z	1.4197	34.6	889	11.3	
	Mk-MRCCSD(T)-F12/CAS orbitals	cc-pVQZ-F12	1.4197	34.6	889	11.3	
Ref. [48]	Best FC+CV+SR		1.4089	38.4	930.2		
Ref. [51]	Experiment (Huber and Herzberg)		1.41193		917	11.2	
Ref. [66]	Experiment (Yang <i>et al.</i> [55])			38.34			
	Stimulated Raman (Martínez <i>et al.</i> [54])		1.412642		916.929	11.3221	

Ref. [43]: the best *ab initio* PES of F₂ with basis-set extrapolated full valence correlation energy and corrections for core–valence correlation, SO coupling, and scalar relativistic effects was recently reported in the work of Bytautas *et al.*

Best CCSD(T) component estimates based on: $D_e = \text{CCSD(T)(FC)/CBS(aV789Z)} + \text{CCSD(T)(CV)/CBS(wCVTQ5)Z} + \text{CCSD(T)(FC)-DKH/cc-pV5Z-DK}$.

of the wavefunction, but rather it is due to an inflexibility of the valence region itself. Extrapolating to the CBS limit leads to a slight shortening of the bond length. We note that the CBS-extrapolated values show that SRCCSD(T), Mk-MRCCSD, and BW-MRCCSD underestimate the F–F bond length (Å) by 0.0030, 0.0062, and 0.0131, respectively, with respect to the experimental estimate by Huber and Herzberg [51]. SS-MRCCSD/CBS underestimates the equilibrium F–F bond length by 0.0063 Å. The SS-MRCCSD/CAS(2,2) calculation provides an equilibrium F–F bond length in the CBS limit of 1.4056 Å, as compared to 1.4089 Å from the very recent best estimated (FC+CV+SR) calculation of Feller *et al.* [48]. The present CAS(2,2)-based SS-MRCCSD calculation generates a PES for F₂ that yields an equilibrium bond length again in close agreement with the CEEIS values (quoted in Table 1) of Bytautas *et al.* [42,44]. The equilibrium distance obtained by

SS-MRCCSD/CBS also agrees very well with the explicitly correlated results (obtained via CC-5/R12+relativity, all-electron correlation calculation) of Ruden *et al.* [52] ($R_e = 1.4122$ Å) and Heckert *et al.* [53] ($R_e = 1.4118$ Å). Our estimated R_e for F₂ in the CBS limit deviates only by 0.007 Å from the value of the high-resolution stimulated Raman spectroscopy experiment [54] which indicates that the SS-MRCC method even at singles–doubles approximation is very effective to compute the equilibrium bond length of the F₂ system. According to Table 1, our SS-MRCCSD calculation in the CBS limit (and also with the largest basis set) agrees well with the current-generation *state-of-the-art* calculations [24,25,36–40,45,46,48,49].

We now focus on the results of vibrational frequencies. The sixth column of Table 1 contains data based on other current-generation works. By far, the most accurate of them are those by Ruden *et al.* [52] and Bytautas *et al.* [42,44].

The vibrational frequency of F_2 computed by SS-MRCCSD with the largest basis sets and SS-MRCCSD/CBS agrees very well with those of experimental results available from high-resolution electronic spectroscopy [51] and from high-resolution stimulated Raman spectroscopy [54]. In the CBS limit, SS-MRCCSD overestimates the harmonic frequency by around 9 cm^{-1} with respect to the accepted experimental values [51,54]. One can see from this table that the frequency obtained with CCSD(T)/best FC+CV+SR due to Feller and co-workers [48] is larger by 13 cm^{-1} over experiment. In the CBS limit, Mk-MRCCSD and BW-MRCCSD overestimate the harmonic frequency by 17 and 46 cm^{-1} , respectively. On the other hand, Ruden *et al.* [52] obtained a value of $\omega_e = 918.9\text{ cm}^{-1}$ (which is based on a high-level CC5/R12 theory including core correlation and relativity corrections), that is, about 1 cm^{-1} larger than the experimental values [51,54]. The same excellent agreement is also found in the case of the values of Bytautas *et al.* [42,44]. The values obtained from the theoretical works of Bytautas *et al.* [42,44], identified as CEEIS in Table 1, differ from the converged experimental values by $\sim 2\text{ cm}^{-1}$ which is contingent upon the explicit inclusion of the effects of core-generated electron correlation, SO coupling, and scalar relativity. It should be noted that most of the other theoretical results (including SS-MRCCSD) listed in Table 1 do not include the contribution due to core–electron correlations and relativity effects (including SO coupling). We can see from Table 1 that all the theoretical results intrinsically overestimate the harmonic frequency of F_2 , while SS-MRCCSD/cc-pVDZ underestimates it. At this point, it is worth mentioning that SRCCSD/CBS overestimates ω_e by more than 100 cm^{-1} , whereas BWCCSD and apB-WCCSD, respectively, overestimates and underestimates the frequency by 46 and 29 cm^{-1} (see Refs. [24,25] for details). Correction due to the triple excitations improves the ω_e value for SRCCSD. The SRCCSD(T) result in the CBS limit deviates from the experimental results by within 20 cm^{-1} .

As with R_e and ω_e , anharmonic constants with SS-MRCCSD agree very well with those of CEEIS and El. sp. best PES [42,44], the maximum deviation (overestimation) of 0.10 cm^{-1} from experiment occurring for the SS-MRCCSD/CBS level of calculation. The corresponding overestimation (i.e., error) in CEEIS and El. sp. best PES [42,44] is around 0.3 and 0.10, respectively, in cm^{-1} . Therefore, the CEEIS calculation with correction for effects of core-generated electron correlation, SO coupling, and scalar relativity leads to errors of similar magnitude to that of our SS-MRCCSD ones. The high accuracy of harmonic frequency and anharmonicity constant indicates the quality of our computed PES.

The dissociation energies, D_e , obtained by SS-MRCCSD with different bases are assembled in the fifth column in Table 1. The importance of using large basis sets and extrapolations to the CBS limit to assess the accu-

