AMES GRANT
NCC2-371
IN-23-CR
329375
P15

Theoretical study of the C-H bond dissociation energy of acetylene

Charles W. Bauschlicher, Jr. and Stephen R. Langhoff
NASA Ames Research Center
Moffett Field, CA 94035

Peter R. Taylor
ELORET Institute[†]
Sunnyvale, CA 94087

Abstract

We present a theoretical study of the convergence of the C-H bond dissociation energy (D_0) of acetylene with respect to both the one- and n-particle spaces. Our best estimate for D_0 of 130.1±1.0 kcal/mole is slightly below previous theoretical estimates, but substantially above the value determined using Stark anticrossing spectroscopy that is asserted to be an upper bound.

[†] Mailing address: NASA Ames Research Center, Moffett Field, CA 94035

I. Introduction

There is currently considerable controversy regarding the C-H dissociation energy of acetylene, D_0(HCC–H). This is in large part due to the low and presumably very accurate value determined by Green, Kinsey, and Field (GKF) [1] using Stark anticrossing spectroscopy. Their result, 126.647(2) kcal/mole, is claimed to be an *upper bound*, and is consistent with the 127±1.5 kcal/mole estimate of Segall *et al.* [2] obtained by measuring the kinetic energy (K.E.) of the hydrogen atom fragment using Doppler multiphoton ionization spectroscopy. However, these values are substantially less than previous theoretical estimates [3,4] and other recent experimental results, such as the D_0 value of 131.3±0.7 kcal/mole measured by Ervin *et al.* [5] using the techniques of negative ion photoelectron spectroscopy and gas phase proton transfer kinetics.

In this Letter we present a theoretical study of the C-H dissociation energy of acetylene, with special emphasis on convergence with improvements in the one- and n-particle basis sets. We examine the n-particle space convergence by performing multireference CI (MRCI) calculations with reference configurations selected at different thresholds from a complete-active-space SCF (CASSCF) wave function. The effect of higher than double excitations is accounted for using either a Davidson correction [6] or the averaged coupled-pair functional method (ACPF) [7]. In fact, since the MRCI technique can treat C_2H_2 and C_2H to equal accuracy, our results are relatively insensitive to correction for higher excitations. We also compare two single-reference treatments, the coupled-pair functional (CPF) method [8] and its modified form (MCPF) [9], with MRCI. As both CPF and MCPF reproduce the MRCI results fairly well, we have performed most of our one-particle basis set convergence studies with these less expensive methods. By employing a well-defined sequence of basis sets of increasing size we are able to estimate the basis set limit dissociation energy with considerable confidence.

Our best estimate of the dissociation energy (D_e), when combined with computed or experimental zero-point corrections, indicates that D_0 is 130.1±1.0 kcal/mole with a high degree of certainty.

II. Methods

The one-particle basis sets employed for carbon in this study are constructed using general contractions based on atomic natural orbitals (ANOs) [10].

We have used two different contractions, [4*s* 3*p* 2*d* 1*f*] and [5*s* 4*p* 3*d* 2*f* 1*g*], of the (13*s* 8*p* 6*d* 4*f* 2*g*) primitive Gaussian set. The *s* and *p* exponents are taken from van Duijneveldt [11] and the polarization functions are given in Ref. 12. For hydrogen, we have used the 8*s* primitive set optimized by van Duijneveldt [11], augmented with a (6*p* 4*d*) polarization set [10]. Three different ANO contractions were considered for hydrogen, namely [3*s* 2*p* 1*d*], [4*s* 2*p* 1*d*], and [4*s* 3*p* 2*d*].

To obtain a balanced treatment of C_2H_2 and C_2H, we have used MRCI and ACPF treatments based on CASSCF wave functions. To minimize size-consistency problems, the D_e value was computed using a supermolecule approach. The CASSCF active space included the C 2*s* and 2*p* and the H 1*s* electrons and orbitals. In C_{2v} symmetry this corresponds to six a_1, two b_1, and two b_2 orbitals, and generates 5180 configuration-state functions (CSFs).

