

# Accurate *ab initio* spectroscopic and thermodynamic properties for the SiC molecule

J. M. L. Martin

Limburgs Universitair Centrum, Department SBM, Universitaire Campus, B-3610 Diepenbeek, Belgium and University of Antwerp (UIA), Institute for Materials Science, Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

J. P. Francois

Limburgs Universitair Centrum, Department SBM, Universitaire Campus, B-3610 Diepenbeek, Belgium

R. Gijbels

University of Antwerp (UIA), Institute for Materials Science, Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

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The spectroscopic properties of the three lowest-lying states  $X^3\Pi$ ,  $A^3\Sigma^-$ , and  $a^1\Sigma^+$  of SiC have been computed accurately using augmented coupled cluster methods and different basis sets. Partition functions have been set up, accounting for anharmonicity, rotation-vibration coupling, centrifugal distortion, and isotope effects. Thermodynamic properties are tabulated in JANAF style from 100 to 6000 K. A critical analysis of the effects of the various contributions is made, as well as an error analysis.

## INTRODUCTION

Silicon carbide (one of whose crystalline phases is also known under the name "carborundum") is of great industrial importance as an abrasive,<sup>1</sup> for applications in high-temperature ceramics,<sup>2</sup> and with potential as a semiconductor.<sup>3</sup>

The SiC molecule has aroused much interest among astrophysicists. It is believed to be an abundant component in carbon stars,<sup>4</sup> stellar atmospheres,<sup>5</sup> and dense interstellar clouds.<sup>6</sup> Only very recently some spectroscopic data on some of its excited states have become available.<sup>7</sup> Its ground and first excited states have been predicted unambiguously to be  $X^3\Pi$  and  $A^3\Sigma^-$ , respectively, in several *ab initio* studies.<sup>4,8-10</sup> However, neither state has been well characterized experimentally.

Recently, the study of small molecules appearing in the vapor of neoceramic materials has attracted much attention from researchers in the area of "chemical vapor deposition" (CVD), as the possible key to an understanding of the mechanism and optimal conditions for CVD.<sup>11</sup> For work with SiC, the availability of adequate thermochemical data for the SiC molecule would be helpful.<sup>12</sup> Present-day theoretical methods are quite capable of producing the kind of accuracy required, if judiciously applied.

The purpose of the present paper is threefold:

- (i) to calculate accurate spectroscopic constants of the three lowest-lying states of SiC;
- (ii) to present thermodynamic functions of chemical accuracy over a wide temperature range;
- (iii) to critically investigate the anharmonic and rotation-vibration effects on the thermodynamic functions. As the rigid rotor-harmonic oscillator (RRHO) approximation is generally applied in thermodynamic studies of polyatomic clusters, such an analysis may indicate whether or not moving beyond this approximation is desirable.

## THEORETICAL METHODS

We first give an overview of recent theoretical studies on SiC. Bruna *et al.*<sup>9</sup> calculated potential energy curves of a number of electronic states using the multireference double excitation configuration interaction (MRD-CI) method of Buenker and Peyerimhoff<sup>13</sup> and a double zeta plus polarization (DZP) basis augmented with bond functions. No dissociation energies nor anharmonic constants were computed in this study; the main emphasis appeared to be on the electronic transition energies between the ground and the lower excited states. Two subsequent papers<sup>14,15</sup> discuss the ionization potential and electron affinity, respectively. Cooper<sup>16</sup> investigated the spin-orbit coupling in the  $X^3\Pi$  state at the self-consistent field (SCF) level using a double zeta Slater type orbital (STO) basis set. Rohlfling and Martin (RM)<sup>4</sup> studied just the ground state with fourth-order Møller-Plesset (MP4) and complete active space self-consistent field/contracted configuration interaction (CASSCF/CCI) methods. They present both dissociation energies and anharmonicity constants, but these are scattered over a wide range among the methods employed. Bauschlicher and Langhoff (BL)<sup>10</sup> studied the  $X^3\Pi$  and  $A^3\Sigma^-$  states using a large atomic natural orbital (ANO)<sup>17</sup> basis set and several sophisticated configuration interaction (CI) methods. Based on comparisons with  $C_2$  and  $Si_2$ , they proposed a "best estimate" of 4.4 eV for the dissociation energy, compared to an experimental upper bound listed in Huber and Herzberg<sup>18</sup> as 4.66 eV. They also noted that the IR intensity would be very weak and that an accurate rotational constant would be more useful. To this end, they came up with a best estimate of 1.719 Å for the bond length. In Bernath *et al.* (BROBM),<sup>7</sup> single- or two-reference configuration interaction with all single and double excitations (CISD) calculations with large (*spdf*) STO basis sets were made to predict bond distance differences between the various states. Combined with