racy of the SS-MRCC dissociation energies is abundantly clear in this table. Compared to the experimental value of Yang *et al.* [55], our SS-MRCCSD/CBS dissociation energy is higher by 3.4 kcal mol^{-1} . The *ab initio* calculation of Feller *et al.* [48] overestimates the D_e value by $0.04\text{ kcal mol}^{-1}$, whereas the CEEIS calculation due to Ruedenberg and co-workers [42,44] underestimates it by $\sim 0.2\text{ kcal mol}^{-1}$. At this juncture, it is worth stressing that Feller and co-workers [48] investigated the influence of different factors that contribute to the estimation of dissociation energy and other molecular structural properties. Beyond the extrapolated FC-CCSD(T) calculation, their composite approach incorporated the extrapolated core–core and core–valence contributions in the frame of CCSD(T) and CCSD(T) with perturbative quadruples [CCSD(T)(Q)], estimated FCI energies along with second-order Douglas–Kroll–Hess (DKH) computations, as well as harmonic and anharmonic contributions to the zero-point vibrational energy. With the ic-MRCI+Q [38], BW-MRCCSD/CBS, and Mk-MRCCSD(T)/CBS methods, we have observed errors of -1.6 , 12.5 , and $-2.32\text{ kcal mol}^{-1}$ in D_e , respectively. The agreement between our computed SS-MRCCSD/CBS and W4.4 [56] values is very good indeed. The application of the most recent variant of the Weizmann-n (Wn) family of model chemistries such as W4.4a and W4.4a yielded 38.25 and $38.24\text{ kcal mol}^{-1}$, respectively. Therefore, our prediction is acceptably accurate as compared to experiment [54]. Our estimated D_e at the CBS limit is also in agreement with the theoretical value of $38.33\text{ kcal mol}^{-1}$ given by Csontos *et al.* [50]. Csontos *et al.* [50] used an approach that is similar to HEAT, which involved CV basis sets up through 8ξ , combined with higher order corrections from CC theory through CCSD(T)(Q) and CCSD(T)(Q)(P) $_{\lambda}$. Therefore, our result is in good agreement with several previous reliable theoretical findings. Our theoretical value in the CBS limit is in close agreement with the D_e ($= 38.23\text{ kcal mol}^{-1}$) listed in the Active Thermochemical Tables (ATcT) [57]. From the results shown in the table, it can be seen that for a small molecule such as F_2 , CCSD(T) can yield the spectroscopic constants fairly well, in spite of its inherent failure at large intermolecular separations.

To demonstrate that this high accuracy of the spectroscopic constants obtained via our CAS(2,2)-based SS-MRCCSD without considering core–electron correlations and relativity effects is not a fluke, we also compare our results with the newly developed Mk-MRCC-F12 computations by Demel *et al.* [45]. Notably, the Mk-MRCCSD-F12/cc-pVXZ results are also in close agreement with the SS-MRCCSD/cc-pVXZ ones. It is worth mentioning that compared to the conventional MRCCSD, the results of MRCCSD-F12 calculations exhibit a much faster convergence with the basis-set quality [36], as expected. Furthermore, the dissociation energy of the extended tailored methods (FXTCCSD/cc-pV5Z = 39.04 and XTCCSD/cc-pV5Z = $40.09\text{ kcal mol}^{-1}$) due to Melnichuk and

Bartlett [46] are in very good agreement with the SS-MRCCSD/CBS value, indicating the ability of the XTCCSD(T) method to successfully address the MR problem as seen in the dissociation of a single bond. In this context, it should be noted that the spectroscopic constants computed at the SS-MRCCSD level with the cc-pVQZ basis are close to the corresponding ones obtained by Demel *et al.* [49] using their Mk-MRCCSD(T)-F12/cc-pVQZ variant. In particular, their equilibrium distance is 1.4060 Å, while we obtained 1.4109 Å; harmonic vibrational frequencies and anharmonicity constants are 925.4 and 11.7 cm⁻¹ compared to 936 and 10.9 cm⁻¹, respectively, while the dissociation energy is 41.2 kcal mol⁻¹ compared to our 41.75 kcal mol⁻¹. The gap between experimental and our SS-MRCC values (and other current-generation MRCC estimates) is not really disappointing, as it has been noted many times by several workers that to reach very high accuracy, besides the basis-set convergence, one has to include full-blown triples–quadruples (and higher) excitations as well as non-adiabatic effects in conjunction with relativistic ones [58]. Notably, the Mk-MRCCSD(T)-F12 results with HF orbitals are in close agreement with the Mk-MRCCSD(T)-F12 estimates with CAS orbitals. Both the Mk-MRCCSD-F12 and Mk-MRCCSD(T)-F12 methods yield values of ω_e considerably higher than the present SS-MRCCSD/CBS value. Overall, the importance of using large basis sets along with the extrapolations to the CBS limit to judge the accuracy and consistency of the MRCC spectroscopic constants is abundantly clear from the above discussion and also results assembled in Table 1. The dynamical correlation and higher angular momentum basis functions are also recognised as important elements for the accurate computation of the PES of other dihalogen molecules discussed below. The error due to SS-MRCCSD calculations can be reduced by considering the effects of higher-than-double non-perturbative excitations.

At this point, we judge the quality of the SS-MRCCSD potential for F₂ as obtained via the vibrational energy level calculations. Such computations provide the most rigorous test of the method designed to compute PESs. This is so since the results depend on the accuracy and the correctness of the computed PES. In fact, for modern structural computations using the the state-of-the-art techniques, theoretical computation of vibrational energies along with frequencies has become almost ‘a must’ for elucidating experimental results, as it helps to interpret and assign experimental infrared or Raman spectra, especially in difficult and questionable cases. It is also worth stressing that the vibrational spectra of diatomic molecules probably furnish the most exacting data available for probing energetic changes along the entire reaction path. They therefore present good tests for *ab initio* methods that aim at describing reaction paths. The approach followed here has proved the method to be a reliable one and has met the expectations as stated above.

Laidig *et al.* [59] performed one of the earliest *ab initio* studies on the vibrational levels of F₂. They calculated the vibrational energy spacings of the lowest five levels using an MR linearised CC method and a basis set of ‘better than’ double zeta plus polarisation quality. The errors in the vibrational level spacings of F₂ vary from 83 to 111 cm⁻¹. There also exists an *ab initio* study [60] of vibrational levels in three electronically excited singlet states of F₂, five levels in two Π states, and 30 levels in a Σ state. Here, the deviations on the calculated harmonic frequencies from the experimental data range from ~ 100 to ~ 700 cm⁻¹. In this context, we also mention investigations of the lowest vibrational levels of the ground state of F₂ [61–63]. The 0→1 transition energy was obtained within 1.7 cm⁻¹ in Ref. [61] and within 48.8 cm⁻¹ in Ref. [63]. Le Roy [64] has discussed in detail how to take long-range interactions into account when deducing dissociation curves following the Rydberg–Klein–Rees procedure from vibrational spectra, a complement that is essential for an accurate determination of dissociation energies by this route. Although the F₂ molecule has been treated in several studies, the best of these by Bytautas *et al.* [42,44] includes core correlations and relativistic effects. The full theoretical route from the *ab initio* calculation of the PES to the entire vibration–rotation spectrum has been traversed by them, without any empirical adjustments, in the ground state of the F₂ molecule. A calculation of a part of the vibrational spectrum of F₂ has been done by Varandas [65] very recently.