All single and double replacements from the CASSCF configuration space would result in prohibitively long CSF expansions, so it was necessary to select occupations based on their importance in the CASSCF wave function. The reference lists for the MRCI and ACPF treatments included all occupations for which the absolute value of the coefficient of any one of the component spin couplings exceeded a designated threshold in the CASSCF wave function, either at the equilibrium or dissociated (supermolecule) geometry. Selection thresholds of 0.05 and 0.025 were employed, resulting in 14 and 39 reference occupations, respectively. Using the latter reference space, the MRCI treatment (denoted MRCI(0.025)) resulted in a CSF expansion exceeding 2.5 million CSFs in the [4*s* 3*p* 2*d* 1*f*/4*s* 2*p* 1*d*] basis, so it was not feasible to consider smaller selection thresholds. However, as we show below, the equilibrium and dissociated geometries are equally well described at the MRCI(0.025) level, so it is unlikely that the MRCI(0.025) dissociation energy will differ significantly from the value that would be obtained either with smaller selection thresholds or with the entire CASSCF configuration space as references. The effect of higher than double excitations was estimated using both the multireference analog of the Davidson correction (denoted +Q) [6] and the ACPF approach [7]. Correlation effects involving the core (C 1*s*) electrons were excluded from consideration, but this is expected to affect D_0 by less than 0.2 kcal/mole [13].

Since the MRCI D_0 values were well reproduced by the much less computationally intensive CPF and MCPF methods, basis set calibration studies were performed using these single-reference-based approaches, following SCF calculations with symmetry and equivalence restrictions imposed. The first-order interacting space restriction is also imposed in the CPF and MCPF calculations. The D_e value is computed as the energy difference between the equilibrium geometry of C_2H_2 and the energy for the $^3\Sigma^+$ state with one hydrogen removed to 100 a_0.

Zero-point vibrational energy contributions to D_0 were computed using CPF wave functions for C_2H_2 and C_2H. The [4*s* 3*p* 2*d* 1*f*/4*s* 2*p* 1*d*] basis was used. Harmonic frequencies were obtained from force constants computed by finite difference methods.

The CASSCF/MRCI and SCF/CPF calculations were performed using the MOLECULE-SWEDEN [14] program system. The calculations were performed on the NASA Ames Central Computer Facility and NAS facility CRAY Y-MP/832 computers.

III. Results and discussion

To determine a definitive C-H bond dissociation energy for acetylene, we must demonstrate convergence in both the one- and *n*-particle spaces. Other errors such as invoking the Born-Oppenheimer approximation, neglect of correlation involving the C 1*s* electrons, and relativistic effects are expected to contribute at most a few tenths of a kcal/mole to D_e. Ideally, we wish to carry out the study of the convergence of the one-particle basis at a high level of correlation treatment so that effects arising from possible coupling between the one and *n*-particle treatments are minimized. The single-reference-based approaches yield D_e values that are within 1.0 (CPF) or 0.7 (MCPF) kcal/mole of our most accurate multireference-based correlation approaches in the [4*s* 3*p* 2*d* 1*f*/4*s* 2*p* 1*d*] contracted basis. This relatively small error combined with the good agreement between the CPF and MCPF approaches indicates that the CPF method should give a reliable estimate of the effect of basis set saturation.

The results of our basis set saturation study are summarized in Table I. The D_e values are computed based on geometries optimized at the MRCI(0.05) level. Only the CPF results are given, since the MCPF dissociation energies are uniformly 0.3 kcal/mole less. The D_e values generally increase with basis set improvement; an exception occurs on going from the [4*s* 3*p* 2*d* 1*f*/3*s* 2*p* 1*d*] to the [4*s* 3*p* 2*d* 1*f*/4*s* 2*p* 1*d*] basis, because the hydrogen 3*s* ANO basis set does not accurately describe the H atom. This shortcoming is remedied with the 4*s* basis, which reproduces the hydrogen atom energy to within 0.2 kcal/mole. Adding an additional *s* through *f* ANO function to carbon and an additional *p* and *d* function to hydrogen increases D_e by only 0.1 kcal/mole, while adding a *g* function to carbon increases it by an additional 0.3 kcal/mole. Thus the [4*s* 3*p* 2*d* 1*f*/3*s* 2*p* 1*d*] basis obtains a fortuitiously good D_e value, because the limitations in the H *s* basis approximately cancel the effect of improving the polarization basis. Additional basis set improvements are likely to further increase D_e slightly (0.1-0.3 kcal/mole), because the correlation energy of C_2H_2 is larger than that of C_2H, and is expected to converge more slowly with the one-particle basis. This claim cannot be made with the same confidence as would be the case for a diatomic dissociation, however, because of the more complicated correlation effects that arise in molecular, as opposed to atomic, fragments.

