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Cyanovinyl radical: an illustration of the poor performance of unrestricted perturbation theory and density functional theory procedures in calculating radical stabilization energies*

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Abstract. Stabilization energies for the 1-cyanovinyl radical ($CH_2{=}C^{\cdot}CN$) have been calculated using a variety of conventional ab initio (Møller–Plesset, quadratic configuration interaction and coupled-cluster) and density functional theory (B-LYP, B3-LYP) procedures, as well as with a range of compound methods. Compared with a high-level benchmark value (that predicts a stabilization energy of 17.1 kJ mol^{-1}), UMP2 and UMP4 give the wrong sign and magnitude of the stabilization energy (both methods predicting destabilization instead of stabilization), while B-LYP and B3-LYP overestimate the degree of stabilization. The RMP2, RMP4, QCISD(T) and CCSD(T) techniques, and several, but not all, variants of G2 and CBS theories give radical stabilization energies in good agreement with the benchmark value.

Key words: Radical stabilization energy – Spin contamination – Unrestricted perturbation theory – Density functional theory

1 Introduction

The stabilities of radicals are often measured by the enthalpy changes for reactions of the type

$$^{\cdot}CH_2X + CH_4 \rightarrow CH_3X + {}^{\cdot}CH_3 \quad (1)$$

or

$$CH_2{=}C^{\cdot}X + CH_2{=}CH_2 \rightarrow CH_2{=}CHX + CH_2{=}C^{\cdot}H \ . \quad (2)$$

Such radical stabilization energies (RSEs) may be derived using either experimental [1] or theoretical [2] data. Although it is well known that there are difficulties associated with the theoretical description of open-shell systems such as radicals, it has commonly been assumed [2] that there will be substantial cancellation of errors for the energies of isodesmic reactions such as 1 or 2. Thus, it has generally been assumed that the RSEs calculated as the energy changes in such reactions should be reliable.

In the present paper, we show that this is not necessarily the case. We examine stabilization energies for the highly spin-contaminated 1-cyanovinyl radical [$CH_2{=}C^{\cdot}CN$, $\langle S^2 \rangle = 1.487$ for the UHF/6-31G(d) wave function] calculated at a variety of commonly used levels of theory and find that several of these methods do not perform well. Some of the poorer calculated RSE values include −64.6 [UMP2/6-311 + G(3df,2p)], −36.9 [UMP4/6-311 + G(3df,2p)], −12.3 [PMP2/6-311 + G(3df,2p)], +42.0 (B-LYP/6-311 + G(3df,2p)] and +33.7 [B3-LYP/6-311 + G(3df,2p)] kJ mol^{-1}, compared with our best estimate of +17.1 kJ mol^{-1}.

2 Theoretical procedures and results

Standard ab initio molecular orbital theory [3] and density functional theory (DFT) [4] calculations were performed with the GAUSSIAN 94 [5], GAUSSIAN 98 [6], ACESII [7] and MOLPRO 96 [8] (with tripu patch installed) computational packages.[1] Calculations were carried out at the HF, MP2, MP4, B-LYP, B3-LYP, QCISD, QCISD(T) and CCSD(T) levels of theory with a variety of basis sets. The frozen-core

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[1] The tripu patch is needed to correct an error that otherwise occurs in MOLPRO 96 when calculating open-shell CCSD(T) energies for species in which there is more than one doubly occupied orbital in an irreducible representation (this was first found by C. Bauschlicher, NASA Ames Research Center)

approximation was employed at all levels of theory unless otherwise indicated. Unrestricted open-shell, restricted open-shell and projected calculations are designated with U, R and P prefixes, respectively.[2] Unless otherwise noted, the unrestricted (U) procedure is implied. The $\langle S^2 \rangle$ value for the $CH_2{=}C^{\cdot}H$ radical in reaction 2 at the UHF/6-31G(d) level is 1.015 compared with 1.487 for $CH_2{=}C^{\cdot}CN$.