The vibrational energy values for the ground electronic state of F₂, as obtained with the SS-MRCCSD method in conjunction with the aug-cc-pVTZ basis set for the first 22 vibrational levels, are given in Table 2. In our present work, we have not considered the higher vibrational levels. Colbourn *et al.* [66] have spectroscopically determined the vibrational levels from $v = 0$ to $v = 22$ of the $^1\Sigma_g^+$ state of F₂. They concluded that the dissociation limit must be higher than the highest observed vibrational level. They further pointed out that an extrapolation of the vibrational levels beyond $v = 22$ to the dissociation limit would be difficult because the gaps between the high vibrational levels are very small and vary rapidly. Moreover, a correct estimation of higher vibrational levels is further hampered due to the intricate or complex interactions of various electronic energy states. In Section IV A of Ref. [42], Ruedenberg and co-workers have mentioned that in the range of internuclear distances (about twice the equilibrium distance), the $^1\Sigma_g$ ground state intersects a $^3\Pi_u$ state, which lies lower at larger internuclear separations. Therefore, there exists a possibility of a non-adiabatic coupling in association with the SO coupling as addressed by Ruedenberg and co-workers in Ref. [42,44]. This intricate interaction may influence the energies of the high-lying vibrational levels. Our theoretically calculated vibrational spectra are compared with the experimentally observed spectrum. Each row in the table is labelled by the vibrational quantum number v in the first

Table 2. Comparison between experimental and *ab initio* calculated vibrational energy level differences $G(v) = G_v - G_0$ in the electronic ground state of F_2 (in cm^{-1}). Entries listed in the third, fourth, and fifth columns are the deviations of the theoretically calculated levels from the corresponding experimental spectroscopic values, i.e., $\Delta(v) = G(v; \text{theor.}) - G(v; \text{expt.})$.

Vibrational levels	Experiment [66]	$\Delta(v)_{\text{CBS}}$ [42]	$\Delta(v)_{(\text{CBS} + \text{CV} + \text{SO} + \text{SR})}$ [42]	$\Delta(v)_{\text{SS-MRCCSD (aug-ccpVTZ)}}$
0	0.00	0.0	0.00	0.00
1	893.90	3.14	-1.82	1.96
2	1764.15	6.41	-2.96	3.81
3	2610.22	9.69	-3.52	5.40
4	3431.53	12.89	-3.63	6.60
5	4227.43	15.94	-3.35	7.38
6	4997.19	18.85	-2.73	7.75
7	5740.05	21.60	-1.84	7.75
8	6455.17	24.22	-0.71	7.48
9	7141.63	26.77	0.62	7.09
10	7798.48	29.29	2.07	6.74
11	8424.67	31.86	3.58	6.65
12	9019.11	34.55	5.00	7.04
13	9580.63	37.40	6.17	8.16
14	10108.02	40.45	6.79	10.26
15	10599.62	44.06	6.83	13.97
16	11053.90	48.34	5.91	19.70
17	11468.96	53.68	3.74	28.18
18	11468.96	53.68	-0.07	43.97
19	12172.25	69.79	-5.94	57.36
20	12452.98	84.18	-12.72	-32.18
21	12678.00	108.31	-18.28	-42.28
22	12830.38	156.70	11.93	-30.60

column. The experimental $G_v - G_0$ values are assembled in the second column in Table 2. It is important to note that the transition energies, i.e., the level differences $G_v - G_0$, can be measured experimentally. The remaining columns in Table 2 provide theoretical estimates in terms of the deviation with respect to the corresponding experimental values: $[\Delta(v) = G(v, \text{theor.}) - G(v, \text{expt.})]$. The third column lists the theoretical non-relativistic CBS spectrum (correlation only between valence electrons) where the dissociation surface was calculated using the CASSCF and MR-CISD levels of theory (including the Davidson correction, MR-CISD+Q). Additional contributions due to core-core and core-valence correlations, SO coupling, and scalar relativistic effects are taken into account in the results reported in the fourth column. The results reported in the third and fourth columns are taken from Table IV of a previously published paper by Bytautas *et al.* [44]. In the last column, we have tabulated our present estimates. The row below $v = 22$ lists the mean absolute deviation (MAD) for each method. Our findings are in good agreement with those obtained by experiment [66]. A comparison of our theoretical spectrum with the experimental spectrum, which had been measured earlier using high-resolution electronic spectroscopy [66], yields an MAD of about 10 cm^{-1} and a minimum of 2 cm^{-1} over the first 14 levels. Almost the same kind of accuracy is obtained for the lower vibrational levels. However, this deviation increases up to 57 cm^{-1} at the $v = 19$ vibrational level. In the case of present calculations, the inaccuracies

for the highly excited vibrational levels possibly can be explained by two factors. First, one expects the description of the energy surface at very low bond lengths to be less accurate, as the interaction between the valence wavefunctions of one atom with the core of the other one is also important for high-lying vibrational levels. Second, there is a total neglect of the relativistic effect(s), which may be crucial in the region of large bond distances. Our observation is also in accordance with the theoretically observed (CBS+CV+SO+SR) vibrational spectrum of Bytautas *et al.* [44]. With the SS-MRCCSD method, we get errors for the vibrational energies having magnitudes similar to those of the errors of the CEEIS treatment which are based on the explicit inclusion of the effects of core-generated electron correlation, SO coupling, and scalar relativity [44]. It is also noteworthy that in our present work, we have exploited CAS(2,2), whereas Bytautas *et al.* used CASSCF in a full valence space. Moreover, vibrational levels obtained from SS-MRCCSD/aug-ccpVTZ PES are also close in proximity with the best estimated CBS values of Bytautas *et al.* [44] obtained by MRCIS-SD+Q calculations incorporating contributions of all-electron correlation in conjunction with SO and scalar relativistic effects. As shown in Table 2, the inclusion of (core-core + core-valence) correlations, SO coupling, and relativistic effects in the valence correlation treatment by utilising MR-CISD+Q calculations decreases the error gap between the experimental results [66] and the theoretical values obtained by Bytautas *et al.* [44].

It should be mentioned here that, in the case of the ground state of F_2 , there is practically no difference in the ω_e values obtained by the analysis of vibrational spectrum and PES. These two values differ by at most a couple of cm^{-1} . The vibrational spectrum of F_2 obtained via the SS-MRCCSD/aug-ccpVTZ energy surface is found to be very accurate. It should be noted that we are able to provide vibrational energy levels with as uniform an accuracy as possible. It is worth noting that we have made no special effort in refining the energy surface obtained via SS-MRCCSD/aug-ccpVTZ calculations and its curvature near the minimum by calculating many energies near the equilibrium distance. In view of this success for one of the more difficult systems such as F_2 , we expect the SS-MRCC methodology to be capable of producing PESs of similar accuracy also for other systems.

We conclude this part by highlighting that the CAS-based SS-MRCCSD formalism can not only yield highly trustworthy PESs even when employed within the smallest of model spaces (thus showing a promise towards better convergence features proportional to the size of the basis sets), but also offer a considerable faith when generating the vibrational spectrum.