their experimental results for the excited  $b^1\Pi$  state, these authors predict  $r_e$  and  $r_0$  values, respectively, of 1.719 and 1.723 Å for the ground state, both of which are expected to be accurate to  $\pm 0.001$  Å. Finally, Müller-Plathe and Laaksonen<sup>19</sup> present numerical Hartree-Fock properties in a very recent paper.

Given the apparent necessity for a multireference expansion in the CI treatments, as well as the high degree of spin contamination in the unrestricted Hartree-Fock (UHF) wave function, it is surprising that no coupled cluster calculations have been attempted. It is well known that coupled cluster theory handles quasidegeneracy quite well, even with a single reference determinant,<sup>20</sup> as well as that the coupled cluster theory with all single and double excitations (CCSD) energy is not affected by the presence of only a single spin contaminant.<sup>21,22</sup> Since it was found in Ref. 4 that a single spin annihilation reduced the value of  $\langle S^2 \rangle$  from 2.50 to 2.02 (compared to 2.0 for a pure triplet state), the decision for a coupled cluster treatment is obvious. From Refs. 4 and 10, it is also apparent that whereas triple excitations are not as important as in  $C_2$ , they should certainly not be neglected. In a multireference-CISD treatment, the most important triple excitations will be included anyway, as excitations to some of the reference configurations. However, in a single-reference coupled cluster treatment, some attempt should be made as to including the  $T_3$  operator.

For heavily spin-contaminated wave functions, it has recently been noted,<sup>23</sup> that single excitations have a large effect on the dissociation energy, which is underestimated by 50% or more when the  $T_1$  operator is only evaluated perturbatively. The authors have also shown that single excitations have a rather large effect on bond distances and harmonic frequencies under the same circumstances.<sup>22</sup> An ideal treatment would then be CCSD + T(CCSD)<sup>24</sup> or QCISD(T),<sup>25</sup> the latter of which is now available to the authors. CCSD + T(CCSD) denotes CCSD augmented by a quasiperturbative correction for connected triple excitations based on converged double substitution amplitudes only. QCISD(T) symbolizes quadratic CISD<sup>25</sup> with a similar quasiperturbative correction for connected triple excitations which is now, however, based on both the single and double substitution amplitudes. QCISD is actually an approximation to CCSD; however, its perturbative triples correction QCISD(T) has the advantage over that in CCSD + T(CCSD) that it is correct to fifth order.<sup>25b</sup> In a recent paper, we showed<sup>26</sup> that effects of single excitations in heavily contaminated systems can be surprisingly well accounted for using a combination of CID (configuration interaction with double excitations only) and CISD, using the Davidson-Silver formula<sup>27</sup> to correct for size inconsistency.

Comparable methods have recently been applied with great success to the  $N_3$  molecule<sup>28,29</sup> using DZP and triple zeta plus polarization (TZP) basis sets, which is in many respects similar to the present one (open-shell ground state, spin contamination, large triples contribution). Regarding the basis set, we had to settle for a compromise between quality and computation time, so we decided on the 6-311G\*<sup>30</sup> basis for carbon, and the McLean-Chandler [6s5p1d] basis set<sup>31</sup> for silicon, with polarization exponents

modified for correlation calculations as suggested by Wong *et al.*<sup>32</sup> This basis set is denoted below as MC-311G(1d). Several basis set extensions were considered to assess their effect on the computed properties. Diffuse functions on C and Si were taken from Refs. 33 and 34, respectively. Standard values<sup>35</sup> were used for the additional C polarization exponents; for Si, the  $d$  function exponents were taken as  $\alpha/2$  and  $2\alpha$  ( $\alpha$  being the single  $d$  function exponent), whereas the  $f$  function exponent was taken as the standard value.<sup>35</sup> To further correct for basis set incompleteness, the G1 theory of Pople and co-workers was then applied.<sup>36</sup>

Part of the calculations were performed using the GAUSSIAN 86 program system,<sup>37</sup> part with the GAUSSIAN 88 package,<sup>38</sup> running on a VaxStation 2000 under VMS 4.7.