Some insight into the *n*-particle requirements can be obtained from an analysis of the work of Curtiss and Pople [3] based on the G1 approach [15], in which electron correlation is handled initially by performing fourth-order Møller-Plesset perturbation theory (MP4) calculations. A correction is then added from quadratic CI (QCI) calculations [16]. For the C-H bond dissociation energy of acetylene, the QCI correction decreases the dissociation energy by a large amount (8.3 kcal/mole). This is a consequence of the fact that a single-reference description of the closed shell $^1\Sigma_g^+$ ground state of C_2H_2 is superior to that of the $^2\Sigma^+$ ground state of the C_2H radical. This suggests that single-reference-based techniques may overestimate the binding energy if infinite-order effects and the contributions of higher excitations are not fully accounted for.

CASSCF wave functions supply a more equivalent description of C_2H_2 and C_2H than SCF wave functions, and thus differential correlation effects are easier to account for using MRCI wave functions. Such CASSCF/MRCI calculations have been found to perform very well in relation to full CI (FCI) benchmark calculations [17], but these have been limited to dissociation to atomic fragments, where the dissociation products were always easier to describe than the molecular system. Since we are unable to perform FCI benchmark calculations for acetylene in double zeta plus polarization (DZP) or better quality basis sets, we have used both the +Q correction and the more rigorous ACPF method to provide independent estimates of the effect of higher excitations.

The D_e values computed using the [4*s* 3*p* 2*d* 1*f*/3*s* 2*p* 1*d*] and

[4*s* 3*p* 2*d* 1*f*/4*s* 2*p* 1*d*] basis sets at various levels of correlation treatment are summarized in Table II. We note again that the D_e values are decreased by about 0.5 kcal/mole if the 3*s* hydrogen basis is replaced by the 4*s* basis, because of the error in describing H atom in the former. Our results demonstrate that the effect of improving the H basis is essentially independent of the level of correlation treatment, thereby justifying our use of CPF wave functions in our basis set study above.

The MRCI+Q and ACPF D_e values are in good agreement at both selection thresholds, but the effect of higher excitations on D_e changes sign as the selection threshold is tightened. This results from the fact that at a threshold of 0.05 the reference configurations provide a better description of C_2H_2 at equilibrium than at dissociation: the weight of the reference configurations in the MRCI wave function is greater at equilibrium. As a consequence, D_e computed using the reference energies is 6 kcal/mole larger than if the CASSCF energies are used. The bias in the reference level description leads to an artificially large correlation energy (defined here as the difference between the MRCI and reference energies) in the dissociated molecule and hence to an overestimated +Q correction that reduces D_e. At the 0.025 threshold, the reference space comprises a nearly identical fraction of the MRCI wave function at the equilibrium and at dissociation, and D_e computed using the reference energies is only 0.6 kcal/mole smaller than the CASSCF value. The 0.025 threshold thus treats equilibrium and dissociation equivalently, resulting in a +Q correction that increases D_e. In addition, since D_e computed from the reference energies is too small, any bias at the 0.025 threshold level would be expected to produce an MRCI D_e value that is too small. We believe that the MRCI(0.025) D_e value of 137.27 kcal/mole should be a lower bound, as higher excitations certainly increase D_e. This is also supported by the good agreement between the ACPF and MRCI+Q calculations. We consider the most accurate D_e values to be those at the ACPF(0.025) level, as they should be near the *n*-particle limit.

One effect that can artificially increase D_e is basis set superposition error (BSSE). We have computed the BSSE at the C_2H equilibrium geometry using the couterpoise method. At the CPF level the BSSE correction is 0.75 and 0.24 kcal/mole in the [4*s* 3*p* 2*d* 1*f*/4*s* 2*p* 1*d*] and [5*s* 4*p* 3*d* 2*f* 1*g*/4*s* 3*p* 2*d*] basis sets, respectively. Thus the relatively small apparent increase in D_e with basis set improvement results from a partial cancellation between the reduction in BSSE and the true increase in D_e. Our correction of 0.2 kcal/mole for further basis set saturation is consistent with observed relationships between basis set incompleteness and BSSE when the basis set is nearly complete. We should also note that use of an isogyric correction would increase D_e by only 0.17 kcal/mole — our computed error in the dissociation energy of H_2.