2.2. Chlorine molecule (Cl_2)

Molecular chlorine (Cl_2) continues to serve as a benchmark system to study photodissociation dynamics, and many experimental [51,67,68] and theoretical [69–75] studies have been reported. The first *ab initio* PES for the Cl_2 molecule was computed by Peyerimhoff and Buenker [69]

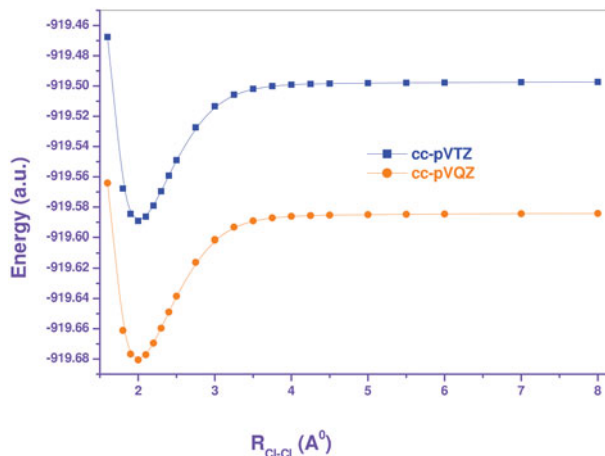


Figure 2. (Colour online) Illustration of the effect of basis-set sizes on the topology of $X^1\Sigma^+ Cl_2$ PESs computed at the level of SS-MRCCSD.

more than 25 years ago and served as the main theoretical basis for analysis of experimental data. In Figure 2, we plot the energy surface of $X^1\Sigma^+ Cl_2$ obtained by SS-MRCCSD with cc-pVXZ basis sets. The topology of the energy surfaces obtained by SS-MRCCSD is almost identical to the shape of the PES obtained via MRCISD calculation in conjunction with SO coupling (SO-MRCISD) at both large and small bond lengths (Figure 2 of Ref. [68]). Table 3 displays the spectroscopic properties derived from the energy surfaces and the results are in good agreement with the available experimental data [51,67,68]. As for F_2 , here we have also obtained consistently

Table 3. Spectroscopic constants for the electronic ground state of the Cl_2 molecule.

Reference	Method	Basis	R_e (Å)	D_e (kcal mol $^{-1}$)	ω_e (cm $^{-1}$)	$\omega_e x_e$ (cm $^{-1}$)
Present	SS-MRCCSD	cc-pVDZ	2.0339	47.52	511.78	2.0127
		cc-pVTZ	2.0044	57.60	550.60	1.9660
		cc-pVQZ	1.9935	56.48	556.18	2.1270
		CBS	1.9871	59.07	558.60	2.2375
Ref. [72]	TZVP	LC-CEPA-3	1.989		585.8	
		LC-CEPA-3+TQ/col/line	2.016		533.9	
		LC-CEPA-3+TQ/explicit	2.013		539.1	
		CCSD	2.003		559.0	
		CCSD(T)	2.011		543.1	
Ref. [69]	MRCISD	[5s5p2d]	3.817	57.42	552	
Ref. [70]	MRCISD	[10s7p2d]	3.820	59.33	560	2.87
Ref. [71]	CCSD(T)	aug-cc-pV(6+d)Z	1.9907		562.7	
		CBS(FC)+CV+ est. FCI	1.9857		563.7	
Ref. [74]	SOCI	[5s5p2d1f1g]	2.017	53.73	549.7	2.78
Ref. [68]	SO-MRCISD	[7s6p3d2f]	2.013	55.34	549	2.98
Ref. [73]	COSCI	aug-cc-pVTZ	1.987	57.88	563	2.86
Ref. [51]	Experiment		1.988	57.07	564.9	
Ref. [67]	Experiment				559.71	2.70
Ref. [68]	Experiment				559.72	2.72

Ref. [72]: LC-CEPA-3+TQ stands for a local contracted single and double configuration interaction (LC-CISD) augment by CEPA-3 like dressing and leading part of linked effects of triples (T) and quadruples (Q) through a series of local four-electron full CI calculations.

correct topological descriptions (without any shoulder) for Cl_2 along a wide range of bonding coordinates with different basis sets, and hence the Dunham method provided very encouraging spectroscopic constants with good accuracy. Inspection of Table 3 shows that although MRS-DCI [69,70] gives a qualitatively correct description of the general trend of the spectroscopic parameters, the absolute error with respect to experiment is higher than that of our SS-MRCCSD values. Our calculated properties for Cl_2 are in good agreement with the best estimated values of Feller and co-workers [71] obtained via CCSD(T)/aug-cc-pV(6+d)Z and CCSD(T)/[CBS(FC)+(CV)+(est. FCI)] calculations. From Table 3, it can be seen that our theoretical results are in better agreement with available experimental data than those of estimates obtained via LC-CEPA-3+TQ/TZVP calculations by Zhang *et al.* [72], indicating that the non-dynamical correlation plays an important role in the computation of PESs. Our results are significantly better than those of CCSD and CCSD(T) values of Zhang *et al.* [72]. It should be noted that the results of LC-CEPA-3+TQ with first column/line and explicit vector dressings are very similar to CCSD ones [72]. As observed in Table 3, the relativistic study within a four-component relativistic framework using the MOLFDIR program package [73] results in much improved agreement with experiment. In Ref. [73], Macedo and de Jong determined a set of electronic energies at different internuclear distances for the ground state and 22 lowest excited states of the Cl_2 molecular system calculated via the four-component relativistic complete open shell CI (COSCI) approach. In contrast to previous theoretical data obtained by Kokh *et al.* (via SO-MRCISD) [68] as well as Asano and Yabushita (using SOCI) [74], our estimated spectroscopic properties for the ground state of Cl_2 are found to be in better agreement with experimental results [51,67,68].

2.3. Bromine molecule (Br_2)

In order to further test the SS-MRCCSD method, we have computed energies and spectroscopic constants for $^1\Sigma_g^+$ Br_2 . Figure 3 summarises the results of the SS-MRCCSD calculations for Br_2 , and the calculated spectroscopic parameters for these PESs are presented in Table 4 together with available experimental data and results from other theoretical works. As in the case of F_2 , extrapolating to the CBS limit yields a slight shortening of the bond length in the case of Cl_2 and Br_2 . Comparing our results with the experimental values available, we found that all the calculated bond lengths for Br_2 are slightly longer than the experimental results, and the reverse is true for Cl_2 . We have observed that the spectroscopic constants for the Cl_2 and Br_2 systems obtained from SS-MRCCSD with a good basis are accurate even on the exclusion of the relativistic effects. We should mention here that the incorporation of the relativistic effect is very crucial to reach the numerical accuracy