The calculated geometry of the 1-cyanovinyl radical is sensitive to the level of theory. We have previously reported [9] that B-LYP/6-31G(d) and B3-LYP/6-31G(d) predict a C_{2v} cumulenic-type structure ($CH_2{=}C{=}C{=}N^{\cdot}$) with a linear CCC arrangement whereas UHF, UMP2, RMP2, QCISD and QCISD(T) with a variety of basis sets all predict C_s vinylic-type structures ($CH_2{=}C^{\cdot}{-}C{\equiv}N$), with CCC bond angles at the radical carbon in the range 135–148°. We have broadened the examination of geometries in the present study to the levels of theory listed in Table 1. With the exception of the larger basis set RMP2 calculations and the smaller basis set B3-LYP calculations, all levels of theory predict substantially bent structures. Importantly, our best calculations, corresponding to URCCSD(T) with the cc-pVTZ basis set (but with f functions restricted to the radical carbon atom), predict a CCC angle of 149.1°.

RSEs have been calculated as energy changes at 0 K for reaction 2. The theoretical procedure that we have chosen to use in the present study as a benchmark for RSEs is a variation of a Martin extrapolation scheme [10] called the Martin-3 method [9]. Martin's techniques in their full implementation have previously been found to yield thermochemical properties of molecules to approximately 1–2 kJ mol^{-1} accuracy [10]. The simplified version represented by Martin-3 would be expected to have slightly lower accuracy.

Stabilization energies for the 1-cyanovinyl radical computed at the HF, MP2, MP4, B-LYP, B3-LYP, QCISD, QCISD(T) and CCSD(T) levels with a variety of basis sets are given in Table 2. Results are presented both for the B3-LYP/6-31G(d) optimized C_{2v} structure and the QCISD/6-31G(d) optimized C_s structure. Zero-point vibrational energy (ZPVE) corrections included in the RSEs were obtained through calculations at the B3-LYP/6-31G(d) level using a scaling factor of 0.9806 [11]. The result obtained with the Martin-3 procedure is included for comparison.

Table 3 lists RSE values that were calculated using a variety of compound methods. Included in the table are results for the G2 [12], G2(MP2) [13] and G2(MP2,SVP) [14] procedures and G2-RAD modifications of these, as well as RSE values calculated with three of Morokuma's G2M techniques [15], the CBS-Q method [16] and three of its CBS-RAD modifications [9], and CBS-APNO [16].[3] Results are reported for both C_s and C_{2v} geometries of the 1-cyanovinyl radical, as calculated by the particular procedure required for the compound method [e.g. UMP2(fu)/6-31G(d) for standard G2]. The ZPVEs used in each case are those for minimum energy structures, i.e. for the C_s structure in those situations where the C_{2v} structure is a saddle point. Because the geometries of the other species in reaction 2 do not display significant sensitivity to the level of theory, the variation in RSE with geometry can largely be taken to reflect the effects in the 1-cyanovinyl radical. In the discussion that follows, we therefore

Table 1. CCC bond angles for fully optimized structures of $CH_2{=}C^{\cdot}CN$ for various correlation methods and basis sets[a]

Theory level	< CCC (deg)
UHF:	
6-31G(d)	146.4
6-311G(df,p)	147.1[b]
UMP2:	
6-31G(d)	135.5
6-311G(d)	135.8
6-311G(d,p)	135.9
6-311 + G(d,p)	135.9
6-311 + G(df,p)	135.9
6-311 + G(2df,p)	137.3
6-311 + + G(3df,3pd)	136.5
UMP2(fu):	
6-31G(d)	135.8
RMP2:	
6-31G(d)	147.9[c]
6-311 + G(2df,p)	180.0[b]
cc-pVTZ	180.0[b]
cc-pVTZ (f on radical C)	180.0[b]
B3-LYP:	
6-31G(d)	180.0
6-311G(d)	180.0
6-311G(d,p)	164.9[d]
QCISD:	
6-31G(d)	143.6
6-311G(d,p)	144.2
QCISD(T):	
6-31G(d)	143.9
URCCSD(T):	
cc-pVTZ (no f)	152.1
cc-pVTZ (f on radical C)	149.1[b]