Potential curves for the  $X^3\Pi$ ,  $A^3\Sigma^-$ , and  $a^1\Sigma^+$  states were evaluated in the range of  $-0.06$  to  $+0.06$  Å around the predicted bond distances in Ref. 7, with a step size of 0.02 Å.  $r_e$  was determined by least-squares fitting of a fourth-degree polynomial to the energies and finding its minimum. The quartic polynomial in  $r$  was then transformed to the dimensionless variable  $(r-r_e)/r_e$ ; from the resulting coefficients, the spectroscopic constants of the most abundant isotopomer  $^{12}C^{28}Si$  were obtained using expressions derived by Dunham.<sup>39</sup>

The partition functions were evaluated using the direct summation technique as implemented in a program by one of the authors (JM). From the partition function  $Q$  as well as its associated moment sums  $Q'$  and  $Q''$ , the thermodynamic functions can then easily be constructed as discussed in Pitzer and Brewer.<sup>40</sup> The summation was carried out over all electronic, vibrational, and rotational levels, including anharmonicity, rotation-vibration coupling, and centrifugal distortion. No approximate factorization of the three partition functions was carried out. Only the translational contribution was evaluated separately. The threshold for summation was set for any temperature at the energy where a given nondegenerate vibronic level would only contribute one part in  $10^8$  to the total partition function.

Isotope effects on the spectroscopic constants were incorporated using the approximate formula suggested by Dunham<sup>39</sup>:

$$Y_{ij}(\text{iso})/Y_{ij} \approx (m/m_{\text{iso}})^{(i+2j)/2} \quad (1)$$

in which  $Y_{10} = \omega_e$ ,  $Y_{20} = -\omega_e x_e$ ,  $Y_{01} = B_e$ ,  $Y_{02} = D_e$ ,  $Y_{11} = -\alpha_e$ , etc., except for some very small correction terms. The partition functions are then constructed separately for each isotopomer and finally averaged using the products of the natural isotope abundances as weight factors. This latter approximation, which holds very well except perhaps for the  $H_2/D_2$  system, was made in the JANAF tables.<sup>41</sup> It is equivalent to assuming the equilibrium constants for isotopic exchange reactions among the different isotopic species to be all unity.

At higher temperatures, excited states above the three lowest should also be accounted for. Since these contributions will be small, we have adopted here the approximation of setting up the partition functions for these using *ab initio* and experimental data for three more excited states  $b^1\Pi$ ,

$c^1\Delta$ , and  $d^1\Sigma^+$  given in BROBM<sup>7</sup> and Bruna *et al.*,<sup>9</sup> and deriving the missing constants using some well-known approximate relationships between spectroscopic constants (*vide infra*).<sup>42</sup>

Finally, spin-orbit coupling should be taken into account. Herzberg<sup>42</sup> gives a first-order expression for the splitting between components of a molecular term as

$$E = E_0 + A\Lambda\Sigma \quad (2)$$

in which  $A$  is the spin-orbit coupling constant, and  $\Lambda$  and  $\Sigma$  represent the components of the electronic angular momentum and of  $S$  along the nuclear axis, respectively. ( $\Lambda$  is 0 for a  $\Sigma^+$  or  $\Sigma^-$  state, 1 for a  $\Pi$  state, 2 for a  $\Delta$  state, etc.).  $E_0$  denotes the energy in the absence of spin-orbit coupling. The  $A$  value for the ground state is computed as  $-37.3 \text{ cm}^{-1}$  by Cooper,<sup>16</sup> who expects his empirically corrected SCF value to be correct to a few  $\text{cm}^{-1}$ ; the other five states included in this calculation do not exhibit first-order term splitting. We here make the assumption that the partition functions of the three component states of  $X^3\Pi$  are very much similar, so the spin-orbit coupling term can be factored out.

## RESULTS AND DISCUSSION

### Spectroscopic constants

Computed spectroscopic constants for the  $X^3\Pi$  state using the MC-311G(1d) basis set and a variety of theoretical models, including normal and projected UHF, MP2, MP3, and MP4(DQ), Pople's infinite-order extrapolation formula, CID and CISD with four different size-consistency corrections, CCD and CCD + ST(CCD) theory, and

finally QCISD and QCISD(T), are listed in Table I. The size-consistency corrections considered were the Davidson (DC),<sup>43</sup> Pople (PC),<sup>44</sup> renormalized Davidson (RDC),<sup>45</sup> and Davidson-Silver (DSC)<sup>27</sup> formulas. It is easily seen that all spectroscopic constants are quite sensitive to the electron correlation method employed. This is an exception to the general finding that anharmonic force constants are quite well described at the Hartree-Fock level.<sup>46</sup> However, in that study, only closed-shell molecules were considered, whereas we are dealing with a heavily spin-contaminated UHF wave function here. When the anharmonic constants at other levels are considered relative to the PUHF constants, a much smaller variation is observed.