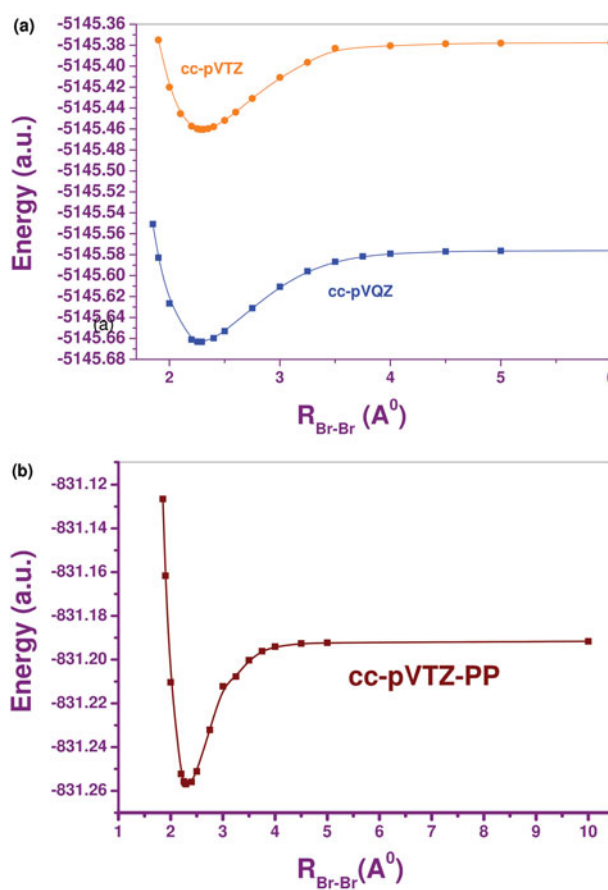


Figure 3. (Colour online) Illustration of the effect of basis-set sizes on the topology of $X^1\Sigma^+$ Br_2 PESs computed at the level of SS-MRCCSD: (a) calculation with cc-pVXZ basis sets and (b) calculation with relativistic pseudo-potential basis sets.

for large systems such as Br_2 and I_2 . As demonstrated by Feller *et al.* [71], both molecular core–valence correlation and molecular SO coupling have modest influence (around $0.8 \text{ kcal mol}^{-1}$) on the value of dissociation energy, D_e , of Br_2 . From the all-electron calculations on Br_2 , both with (cc-pV5Z-DK basis set) and without (cc-pV5Z basis set) relativistic effects using the DKH Hamiltonian, by Dolg and co-workers [34], the effects of scalar relativity on the spectroscopic constants are determined to be -0.0023 \AA on R_e , 1.2 cm^{-1} on ω_e , and $20.54 \text{ kcal mol}^{-1}$ on D_e . As reported by Feller *et al.* [71], both core–valence correlation and SO coupling have modest effects on the D_e of Br_2 , increasing it by $\sim 0.8 \text{ kcal mol}^{-1}$. The most simple and straightforward way to incorporate the scalar relativistic effects is through the use of relativistic PPs, which are constructed from fully relativistic all-electron atomic calculations. As a result of this, in such heavy systems, relativistic PPs not only diminish the number of electrons and basis size, but also, more importantly, help to incorporate scalar relativistic effects in a non-relativistic-like computation. The PPs introduced with cc-pVXZ-PP [34] are of very

Table 4. Spectroscopic constants for the electronic ground state of the Br₂ molecule.

Reference	Method	Basis	R_e (Å)	D_e (kcal mol ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)
Present	SS-MRCCSD	cc-pVDZ	2.3697	51.45	293.74	1.523
		cc-pVTZ	2.2976	53.95	322.60	1.519
		cc-pVQZ	2.2800	55.26	327.38	1.504
		CBS	2.2706	56.05	329.61	1.4939
		cc-pVTZ-PP	2.2929	54.97	333.47	1.408
Ref. [71]	CCSD(T)	aug-cc-pV5Z	2.2945		327.4	
	CCSD(T)	CBS(FC)+CV+ est. FCI	2.2816		330.3	
Ref. [34]	CCSD(T)	cc-pVDZ-PP	2.3406	38.10	300.0	1.16
	CCSD(T)	cc-pV5Z-PP	2.2920	50.85	326.1	1.01
Ref. [78]	CCSD(T)	All-electron/cc-pV5Z-DK	2.2921	50.86	326.3	1.01
	CCSD(T)-F12x	cc-pVDZ-F12	2.2764		330.7	1.02
		cc-pVTZ-F12	2.2793		328.8	1.02
		cc-pVQZ-F12	2.2767		330.5	1.01
		aug-wCV[Q5]Z-PP	2.2740		331.2	0.99
Ref. [80]	CCSD(T)-F12b/valence	VDZ-F12-F12	2.2899 (2.2760)	51.41 (51.04)	327.83 (329.57)	1.01 (1.02)
		VDZ-F12-F12	2.2914(2.2779)	51.06 (51.23)	325.95 (328.31)	1.01 (1.02)
		VDZ-F12-F12	2.2894 (2.2762)	51.53 (51.90)	327.44 (330.23)	1.01 (1.01)
Ref. [76]	CCSD(T)	CBS	2.2874 (2.2740)	52.09 (52.54)	328.18 (331.23)	0.99 (0.99)
	AF-QMC	cc-pVDZ-PP	2.321	42.1	314	
	AF-QMC	cc-pVTZ-PP	2.279	52	336	
Ref. [77]	DMC/1-det		2.274	50.6	346	
	DMC/multideterminant		2.286	49.46	323	
Ref. [81]	NR-CCSD(T)	pVTZ	2.315	46.1	316	
	DC-CCSD(T)	pVTZ	2.361	39.1	312	
	DHF-CCSD(T) (Ext. Basis)		2.685	35.283	217	0.58
Ref. [51]	Experiment		2.2810	45.9	325.31	1.079

Ref. [77]: quadrupole-zeta quality basis set by augmenting the triple-zeta sets with (1s, 1p, 1d, 1f, 1g) uncontracted functions and optimising the exponents at the RHF level.

Ref. [80]: The entries in parentheses indicate the results corresponding to the (val+3d) Correlation space. The CBS [79] reference values were obtained from extrapolation of conventional CCSD(T)/aug-cc-pwCVnZ-PP calculations with $n = Q$ and 5.

high quality, as has been checked by comparing relativistic all-electron estimations with those obtained using these PPs [34]. Considering this aspect, we have also computed PESs and spectroscopic constants of Br₂ using the cc-pVTZ basis in conjunction with pseudo-potentials. In Table 4, we summarise our estimates of the dissociation energy, equilibrium bond length, angular frequencies, and anharmonicity constant for Br₂ using the SS-MRCCSD method with the cc-pVTZ-PP basis set. As shown in the table, the deviation of our SS-MRCCSD results with cc-pVTZ-PP from experimental estimates is also acceptably small. SS-MRCCSD/cc-pVTZ-PP results also indicate that the results obtained via SS-MRCCSD with correlation consistent non-relativistic basis sets are in acceptably good agreement. Our results are also in very good agreement with the previous relativistic (CCSD(T) + all-electron/cc-pV5Z-DK) results [34]. In Br₂, the discrepancy between the SS-MRCCSD/cc-pVTZ-PP and experimental dissociation energies could be also due to the large-core pseudo-potential. Table 4 shows that the SS-MRCCSD/cc-pVXZ-PP and AF-QMC/cc-pVXZ values [76] exhibit roughly comparable agreement with exact values in the case of Br₂. In passing, we also mention that the diffusion Monte Carlo (DMC) values [77] obtained with single and multiple determinants agree well with our