[a] From Ref. [9] unless otherwise noted
[b] Present work
[c] A second minimum occurs for CCC = 180.0°, lying 0.8 kJ mol^{-1} above the C_s bent structure
[d] A C_{2v} structure is reported in Ref. [9] for the 1-cyanovinyl radical at this level of theory but frequency calculations show such a structure to be a saddle point

[2] RMP2 calculations were performed using GAUSSIAN 94 and the keyword ROMP2; RMP4 calculations were carried out with ACESII; URCCSD(T) calculations were carried out using MOLPRO 96 with the UCCSD(T) keyword (which is the restricted open-shell CCSD(T) calculation in MOLPRO 96 that is the same as the restricted open-shell coupled-cluster method in ACESII); RRCCSD(T) calculations were performed using MOLPRO 96 and the RCCSD(T) keyword

[3] G2-RAD differs from G2 in that RMP energies are used instead of the standard UMP energies and the ultimate electron correlation level is the URCCSD(T) method of MOLPRO 96 rather than UQCISD(T). Geometries used include QCISD/6-31G(d), RMP2/6-31G(d) or B3-LYP/6-31G(d) while ZPVEs are calculated from scaled B3-LYP/6-31G(d) vibrational frequencies

Table 2. Stabilization energies of the $CH_2{=}C^{\cdot}CN$ radical calculated with a variety of correlation procedures and with several basis sets (0 K, kJ mol^{-1})[a]

Basis set	6-31G(d)		6-311 + G(d,p)		6-311 + G(2df,p)		6-311 + G(3df,2p)	
Geometry	B3[b]	QCI[c]	B3[b]	QCI[c]	B3[b]	QCI[c]	B3[b]	QCI[c]
UHF	30.5	36.4	29.6	34.4	30.0	34.6	29.0	34.3
UMP2	−76.5	−61.2	−80.0	−64.1	−77.0	−64.0	−79.4	−64.6
PMP2[d]	17.4	16.4	15.2	14.5	16.9	13.4	14.7	12.9
PMP2[e]	−15.7	−10.2	−17.4	−11.6	−14.7	−11.7	−16.9	−12.3
RMP2	15.9	16.1	14.7	15.3	21.4	17.1	19.5	16.7
UMP4	45.9	−34.0	−50.2	−37.5	−45.5	−36.3	−48.0	−36.9
PMP4[d]	35.7	32.8	32.2	30.2	35.6	30.0	33.2	29.4
PMP4[e]	4.8	8.0	1.9	5.8	6.3	6.6	3.8	6.0
RMP4	14.7	16.6	13.6	16.1	20.0	18.0	18.4	17.7
B-LYP	47.0	39.3	41.8	35.5	42.7	36.4	42.0	36.2
B3-LYP	37.8	33.0	33.4	29.3	34.5	30.3	33.7	30.0
QCISD	3.1	11.5	2.4	11.1	6.9	12.3		
QCISD(T)	5.1	12.4	3.9	11.7	9.6	13.7		
CCSD(T)	5.1	12.1	3.5	11.1	9.0	12.8		
URCCSD(T)	11.0	16.8	9.8	16.1	15.6	17.9		
RRCCSD(T)	9.1	15.4	7.9	14.7	13.4	16.3		
Martin-3[f]								17.1

[a] All radical stabilization energies (RSEs) were calculated as the energy change for reaction 2 and corrected with scaled (by 0.9806) B3-LYP/6-31G(d) ZPVEs
[b] These calculations were performed on B3-LYP/6-31G(d) optimized geometries
[c] These RSEs were evaluated using QCISD/6-31G(d) optimized geometries
[d] The energies used were those with the leading spin-contaminant annihilated
[e] The energies used were those with the first four spin-contaminants annihilated
[f] The Martin-3 energy for the 1-cyanovinyl radical was calculated on the CCSD(T)(fu)/cc-pVTZ geometry (optimized without f functions). See Ref. [9]