It would be interesting to see, how much of the remaining difference is due to geometry change effects. Since the coefficients of the Dunham polynomial are not explicitly dependent on bond length, one could make the assumption that the Dunham coefficients  $a_0$ ,  $a_1$ , and  $a_2$  are approximately constant for the different methods. It is then easily shown that

$$\omega_e x_e(r_1)/\omega_e x_e(r_2) = (r_2/r_1)^2, \quad (3)$$

$$\alpha_e(r_1)/\alpha_e(r_2) = (r_2/r_1)^3. \quad (4)$$

Upon changing from the projected unrestricted Hartree-Fock (PUHF) to the projected Møller-Plesset second-order (PMP2) geometry, this would result in 10% and 6% increases in  $\alpha_e$  and  $\omega_e x_e$ , respectively. Oddly enough, this approximation holds better with increasing order of perturbation theory, but fails when single or triple excitations are introduced for the first time. Apparently, both of them have

TABLE I. Computed spectroscopic constants for the  $X^3\Pi$  state [MC-311G(d)].

Method	$D_e$ (eV)	$D_0$ (eV)	$r_e$ (Å)	$r_0$ (Å)	$B_e$ ( $\text{cm}^{-1}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$\omega_e x_e$ ( $\text{cm}^{-1}$ )	$10^3 \alpha_e$ ( $\text{cm}^{-1}$ )
UHF	2.55	2.49	1.765	1.769	0.644 66	826.5	2.72	5.85
MP2	3.49	3.43	1.706	1.711	0.690 05	892.3	6.76	8.53
MP3	3.37	3.32	1.709	1.714	0.687 50	886.4	6.62	8.53
MP4DQ	3.27	3.22	1.712	1.717	0.685 08	884.2	6.46	8.40
MP4SDQ	3.37	3.31	1.711	1.716	0.686 04	905.0	7.39	8.43
MP <sub>x</sub> <sup>a</sup>	3.22	3.17	1.713	1.718	0.684 24	882.6	6.37	8.36
CCD	3.24	3.18	1.713	1.718	0.683 85	885.2	6.27	8.19
CCD(T)	3.36	3.31	1.710	1.715	0.686 47	894.3	6.83	8.36
CCD(ST)	3.50	3.44	1.711	1.716	0.685 47	924.0	7.54	7.98
PUHF	2.74	2.69	1.763	1.767	0.645 79	879.7	5.53	6.07
PMP2	3.71	3.65	1.712	1.717	0.684 51	936.5	7.00	7.62
PMP3	3.59	3.53	1.718	1.723	0.680 12	918.9	6.35	7.42
PMP4	3.49	3.43	1.721	1.725	0.678 00	917.5	6.35	7.35
PMP <sub>x</sub> <sup>a</sup>	3.44	3.38	1.722	1.726	0.677 22	915.9	6.30	7.31
CID	3.02	2.96	1.718	1.723	0.680 08	874.3	5.66	7.99
CID + PC	3.24	3.19	1.713	1.718	0.684 12	883.8	6.39	8.33
CID + DC	3.21	3.16	1.712	1.718	0.684 59	884.7	6.45	8.35
CID + RDC	3.24	3.18	1.712	1.717	0.685 15	886.2	6.57	8.41
CID + DSC	3.27	3.22	1.711	1.716	0.685 86	888.1	6.72	8.47
CISD	3.22	3.17	1.720	1.725	0.678 58	924.6	7.08	7.32
CISD + PC	3.68	3.62	1.720	1.724	0.678 24	988.9	11.05	6.10
CISD + DC	3.63	3.57	1.719	1.723	0.678 99	983.3	10.47	6.28
CISD + RDC	3.71	3.65	1.720	1.724	0.678 48	999.5	11.54	5.96
CISD + DSC	3.83	3.76	1.721	1.725	0.677 60	1024.4	13.26	5.50
CCD(T) + S(DSC)	3.92	3.85	1.721	1.724	0.678 10	1029.6	13.22	5.43
QCISD	3.72	3.66	1.727	1.731	0.672 81	970.4	8.27	6.04
QCISD(T)	3.93	3.87	1.732	1.735	0.669 36	976.4	8.88	5.69