estimated dissociation energies, vibration frequencies, and equilibrium bond lengths of Br₂, indicating the quality of our computations. In the DMC calculations, Al-Saidi [77] used the recent scalar-relativistic energy-consistent HF pseudo-potentials which are non-singular at the origin. It is worth noting that the DMC/multideterminant values are generally in better agreement with the experimental values. Furthermore, a comparison with the results obtained via the computation of an explicitly correlated CCSD(T)-F12 method with orbital-pair-specific Slater-type geminals [78] also supports the accuracy and reliability of SS-MRCCSD results for Br₂. Our spectroscopic constants extracted from SS-MRCCSD/cc-pVTZ-PP PES are also in good agreement with results of FC-CCSD(T)/CBS [79] and CCSD(T)-F12 [80]. In a nutshell, the results using SS-MRCCSD/cc-pVTZ-PP show good agreement with those obtained via the recently developed explicitly correlated CC method(s) which include high-level correlation corrections, core correlation, scalar relativistic effects, and SO effects [78,79] confirming the utility of the SS-MRCC method. It is worth noting that spectroscopic constants for Br₂ obtained from CCSD(T) calculations [34,71] with very large basis sets, including the CBS limit, still deviated reasonably from experimental values as that of the present SS-MRCCSD

calculation. However, overall, our results are in good agreement with the previous current-generation estimates considering the size of the basis sets in association with the approximations engaged. An important note concerns the comparison of the SS-MRCCSD values with the experimental values. Although the cc-pVQZ results are very close to the basis-set limits, the deviations from the experimental values are quite large. This might be due to large contributions from higher excitations. The effect emerges mainly from the valence electrons, and is probably due to the rather small highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap in the Br₂ molecule [78]. Table 4 also demonstrates the fact that our results are better than that of the relativistic and non-relativistic CCSD(T) results obtained by Visscher and Dyall [81]. In passing, we should mention that the results of the *ab initio* method based DKH Hamiltonian can help us to identify the impact of the PP approximation in molecular calculations. It should be noted that in Cl₂ and Br₂, core–valence correlation effects are significant, in particular on the equilibrium bond lengths and also on the dissociation energy.

2.4. Iodine molecule (I₂)

Finally, we focus on the computation of I₂ as it is one of the favourite species studied in molecular spectroscopy because of its attractive optical properties. One of the difficulties in the theoretical estimation of spectroscopic parameters (considered here) as well as the pre-dissociation dynamics of I₂ arises from the absence of accurate *ab initio* PESs. In general, *ab initio* computations on systems containing iodine are not simple and straightforward, owing to the large number of electrons involved and relativistic effects. The spectroscopic properties of I₂ have been the subject of various experiments [51,82] and theoretical [34,81,83–88] investigations, only a few of which can be cited here. The theoretical determination of the ground state I₂ requires proper accounting for the effects of relativity (in particular, the SO interaction) and correlations. The relativistic effects increase on going from F to I. The majority of the calculations are valence electron calculations, where the core is represented by a relativistic pseudo-potential. It was reported before that core–valence correlation has strong effects on the dissociation energy surface of I₂ [34,71,83]. In the present work, cc-pVDZ-PP and cc-pVTZ-PP basis sets of Peterson *et al.* [34] have been used. As already mentioned, such type of basis sets are very useful to treat relativistic systems using non-relativistic code. The PP has an obvious advantage over the elaborate all-electron correlated basis sets by having a precise accounting of the scalar and SO relativistic effects and by simultaneously being smaller as compared to the all-electron sets owing to replacement of the energetically low-lying core electrons by the effective core potential. For I₂, no extensive studies

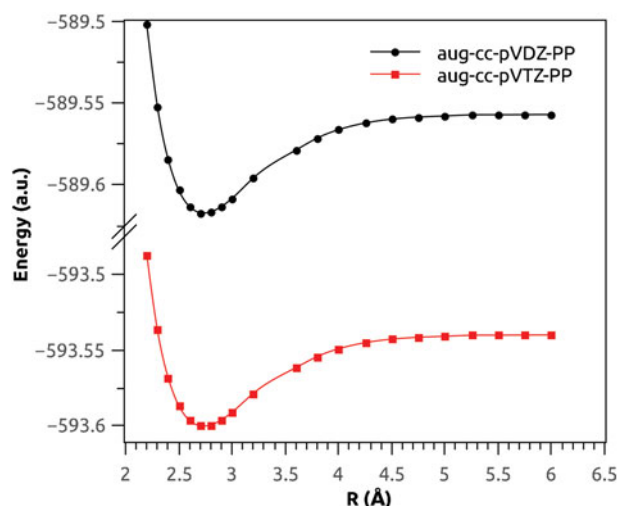


Figure 4. (Colour online) Illustration of the effect of basis-set sizes on the topology of $X^1\Sigma^+$ I₂ PESs computed at the level of SS-MRCCSD.

of basis-set convergence have been carried out. It is important to note that as the basis sets used here are rather small, basis-set superposition errors are not negligible and need to be corrected for. The aim of our present calculations is to demonstrate the applicability of the SS-MRCC method rather than provide definitive potential functions or spectroscopic constants, and basis sets of moderate size are therefore used. Here, the ground state spectroscopic constants of the iodine molecule have been determined through the computation of PESs via our SS-MRCCSD code with cc-pVXZ-PP ($X = D$ and T).

The PESs computed via the SS-MRCCSD method with different basis sets are summarised in Figure 4. SS-MRCCSD gave a qualitatively correct description for the whole region, including the dissociation limit, as the spectroscopic constants indicate. The spectroscopic constants extracted from these PESs are assembled in Table 5. Available experimental data and some previous theoretical results [83,88] are also listed for comparison. In addition, all-electron calculations using the DHK Hamiltonian (cc-pV5Z-DK) [34] have been included in our discussion. To judge the quality of our results, we have also considered the results obtained via the relativistic Fock-space MRCC (RFS-MRCC) method [85,87] and DMC results [77]. From the data assembled in the table, it is evident that the accurate estimation of the spectroscopic constants for I₂ is not only difficult, but also challenging. As shown in the table, the comparison of the SO relativistic effective core potential based FS-MRCCSD (SOREP-FS-MRCCSD) calculation with SS-MRCCSD/cc-pVTZ-PP calculations indicates that SOREP-FS-MRCCSD [87] yields similar bond lengths. Nevertheless, it should be stressed that there is still very good agreement between the average relativistic effective core potential (AREP)-FS-MRCCSD and

Table 5. Spectroscopic constants for the electronic ground state of the I₂ molecule compared to experiment.