Table 3. Stabilization energies for the $CH_2{=}C^{\cdot}CN$ radical calculated using a variety of compound methods (0 K, kJ mol^{-1})

Method	RSE (C_s)[a]	RSE (C_{2v})[b,c]
G2	6.1	3.9
G2(MP2)	5.5	2.7
G2(MP2,SVP)	4.4	1.5
G2-RAD(QCISD)[d]	17.7	14.1
G2(MP2)-RAD(QCISD)[d]	17.5	14.0
G2-RAD(RMP2)[d]	18.5	12.2
G2(MP2)-RAD(RMP2)[d]	18.3	12.0
G2-RAD(B3-LYP)[d]	14.3	14.3
G2(MP2)-RAD(B3-LYP)[d]	14.2	14.2
G2(MP2,SVP)-RAD(B3-LYP)[d]	14.6	14.6
G2M(RCC)	11.6	9.7
G2M(RCC,MP2)	9.7	7.8
G2M(rcc,MP2)	7.9	6.0
CBS-Q	10.7	21.4
CBS-RAD(QCISD,QCISD)[e]	18.9	20.4
CBS-RAD(RMP2,B3-LYP)[e]	23.0	19.2
CBS-RAD(B3-LYP,B3-LYP)[e]	25.5	25.5
CBS-APNO	18.7	15.3
Martin-3	17.1	

[a] Results for C_s-optimized structures of the 1-cyanovinyl radical
[b] Results for C_{2v}-optimized structures of the 1-cyanovinyl radical
[c] In cases where the C_{2v}-optimized geometry is a saddle point, the ZPVE was assumed to be the same as that for the C_s minimum energy structure
[d] The method used for optimizing geometries is shown in parentheses after RAD. See text
[e] The methods used for optimizing geometries and obtaining ZPVEs are shown in parentheses after RAD. See text

interpret the larger of the C_s or C_{2v} RSE values as corresponding to the better description of the 1-cyanovinyl radical for the particular method (simple or compound).

3 Discussion

It can be seen from Table 2 that the effect of choice of geometry [i.e. the B3-LYP/6-31G(d) C_{2v} structure or the QCISD/6-31G(d) C_s structure] on calculated RSE values

can be significant. The geometry effect ranges from 0.7 kJ mol^{-1} (for RMP4) to about 15 kJ mol^{-1} (for UMP2). With the largest basis sets, most levels of theory prefer a C_s structure, but notable exceptions include PMP, RMP, B-LYP and B3-LYP.

When QCISD/6-31G(d) optimized geometries are used, the calculated RSE values for the 1-cyanovinyl radical have essentially converged with respect to the basis set at the 6-311+G(2df,p) stage. The changes in stabilization energies upon going to the larger 6-311+G(3df,2p) basis set are invariably less than 1 kJ mol^{-1}. Even the smaller 6-311+G(d,p) basis set performs well, with results in all cases being within 2 kJ mol^{-1} of the 6-311+G(3df,2p) values. However, for the B3-LYP/6-31G(d) geometries, the changes from 6-311+G (d,p) to 6-311+G(3df,2p) can be as large as 5 kJ mol^{-1}.

The Martin-3 method predicts a stabilization energy for the 1-cyanovinyl radical of 17.1 kJ mol^{-1}, and we have found this value to be stable with respect to various modifications in the method to about 2 kJ mol^{-1}. Comparison of this benchmark value with results obtained using a variety of correlation levels (Table 2) indicates that the UMP2 and UMP4 methods perform particularly poorly, giving the wrong sign for the stabilization energy of the 1-cyanovinyl radical, i.e. predicting that the cyano substituent is destabilizing rather than stabilizing. The RSEs are 50–80 kJ mol^{-1} lower than the Martin-3 value. The deviations in these cases may be attributed to incomplete cancellation of errors for the two sides of reaction 2, arising because of the poor UMP description of the highly spin contaminated 1-cyanovinyl radical. Projecting out the leading spin contaminant from the UMP2 and UMP4 energies with the PMP procedure results in a large increase in the stabilization energy. More complete PMP annihilation of spin contamination decreases the RSE values but the results are not particularly good. RMP2, RMP4, QCISD, QCISD(T) and the various CCSD(T) methods all give stabilization energies that agree well with the benchmark value. B-LYP and B3-LYP overestimate the stabilization energies by 16–25 kJ mol^{-1}, with B3-LYP performing slightly better than B-LYP.