<sup>a</sup> Corrected with Pople's infinite-order extrapolation formula (J. A. Pople, M. J. Frisch, B. T. Luke, and J. S. Binkley, *Int. J. Quantum Chem. Symp.* 17, 307 (1983)).

some influence, not only on the equilibrium bond length and the harmonic force constant, but even on the anharmonicity. This itself is again a consequence of the spin-contaminated radical character of the wave function.

Projection and annihilation of higher contaminants than quintuplets show almost no change in energy or  $\langle S^2 \rangle$ : The spin contamination is adequately removed by a single projector. As neither the CCSD nor the CISD or QCISD energies are affected by a single spin contaminant,<sup>21,22</sup> these methods should be no less reliable than usual.

The Davidson-corrected CISD potential curves all exhibit excessive anharmonicity, which is not seen in the uncorrected curves, nor in the corrected CID curves. Incidentally, the size-consistency corrections are all very large,  $(1-c_0)^2$  being about 0.12 and varying quite substantially even over the small distance sampled. All coefficients are quite sensitive to the degree of the fit or interpolation, which is not the case with any of the other methods.

The QCISD and QCISD(T) frequencies are in excellent agreement with the "best theoretical estimate" of  $975 \pm 10 \text{ cm}^{-1}$  by RM,<sup>4</sup> which was produced using an empirical error correction. Very good agreement is also observed for both methods with the best estimate of  $962 \text{ cm}^{-1}$  by BL.<sup>10</sup> It should be noted that the basis set employed here is only of TZP quality, whereas the RM basis set was of TZ(2*d*) quality and BL used a TZ(2*df*) ANO contraction of a very large primitive set. Apparently, the QCISD and QCISD(T) electron correlation methods are complete enough to obtain good accuracy even with smaller basis sets. The extrapolated value of  $1.719 \pm 0.001 \text{ \AA}$  for the bond distance by BROBM<sup>7</sup> is quite well reproduced by the projected MP methods, as well as by the size-consistency corrected CISD methods. Oddly enough, the QCISD and QCISD(T) methods produce longer bond lengths, which might be a basis set effect; computed MP2–4 bond lengths are consistently longer (by 0.008, 0.007, and 0.006 Å, respectively) than with the RM basis.

Concerning the dissociation energies, the most remarkable feature is the large effect of single excitations. Taken as

the difference between CCD and QCISD values, it is no less than 0.48 eV! The triple excitation contribution 0.21 eV is comparable to the 0.18 eV difference between MP4(SDQ) and MP4(SDTQ) in the RM study. This value is itself intermediate between the large 0.41 eV contribution in the  $a^3\Pi$  state of  $C_2$  and the small 0.13 eV contribution in the  $X^3\Sigma^-$  state of  $Si_2$ . The difference with the RM basis set is quite small [0.01 eV at the MP4(DQ) level], whereas the difference between the RM and the BL basis sets was 0.20 eV at the Davidson-corrected MRD-CI level. This indicates that the effect of *f* functions on the dissociation energy should not be neglected.

As expected, the situation for the  $A^3\Sigma^-$  state is quite different. Table II lists the computed spectroscopic constants with several methods. Projected and unprojected MP results are virtually identical to each other, because no appreciable spin contamination is present. Correspondingly, single excitations have no anomalous effects on the dissociation energy and the CCD + ST(CCD) spectroscopic parameters given should be very close to the full CI limit within this basis set. Indeed, the QCISD(T) results are hardly different from those at the CCD + ST(CCD) level. From the QCISD(T)  $D_e$ 's for each state, a rather high  $T_e$  value of  $4356 \text{ cm}^{-1}$  is found. Neglect of triple excitations reduces this value to  $4037 \text{ cm}^{-1}$ , compared to the large basis set multi-reference second order configuration interaction (MR-SOCI) result of  $3619 \text{ cm}^{-1}$  by BROBM. BL suggest a value of "about  $4000 \text{ cm}^{-1}$ " based on their high-level calculations. It should be remarked that neither treatment includes triple excitations properly, which might be responsible for part of the disagreement.