Reference	Method	Basis	R_e (Å)	D_e (kcal mol ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)
Present	SS-MRCCSD	cc-pVDZ-PP	2.7284	42.95	210.76	0.75
		cc-pVTZ-PP	2.7195	40.89	214.28	0.77
Ref. [71]	CCSD(T)	aug-cc-pRV5Z	2.6728		220.8	
	CCSD(T)	CBS(FC)+CV+ est. FCI	2.6473		225.2	
Ref. [34]	CCSD(T)	cc-pVDZ-PP	2.7437	33.31	199.1	0.58
	CCSD(T)	cc-pV5Z-PP	2.6755	46.23	221.4	0.52
	CCSD(T)	All-electron/cc-pV5Z-DK	2.6810	45.99	220.9	0.51
Ref. [85]	DC/FS-MRCCSD		2.691	33.90	214	0.50
	DCG/FS-MRCCSD+BSSE		2.711	30.44	209	0.53
Ref. [83]	PP-MCSCF-MRCISD		2.769	17.526	185	0.80
Ref. [81]	NR-CCSD(T)	pVTZ	2.712	42.3	217	
	DC-CCSD(T)	pVTZ	2.717	29.6	206	
Ref. [84]	DHF-CCSD(T)[Ext. Basis]		2.685	35.283	217	0.58
	PP-CCSD(T)		2.685	35.283	217	0.58
Ref. [87]	AREP-FS-MRCCSD		2.678	39.89		
	SOREP-FS-MRCCSD		2.692	29.52		
Ref. [88]	GCS-CI(10,12)	Dyall's VTZ	2.75	19.14	168	
	GMC-PT(10,12)		2.70	32.05	205	
	GCS-CI(10,24)		2.78	23.29	163	
	GMC-PT(10,24)		2.70	31.82	205	
Ref. [77]	DMC/1-det		2.663	46.30	246	
	DMC/multideterminant		2.674	45.76	205	
Ref. [89]	MRCI+Q		2.687	44.9	219.5	0.512
Ref. [91]	CCSD(T)	pVTZ	2.686 (2.703)		214 (204)	
Ref. [51]	Experiment		2.6663	35.90	214.5	0.61

Ref. [91]: the entries in parentheses indicate the results corresponding to the two-component scheme.

SS-MRCCSD/cc-pVXZ-PP results. AREP-FS-MRCCSD [87] and SS-MRCCSD/cc-pVXZ-PP calculations on I₂ also yielded dissociation energies within few kcal mol⁻¹ from each other. Errors of SS-MRCCSD/cc-pVTZ-PP with respect to experiment of about 5 kcal mol⁻¹ imply that the contribution from relativistic and core–valence effects is also important to estimate experiment results. At the MCSCF/MRSDCI+Q level of calculation, Teichteil and Pelissier [83] find a bond distance of 2.75 Å without the SO operator and 2.77 Å with the SO operator, and the ω_e values are 199 and 185 cm⁻¹, respectively. As reported by Feller *et al.* [71], the contributions from molecular core–valence correlation and molecular SO coupling also have strong effects on the D_e of I₂, increasing it by a total of ~4 kcal mol⁻¹. Near the basis-set limit, the DHF-CCSD(T) [81] spectroscopic constants are in very good agreement with the estimates of SS-MRCCSD/cc-pVTZ-PP. The bond lengths, angular frequency, and anharmonicity of vibrations obtained with SS-MRCCSD and RFS-MRCCSD [85] are in good agreement with each other with respect to the experimental results, compared to the dissociation energies. It should be stressed that the dissociation energy for I₂ is 50.37 kcal mol⁻¹ if SO effects have been approximately removed from the experimental dissociation energy using the atomic splitting of Moore [34]. Our results exhibit better overall accuracy and a more uniform behaviour than CCSD(T) [84] even with extended basis

sets in computing spectroscopic constants [81]. CCSD(T) values [81,84] imply that the contribution from non-dynamical correlation should also be considered important to estimate experiment results. On comparison with the all-electron CCSD(T)/cc-pV5Z-DK results also shown in Table 5, it is found that the SS-MRCCSD/cc-pVTZ-PP bond length is larger by around 0.04 Å. The corresponding differences in D_e is about 5 kcal mol⁻¹. It is notable that our SS-MRCCSD/cc-pVTZ-PP dissociation energy for I₂ agrees with the DMC/multideterminant estimates. Our extracted spectroscopic constants are also in agreement with MRCI+Q results of Kalemios *et al.* [89]. Our results are similar to those found in the studies of DIM+SO ($R_e = 2.672$ Å, $\omega_e = 213$ cm⁻¹, and $D_e = 33.30$ kcal mol⁻¹) by Vala *et al.* [90]. Results in Table 5 show that the bond lengths and harmonic frequencies obtained with SS-MRCCSD/cc-pVTZ-PP agree well with those computed with the two-component CC method and CC approach including SO coupling at the HF-SCF level of Wang *et al.* [91]. Our numerical data at the SS-MRCCSD/cc-pVTZ-PP level of theory compare reasonably with the existing experimental values considering the size of the molecule and the approximations engaged.

It is apparent from the aforesaid issues that the differences between our and experimental results are somewhat larger for the iodine cases as compared to the other halogens. To a certain extent, similar observations are also found by other works. Differences of our results with respect to

the experimental ones are as expected due to the omission of core–valence correlation and SO coupling, as well as residual basis-set incompleteness [34,81,83–87]. Teichteil and Pelissier [83] have also studied the importance of core–valence polarisation effects by comparing seven-electron pseudo-potential results with 17-electron pseudo-potential results and have found a small effect ($<0.003 \text{ \AA}$) using the MCSCF/MRSDCI+Q level of theory, but a contraction of 0.02 \AA when using second-order perturbation theory after the MCSCF step. A recent work by [34] where DKMP2 results have been compared with and without correlating the d electrons also has given a contraction of 0.02 \AA . This makes it likely that the core–valence correlation is at least partly responsible for the discrepancy between our results and experimental results. As demonstrated by previously published works [34,81,83–87], both molecular core–valence correlation and molecular SO coupling in conjunction with the basis sets have strong effects on the D_e of I_2 . The relativistic correction for D_e (kcal mol^{-1}) of I_2 is 212.5 due to DKH/VTZ calculations vs. 212.7 of four-component, CCSD(T)/VTZ, where the non-relativistic result is taken from the VTZ D_e of Visscher and Dyall [81] (see Ref. [71]). It is worth noting that the SO splitting of Cl, Br, and I is 881, 3685, and 7603 cm^{-1} , respectively. To improve the calculated spectroscopic properties, core–valence correlation effects can be included in the pseudo-potentials. It can be seen from Table 5 that the present method offers a balanced and economical description of the ground state spectroscopic constants similar in quality to more costly SRCC approaches with higher order cluster operators. As already mentioned, a comparison with other theoretical works is not always straightforward due to method and basis-set differences and also differences in the use of a semi-empirical core–valence polarisation potential in some computations considered here. It is worth noting that the relativistic pseudo-potential schemes in conjunction with the SS-MRCCSD approach reproduce the effects of relativity in a reliable way. We also found that our relativistic pseudo-potential calculations exhibit good agreement with all-electron calculations.

At this point, we would also like to mention that the chemical bonding in dihalogen molecules hides many interesting yet not fully understood specific features. The apparent discrepancy in the bond energies that should decrease as one moves down ($F \rightarrow I$) in the periodic table is one of them. In representative element groups, the homonuclear diatomic bonding dissociation energy decreases as one moves down in the periodic table. However, in the halogen group, the chlorine molecule has the largest bond energy. The bond distance of the fluorine molecule is also considered to be a bit longer than expected for a first-row diatomic molecule. From the present study, it is found that the calculated values of the dissociation energy exhibit the trend $I_2 > Cl_2 > Br_2 > F_2$, as also observed experimentally. This is usually explained by enhanced Pauli repulsion between

the occupied $p(\pi)$ orbitals, which is particularly strong in F_2 because it has the shortest bond of the dihalogens. It is also important to note the similarities and differences in their potential surfaces.