To obtain our best estimate for D_e, we must correct the ACPF(0.025) values for basis set incompleteness. We add 0.4 kcal/mole for improving the one-particle basis from [$4s\ 3p\ 2d\ 1f/4s\ 2p\ 1d$] to [$5s\ 4p\ 3d\ 2f\ 1g/4s\ 3p\ 2d$], based on the CPF results of Table I. We further increase our value by 0.2 kcal/mole to account for the addition of h and higher angular momentum functions and saturation of the $l \leq 5$ shells on carbon, as well as f functions and saturation of the $l \leq 2$ shells for hydrogen. Therefore our best estimate for D_e is about 138.2 kcal/mole. To this we assign an uncertainty of 0.7 kcal/mole to encompass the value before correction for basis set incompleteness; this error is of the same magnitude as the error in the bond dissociation energy of CH radical [12].

In order to compare our results with the experimentally determined D_0 values, we must correct our computed D_e values for zero-point energy. Vibrational energies for both C_2H_2 and C_2H are compared with experiment [18-20] in Table III. The CPF method gives harmonic frequencies for C_2H_2 that agree well with experiment [18]. The maximum error is only 47 cm^{-1} (for the symmetric CH stretch) and the error in the zero-point energy is 0.15 kcal/mole. However, the zero-point energy of C_2H is less easy to estimate reliably. The ν_3 band (CH fundamental) has not been conclusively assigned from experiment, and the original assignment [21] of this band as 3612 cm^{-1} based on isotopic studies of infrared absorptions is almost certainly incorrect. Not only is it in substantial disagreement with our CPF value (3328 cm^{-1}), but if it is used in an empirical force constant/bond length correlation formula [21] it leads to a ridiculously short C-H bond length of 1.915 a_0. Our computed frequency gives a bond length estimate of 1.996 a_0 using the same formula, in much better agreement with the actual CPF value of 2.016 a_0. Hence we prefer our computed value for the CH stretch. (Note, however, that a larger value, 3550 cm^{-1}, is obtained in the *ab initio* study of Peric *et al.* [22].) The C-C stretch and bending fundamentals are even more difficult to compute accurately, owing to the strong interaction between these two modes induced by the avoided crossing of the lowest $^2A'$ state with the $^2A'$ component of the $^2\Pi$ state near its minimum at a C-C bond length of 2.5 a_0. For the purpose of computing the zero-point correction we have used the experimental ν_2 value [19] of 371.6 cm^{-1} and have considered both the experimental [20] and CPF values for ν_1.

The zero-point energy for C_2H is 8.45 and 8.70 kcal/mole using (ν_1, ν_2, ν_3) values (cm^{-1}) of (1840, 371, 3328) and (2017, 371, 3328) for C_2H, respectively. Combining these with the experimental zero-point energy of 16.68 kcal/mole for C_2H_2 leads to a total zero-point correction of 8.23 and 7.98 kcal/mole. These values are similar to the value of 8.05 kcal/mole used by Curtiss and Pople [3]. Since it is highly unlikely that the zero-point energy of C_2H could be less than the first set of values, 8.23 kcal/mole must be considered to be an upper bound to the zero-point correction. Combining these zero-point corrections with our best estimate of 138.2 kcal/mole for D_e leads to D_0 values of 130.0 and 130.2 kcal/mole. We thus take our best estimate of D_0 to be 130.1 kcal/mole, and add an additional 0.3 kcal/mole to our error bars for uncertainties in the zero-point correction. We feel that our estimate of 130.1±1.0 kcal/mole has a 90% probability of encompassing the true value. In view of our expectation that we will approach D_0 from below it seems likely that the actual value will lie in the upper half of our estimated uncertainty.