Standard G2, G2(MP2) and G2(MP2,SVP) methods predict RSE values that are 10–13 kJ mol^{-1} below the Martin-3 result (Table 3). The various G2-RAD, G2(MP2)-RAD and G2(MP2,SVP)-RAD procedures on the other hand give stabilization energies that are all within 3 kJ mol^{-1} of the Martin-3 value. A breakdown of the difference of 11.6 kJ mol^{-1} in the RSE calculated by G2-RAD(QCISD) compared with that calculated by G2 shows that this may be attributed mainly to a combination of changes in geometry (+11.3 kJ mol^{-1}), ZPVE (−4.0 kJ mol^{-1}) and correlation method (+4.5 kJ mol^{-1}). The three G2M procedures of Morokuma predict stabilization energies that are 5–9 kJ mol^{-1} lower than the benchmark result, with G2M(RCC) performing slightly better than G2M(RCC,MP2) and G2M(rcc,MP2). CBS-Q strongly prefers a C_{2v} structure and the associated RSE value is overestimated by about 4 kJ mol^{-1}. The full CBS-RAD method, i.e. CBS-RAD(QCISD,QCISD), gives an RSE that lies about 3 kJ mol^{-1} above Martin-3. The two modifications of CBS-RAD in Table 3 overestimate the RSE by 6–9 kJ mol^{-1}. The different results obtained by the various CBS-Q and CBS-RAD procedures (for C_s 1-cyanovinyl geometries) are largely associated with changes in the geometry of the 1-cyanovinyl radical used in the calculations. In that sense, the good result obtained with CBS-RAD(QCISD,QCISD) with a C_s geometry is partly fortuitous since CBS-RAD(B3-LYP,B3-LYP) gives a lower energy for the 1-cyanovinyl radical. CBS-APNO predicts a stabilization energy that is in good agreement with the Martin-3 value.

4 Conclusions

The most important result to emerge from the present study is that, for highly spin contaminated species such as the 1-cyanovinyl radical, stabilization energies calculated using UMP energies may be significantly in error, both quantitatively and qualitatively. This failure arises because the assumption of cancellation of errors in the isodesmic reaction that measures the stabilization energy (reaction 2) is not valid in such cases. DFT procedures are not subject to such substantial errors but they do overestimate the stabilization energy. The RMP methods, on the other hand, predict RSE values that are close to the benchmark result. All the compound theoretical techniques investigated in the present study correctly predict the 1-cyanovinyl radical to be stabilized. Of these methods, G2-RAD and CBS-APNO predict the best quantitative RSE values. In particular, the G2-RAD procedures perform better than the standard G2 methods. The RSEs are found not to be very sensitive to the particular G2 additivity scheme used. However, the geometry employed for the 1-cyanovinyl radical has an important influence on the calculated RSE.