Although the agreement of SS-MRCCSD with sophisticated CC calculations is in general very good, even with larger basis sets (in our series), the spectroscopic constants are still not satisfactorily converged to the spectroscopic accuracy, as one would desire. In contrast to F_2 and Cl_2 , in the more complex systems, Br_2 and I_2 , we have a less satisfactory performance of the SS-MRCCSD scheme. While the calculated results shown here are not free from approximation, and thus not exact, it is nonetheless significant that of all X_2 , Br_2 and I_2 show discrepancy between our calculation and the experimental data. The cause of this discrepancy is: (1) the absence of the relativistic effects in the computation, (2) exclusion of higher than double excitations in the working equations, and (3) the increased number of electrons (implying a rather large CAS). Actually, in F_2 , Cl_2 , and Br_2 , the active orbitals mainly consist of atomic p , d , and f orbitals, respectively. To increase the accuracy, one can suggest the inclusion of appropriate sets of orbitals in the active space. However, the resulting dimension of the CAS space would make the corresponding numerical calculations most unpractical, especially for Cl_2 and Br_2 . Recent studies at the MR-CISD+Q level [41–44] demonstrate the importance of the flexibility of the reference space in the description of PESs in the case of the F_2 molecule. For Cl_2 and Br_2 calculations, using a rather large CAS cannot even provide a qualitatively acceptable form of the PES due to the strong importance of the dynamical correlation of the inner electrons along with relativistic effects. In our opinion, in order to get a quantitative agreement of the spectroscopic constants with the corresponding experimental data, inclusion of the intricate interplay of these effects is inevitable. It is noteworthy that in order to make contact with physical reality, using large basis sets and extrapolations to the CBS limit is essential, though we have not explored this aspect in the case of Br_2 and I_2 . Moreover, the accurate X_2 PES study presented here, for the ground state, is of fundamental importance to many issues, including atom–atom collisions, prediction of cluster structures, and chemical reactivity of the systems.

3. Conclusion

The concept of PESs involving bond breaking is a central idea to the field of reaction dynamics and quantum chemistry. Accurate estimation of PESs, which are contingent upon the accurate treatment of the intricate interplay of non-dynamical and dynamical correlation effects over the dissociation path, is important for any reliable spectroscopic study. In particular, the enormous advances in spectroscopic techniques have prompted such a need. In view of their simplicity, diatomic molecules offer an

important ground for such investigations. The importance of the X_2 ($X = F, Cl, Br, \text{ and } I$) systems as laser media, as well as their important role in atmospheric chemistry, provides motivation for trying to understand them better.

The non-relativistic SS-MRCC method (that relies on a small reference space) with the singles–doubles truncation scheme in conjunction with the correlation consistent basis sets is used to investigate PESs of homonuclear diatomic halogens, X_2 . In the present paper, the contributions of electron correlations involving the core have not been included. The key idea of the MRCC method used here is to treat the largest components of the exact wavefunction on an equal footing by including them in a zeroth-order reference in an intruder-free manner. The method is well defined on the whole PES of a chemical reaction as long as the target state is well separated from the virtual one and if an appropriate active space is chosen. Thus, the method can be very useful in the description of the bond-breaking process and electronic states displaying pronounced quasi-degeneracy. We assess the accuracy of the PES by computing spectroscopic constants using Dunham polynomials analysis (by exploiting sixth-degree polynomial fitting). The complete basis-set limit of these spectroscopic constants has been determined. Our results are in good agreement with the current-generation theoretical estimates and experimental results. Present computations of the PES and spectroscopic constants of X_2 are used to assess the quality of the basis sets with relativistic pseudo-potentials when combined with MRCC. The SS-MRCCSD results also provide evidence for concluding that the basis sets with relativistic pseudo-potentials are adequate for high-accuracy computation of PESs and spectroscopic constants. To established accuracy, we have compared our computed spectroscopic constants with extensive conventional CCSD(T) calculations using a variety of orbital basis sets and different ansätze for the explicitly correlated wavefunctions. Present results bolster our belief that treating the correlation factor separately for each reference is appropriate to compute dissociation energy surfaces.

The ground state SS-MRCCSD/aug-ccpVTZ potential surface of F_2 is also used to compute the vibrational levels up to $v = 22$. Colbourn *et al.* experimentally determined these vibrational spectra by means of high-resolution electronic spectroscopy. The absolute deviation between the first 17 experimentally observed and our calculated levels turns out to be $2\text{--}28\text{ cm}^{-1}$. The maximum deviations, viz., between 28 and 57 cm^{-1} , occur only for the levels $v = 18\text{--}22$. The range of the spectral deviations for the non-relativistic SS-MRCCSD/aug-ccpVTZ potentials can be taken as indicative of the error bar inherent in the present *ab initio* calculations of the vibrational levels. Incorporation of correction due to the core-generated electron correlation and relativistic effect may provide further improvement to the agreement between experimental and our theoretical values. However, the close agreement of our theoretical

vibrational spectrum with the corresponding experimental ones is contingent upon the balanced and accurate treatment of the both correlation effects over the entire range of internuclear distances of $F\text{--}F$, and the reported agreement expressly supports the quality of our computed PES. Our estimated vibrational levels are in good agreement with those obtained from experiment in comparison to the non-relativistic, valence-shell-only correlated CBS estimates of Bytautas *et al.* [44]. The very close agreement between the SS-MRCCSD/aug-ccpVTZ results and the best estimated (which is complemented by determining the energy contributions that arise from the electron correlations that involve the core electrons as well as the contributions that are due to SO coupling and scalar relativistic effects) vibrational energy levels of Bytautas *et al.* [44] is also noteworthy. We should also mention here that the relative accuracy of the computed vibrational energies via the SS-MRCC method in conjunction with small CAS and singles–doubles truncation of cluster operators is non-uniform in nature, which is obviously not desirable. However, the non-uniformity is not significant in general. This is also even in the case of *state-of-the-art* correlation energy extrapolation by intrinsic scaling (CEEIS) calculations by Ruedenberg and co-workers. The present computations further emphasise the utility of the method for theoretical descriptions of the vibrational spectrum of the ground states in MR systems, say, single-bond dissociations. Accuracy of our estimates with respect to experiment can be improved by considering the core–valence correlation and SO coupling as well as basis-set completeness. In the near future, we will also explore more studies to demonstrate how SS-MRCC calculations with different truncation schemes can have an impact on the estimation of the vibrational energy spectrum of interesting and computationally challenging molecular systems.

It is also possible to improve the results of SS-MRCCSD calculations by approximately accounting for higher than double excitations. The accuracy of the SS-MRCC method can be pushed further by taking into account larger CI expansions, i.e., by increasing the dimension of the model space. Finally, the present results with small reference spaces, in conjunction with the previous study of the dissociation energy surface, show that the state specific method of MRCC works well along reaction paths where the zeroth-order reference function is strongly multiference in nature.

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