As can be seen from Table III, the computational behavior of the  $a^1\Sigma^+$  state could hardly be more different from that of the  $X^3\Pi$  state. With the exception of MP2, the anharmonic constants at the other levels can be approximated quite well using the displaced-curve approximation outlined in Eqs. (3) and (4). The state is unbound at the HF level, but has a markedly high correlation energy. Oscillation of the MP series occurs. As a consequence of this, the MP2 spec-

TABLE II. Computed spectroscopic constants for the  $A^3\Sigma^-$  state [MC-311G(*d*)].

Method	$D_e$ (eV)	$D_0$ (eV)	$r_e$ (Å)	$r_0$ (Å)	$B_e$ ( $\text{cm}^{-1}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$\omega_e x_e$ ( $\text{cm}^{-1}$ )	$10^3 \alpha_e$ ( $\text{cm}^{-1}$ )
UHF	1.86	1.80	1.765	1.768	0.644 01	1002.6	4.61	4.14
MP2	3.40	3.35	1.810	1.814	0.612 75	865.1	5.67	5.46
MP3	3.34	3.28	1.808	1.811	0.614 21	881.2	4.81	5.01
MP4(DQ)	3.22	3.16	1.804	1.808	0.616 63	894.7	4.54	4.79
MP4(SDQ)	3.26	3.21	1.809	1.812	0.613 56	879.9	4.81	4.46
CCD	3.16	3.11	1.803	1.806	0.617 62	898.0	4.47	4.78
CCD + T(CCD)	3.33	3.27	1.813	1.817	0.610 63	868.7	4.50	5.03
CCD + ST(CCD)	3.37	3.32	1.818	1.822	0.607 59	855.2	4.48	5.17
PUHF	1.81	1.75	1.765	1.768	0.644 27	1003.9	4.60	4.13
PMP2	3.38	3.33	1.810	1.814	0.612 98	866.1	5.67	5.46
PMP3	3.33	3.28	1.808	1.811	0.614 34	881.6	4.84	5.01
PMP4	3.21	3.16	1.804	1.808	0.616 75	895.1	4.31	4.77
CISD	2.91	2.85	1.799	1.803	0.620 01	907.7	4.40	4.71
CISD + PC	3.25	3.19	1.814	1.817	0.610 36	869.4	3.30	4.62
QCISD	3.22	3.17	1.808	1.812	0.613 84	881.4	4.83	4.45
QCISD(T)	3.39	3.34	1.819	1.823	0.606 56	851.2	4.89	4.53

TABLE III. Computed spectroscopic constants for the  $a^1\Sigma^+$  state [MC-311G( $d$ )].

Method	$D_e$ (eV)	$D_0$ (eV)	$r_e$ (Å)	$r_0$ (Å)	$B_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$10^3 \alpha_e$ (cm <sup>-1</sup> )
HF	-0.45	-0.52	1.626	1.629	0.759 53	1148.2	6.51	5.28
MP2	3.06	3.00	1.684	1.687	0.708 19	989.1	6.70	6.23
MP3	2.38	2.31	1.652	1.655	0.735 23	1088.0	6.61	5.52
MP4DQ	2.35	2.29	1.661	1.664	0.727 46	1058.7	6.44	5.67
MP4SDQ	2.69	2.63	1.669	1.672	0.720 91	1035.2	6.65	5.95
MP <sub>x</sub>	2.29	2.22	1.661	1.664	0.727 69	1060.6	6.38	5.64
CCD	2.36	2.30	1.663	1.667	0.725 57	1052.8	6.71	5.78
CCD + T(CCD)	2.83	2.77	1.678	1.682	0.712 66	1004.6	6.94	6.24
CCD + ST(CCD)	3.07	3.01	1.682	1.686	0.709 77	992.8	7.10	6.43
QCISD	2.96	2.89	1.657	1.660	0.731 54	1080.8	7.04	5.75
QCISD(T)	3.39	3.33	1.666	1.670	0.722 99	1053.1	7.36	6.02