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References

1. (a) Hawari JA, Kanabus-Kaminska JM, Wayner DDM, Griller D (1986) In: Viehe HG, Janousek Z, Merenyi R (eds) Substituent effects in radical chemistry. Reidel, Louvain-la-Neuve, p 91; (b) Ruchardt C, Beckhaus H-D (1986) Top Curr Chem 130:1; (c) Timberlake JW (1986) In: Viehe HG, Janousek Z, Merenyi R (eds) Substituent effects in radical chemistry. Reidel, Louvain-la-Neuve, p 271; (d) Sustmann R, Korth H-G (1990) Adv Phys Org Chem 26:131; (e) Bordwell FG, Satish AV (1994) J Am Chem Soc 116:8885; (f) Ponomarev D, Takhistov V (1997) J Mol Struct 435:259; (g) Wayner DDM, Clark KB, Rauk A, Yu D, Armstrong DA (1997) J Am Chem Soc 119: 8925
2. (a) Lehd M, Jensen F (1991) J Org Chem 56:884; (b) Leroy G, Sana M, Wilante C (1991) J Mol Struct (Theochem) 228:37; (c) Espinosa-Garcia J, Olivares del Valle FJ, Leroy G, Sana M, Wilante C (1992) J Mol Struct (Theochem) 258:315; (d) Pasto DJ (1992) J Org Chem 57:1139; (e) Arnaud R, Grand A, Subra R (1993) J Mol Struct (Theochem) 283:101; (f) Wu Y-D, Wong C-L (1995) J Org Chem 60:821; (g) Fox T, Kollman PA (1996) J

Phys Chem 100:2950; (h) Jursic BS, Timberlake JW (1996) Tetrahedron Lett 37:6473; (i) Wu Y-D, Wong C-L, Chan KWK, Ji G-Z, Jiang X-K (1996) J Org Chem 61:746; (j) Cioslowski J, Liu G, Moncrieff D (1997) J Am Chem Soc 119:11452; (k) Davidson ER, Chakravorty S, Gajewski JJ (1997) New J Chem 21:533; (l) Korth H-G, Sicking W (1997) J Chem Soc Perkin Trans 2 715; (m) Jursic BS (1998) J Mol Struct (Theochem) 422:253

3. Hehre WJ, Radom L, Schleyer P v R, Pople JA (1986) Ab initio molecular orbital theory. Wiley, New York
4. (a) Jones RO, Gunnarsson O (1989) Rev Mod Phys 61:689; (b) Parr RG, Yang W (1989) Density functional theory of atoms and molecules. Oxford University Press, New York; (c) Labanowski JK, Andzelm JW (eds) (1991) Density functional methods in chemistry. Springer, Berlin Heidelberg New York; (d) Ziegler T (1991) Chem Rev 91:651; (e) Seminario JM, Politzer P (1995) Modern density functional theory: a tool for chemistry. Elsevier, Amsterdam
5. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheesman JR, Keith T, Petersson A, Montgomery A, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA (1995) GAUSSIAN 94. Gaussian, Pittsburgh, Pa
6. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) GAUSSIAN 98. Gaussian, Pittsburgh, Pa
7. (a) Stanton JF, Gauss J, Watts JD, Lauderdale WJ, Bartlett RJ (1992) ACESII. Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainsville, Fla; (b) Stanton JF, Gauss J, Watts JD, Lauderdale WJ, Bartlett RJ (1992) Int J Quantum Chem Symp 26:879
8. Werner HJ, Knowles PJ with contributions from Almof J, Amos RD, Deegan JO, Elbert ST, Hampel C, Meyer W, Peterson K, Pitzer R, Stone AJ, Taylor PR, Lindh R, Mura ME, Thorsteinsson T MOLPRO 96 (a package of ab initio programs). University of Birmingham, UK
9. Mayer PM, Parkinson CJ, Smith DM, Radom L (1998) J Chem Phys 108:604
10. Martin JML (1996) Chem Phys Lett 259:669
11. Scott AP, Radom L (1996) J Phys Chem 100:16502
12. Curtiss LA, Raghavachari K, Trucks GW, Pople JA (1991) J Chem Phys 94:7221
13. Curtiss LA, Raghavachari K, Pople JA (1993) J Chem Phys 98:1293
14. Smith BJ, Radom L (1995) J Phys Chem 99: 6468
15. Mebel AM, Morokuma K, Lin MC (1995) J Chem Phys 103:7414
16. Ochterski JW, Petersson GA, Montgomery JA Jr (1996) J Chem Phys 104:2598