Our theoretical estimate of 130.1±1.0 kcal/mole is compared with other recent experimental [1,2,5,23,24] and theoretical [3,4,25] determinations in Table IV. The agreement between the theoretical calculations is reasonably good, especially considering that the D_0 value of Curtiss and Pople [3] is likely to be slightly too high as a result of underestimating the effects of electron correlation in C_2H and favoring C_2H_2 somewhat. The calculations of Montgomery and Petersson [4] were performed at the QCI level; they include extrapolation to an estimated complete basis set limit. Their result is a little higher than ours: it is tempting to ascribe this again to the tendency of single-reference-based methods to favor C_2H_2. In this regard we note that the QCISD(T) energy for C_2H is 1.39 kcal/mole above the FCI energy in an STO-3G basis [26], so the RMS error bars in Ref. 4, determined from atomization energies for simpler systems, may be too optimistic for acetylene. Montgomery and Petersson obtain an excellent electron affinity (EA) for C_2H, which would suggest that their correlation treatment is not biased towards the closed-shell system, although this could result from a cancellation of errors that may not occur in the calculation of the dissociation energy. On balance, we conclude that our results and those of Montgomery and Petersson are essentially in agreement. Very recently, Wu and Carter [25] have obtained a D_0 value of 129.7 kcal/mole using an MRCI treatment in a DZP basis and a zero-point correction derived from experimental harmonic frequencies. Their result is very similar to ours, especially considering that basis set improvements will probably increase their value.

The agreement between our value and recent experimental measurements is also satisfactory, excluding the recent experiment interpreted as providing an upper bound of 126.647 kcal/mole by GKF [1]. The validity of their upper bound rests on the contention that observed increases in molecular decay rates are due to predissociation rather than any other Stark-induced nonradiative or radiative phenomenon. Although these authors carefully consider various alternatives, it still seems likely that another explanation exists, considering the wealth of data supporting a D_0 value of greater than 129.0 kcal/mole.

IV. Conclusions

We have presented a systematic study of the C-H bond dissociation energy in acetylene with respect to improvements in both the one- and n-particle treatments. Our best estimate for the D_0 value of 130.1±1.0 kcal/mole is in good agreement with several recent experiments and theoretical calculations. Considering that we estimate that our error bars have a better than 90% probability of encompassing the correct D_0 value, we question the recent upper bound inferred from Stark anticrossing spectroscopy.

Acknowledgement:

Part of this work was performed under a grant of computer time provided by the NAS Facility. P. R. Taylor was supported by NASA grant NCC 2-371. We would like to thank E. A. Carter, W. C. Lineberger, and G. A. Petersson for communicating results in advance of publication.

REFERENCES

1. P. G. Green, J. L. Kinsey, and R. W. Field, J. Chem. Phys. **91** (1989) 5160.
2. J. Segall, R. Lavi, Y. Wen, and C. Wittig, J. Phys. Chem. **93** (1989) 7287.
3. L. A. Curtiss and J. A. Pople, J. Chem. Phys. **91** (1989) 2420.
4. J. A. Montogmery and G. A. Petersson, Chem. Phys. Letters, in press.
5. K. M. Ervin, S. Gronert, S. E. Barlow, M. K. Gilles, A. G. Harrison, V. M. Bierbaum, C. H. DePuy, W. C. Lineberger, and G. B. Ellison, J. Am. Chem. Soc. (submitted).
6. M. R. A. Blomberg and P. E. M. Siegbahn, J. Chem. Phys. **78** (1983) 5682. See also S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. **8** (1974) 61.
7. R. J. Gdanitz and R. Ahlrichs, Chem. Phys. Letters **143** (1988) 413.
8. R. Ahlrichs, P. Scharf, and C. Ehrhardt, J. Chem. Phys. **82** (1985) 890.
9. D. P. Chong and S. R. Langhoff, J. Chem. Phys. **84** (1986) 5606.
10. J. Almlöf and P. R. Taylor, J. Chem. Phys. **86** (1987) 4070.
11. F. B. van Duijneveldt, IBM Research Report No. RJ 945 (1971).
12. C. W. Bauschlicher and S. R. Langhoff, Chem. Phys. Letters **135** (1987) 67.
13. C. W. Bauschlicher, S. R. Langhoff, and P. R. Taylor, J. Chem. Phys. **88** (1988) 2540.
14. MOLECULE-SWEDEN is an electronic structure program system written by J. Almlöf, C. W. Bauschlicher, M. R. A. Blomberg, D. P. Chong, A. Heiberg, S. R. Langhoff, P.-Å. Malmqvist, A. P. Rendell, B. O. Roos, P. E. M. Siegbahn, and P. R. Taylor.
15. J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, J. Chem. Phys. **90** (1989) 5622.
16. J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. **87** (1987) 5968.
17. C. W. Bauschlicher, S. R. Langhoff and P. R. Taylor, Adv. Chem. Phys. (in press).
18. G. Strey and I. M. Mills, J. Mol. Struct. **59** (1976) 103.
19. H. Kanamori and E. Hirota, J. Chem. Phys. **89** (1988) 3962.
20. H. Kanamori, K. Seki, and E. Hirota, J. Chem. Phys. **87** (1987) 73.

21. M. E. Jacox, Chem. Phys. **7** (1975) 424.

22. M. Peric, S. D. Peyerimhoff, and R. J. Buenker, paper communicated to the authors by R. F. Curl.

23. A. M. Wodtke and Y. T. Lee, J. Phys. Chem. **89** (1985) 4744.

24. H. Shiromaru, Y. Achiba, K. Kimura, and Y. T. Lee, J. Phys. Chem. **91** (1987) 17.

25. C. J. Wu and E. A. Carter, J. Am. Chem. Soc, submitted for publication.

26. P. M. W. Gill, J. A. Pople, L. Radom, and R. H. Nobes, J. Chem. Phys. **89** (1988) 7307.

Table I. Basis set calibration studies of D_e at the CPF level.

Basis set	Energy(E_h)		D_e(kcal/mole)[a]
	Molecule[b]	Fragment[c]	
[4s 3p 2d 1f/3s 2p 1d]	−77.183339	−76.962320	138.7
[4s 3p 2d 1f/4s 2p 1d]	−77.183994	−76.963765	138.2
[5s 4p 3d 2f/4s 3p 2d]	−77.191595	−76.971225	138.3
[5s 4p 3d 2f 1g/4s 3p 2d]	−77.197034	−76.976115	138.6

[a] The MCPF D_e values are uniformly 0.3 kcal/mole smaller.

[b] R(C-C)=2.292 and R(C-H)=2.010 a_0.

[c] R(C-C)=2.308 and R(C-H)=2.016 a_0.

Table II. Study of the convergence of D_e(kcal/mole) with respect to the n-particle treatment.

Basis set	Method[a]					
	CPF	MCPF	MRCI(0.05)	ACPF(0.05)	MRCI(0.025)	ACPF(0.025)
[$4s$ $3p$ $2d$ $1f$/$3s$ $2p$ $1d$]	138.69	138.37	137.70(137.55)	137.31	137.27(138.19)	138.05
[$4s$ $3p$ $2d$ $1f$/$4s$ $2p$ $1d$]	138.19	137.87	137.20(137.06)	...	...	137.55

[a] Values in parentheses include the multireference +Q correction.

Table III. CPF harmonic frequencies(cm^{-1}) for C_2H_2 and C_2H.

Mode	Harmonic frequencies	
	Theory	Experiment[a]
A. C_2H_2		
σ_g(CH stretch)	3544	3497
σ_g(CC stretch)	2034	2011
σ_u(CH stretch)	3444	3415
π_g(bend)	616	624
π_u(bend)	761	747
B. C_2H		
ν_1(CC stretch)	2017	1840.6[b]
ν_2(bend)	275	371.6[c]
ν_3(CH stretch)	3328	...

[a] Ref. 18.

[b] Ref. 20.

[c] Ref. 19.

Table IV. Summary of recent experimental and theoretical D_0 values (kcal/mole) for acetylene.

D_0(HCC–H)	Method	Ref.
	Experimental	
$\leq$126.647±0.002	Stark anti-crossing spectroscopy	1
127.±1.5	$HCCH + h\nu \rightarrow C_2H + H(K.E.)$	2
131.3±0.7	$\Delta H_{acid}(HCCH) + EA(C_2H) - IP(H)$	5
132.±2	$HCCH + h\nu \rightarrow C_2H(K.E.) + H$	23
132.6±1.2	photoionization of HCCH	24
	Theoretical	
133.5±2.3	G1	3
131.54±0.45	QCI	4
129.7	MRCI	25
130.1±1.0	MRCI	This work