troscopic constants benefit from a fortunate error compensation to yield values in excellent agreement with those at the CCD + ST(CCD) level, which one should expect to be quite close to the full CI limit for this closed-shell species. Note the small, but nonnegligible effect of single excitations on  $r_e$ , as well as the quite significant triple excitation effect. The harmonic frequency was computed as 955 cm<sup>-1</sup> by BROBM, using a very large QZ(3d 2f)STO basis set and Davidson-corrected multireference second-order CI. A prediction of 927 cm<sup>-1</sup> was made using the same method [and a restricted open-shell Hartree-Fock (ROHF) wave function] for the  $X^3\Pi$  state, so, based on the deviation of this value from the "best theoretical estimates," the CCD(ST) value should be quite close to the actual one. Similar considerations apply for the bond length. Oddly enough, when the calculations were repeated at the QCISD and QCISD(T) levels, all spectroscopic constants were affected significantly. Apparently the problems associated with not including the  $\exp(T_1 + T_2)$  ansatz to infinite order are not necessarily restricted to UHF species with heavy spin contamination. Also, the account of triple excitations is much more complete in the present method than in CCD + ST(CCD), which explains the difference in triple excitation contribution. At this level, the  $a^1\Sigma^+$  state lies much closer ( $T_e = 4355$  cm<sup>-1</sup>) to the ground state than was previously believed (cf. the  $T_e$  values of 6856 cm<sup>-1</sup> by Bruna *et al.*,<sup>9</sup> and of 6628 cm<sup>-1</sup> by Lutz and Ryan<sup>8</sup>); in this sense, it compares well to the MR-SOCI result of 5079 cm<sup>-1</sup> obtained by BROBM.

Because the size-consistency corrected CI methods apparently fail to produce a good rendition of the potential curve for the ground state, these methods were abandoned in the study of basis set effects.

Adding a second set of  $d$  functions to each atom results in the spectroscopic parameters for the  $X^3\Pi$  state given in Table IV. Principal features are: (a) a systematic shortening of the bond distance, which decreases as the electron correlation method is improved; (b) an almost negligible effect on the dissociation energy; (c) a consistent lowering of the harmonic frequency by about 15 cm<sup>-1</sup>. The QCISD(T) value of 959 cm<sup>-1</sup> is in excellent agreement with the empirically corrected value of  $962 \pm 10$  cm<sup>-1</sup> by RM. Although the MC-311G(2d) basis set is quite comparable to the one used by RM, slightly lower (about 0.05 eV)  $D_e$  values are consistently obtained. The main difference between both basis sets appears to lie in the values for the polarization exponents. Our computed harmonic frequencies and anharmonicity constants are also consistently lower.

One might argue that since Si has a greater tendency than C to form compounds with significant  $d$  character, the Si atom should be given more polarization functions than the C atom, as Larsson<sup>47</sup> did in his study. We investigated the effect of this by using the 6-311G( $d$ ) basis on C and its MC-311G(2d) partner on Si. Our findings, summarized in Table V, are that  $D_e$  is hardly affected; however, a much smaller decrease of about 4 cm<sup>-1</sup> (compared to the singly polarized basis set) is found for the harmonic frequency, whereas the bond distance is significantly shorter (and thus closer to the

TABLE IV. Computed spectroscopic constants for the  $X^3\Pi$  state [MC-311G(2d)].

Method	$D_e$ (eV)	$D_0$ (eV)	$r_e$ (Å)	$r_0$ (Å)	$B_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$10^3 \alpha_e$ (cm <sup>-1</sup> )
UHF	2.59	2.54	1.759	1.763	0.648 80	825.1	2.41	5.89
MP2	3.51	3.46	1.699	1.704	0.695 60	888.3	7.20	9.26
MP3	3.35	3.29	1.703	1.709	0.691 89	876.4	6.92	9.30
MP4DQ	3.18	3.13	1.707	1.713	0.688 73	871.4	6.53	9.10
MP4SDQ	3.32	3.26	1.707	1.712	0.689 07	892.2	7.44	9.00
PUHF	2.78	2.72	1.759	1.764	0.648 54	878.2	5.89	6.17
PMP2	3.72	3.67	1.708	1.713	0.688 07	929.2	7.10	8.05
PMP3	3.56	3.50	1.715	1.720	0.682 63	905.0	6.25	7.89
QCISD	3.65	3.59	1.725	1.729	0.674 39	952.7	6.89	6.32
QCISD(T)	3.88	3.82	1.730	1.734	0.670 57	959.3	6.49	5.84

TABLE V. Computed spectroscopic constants for the  $X^3\Pi$  state [MC-311G(2*d* on Si, 1*d* on C)].

Method	$D_e$ (eV)	$D_0$ (eV)	$r_e$ (Å)	$r_0$ (Å)	$B_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$10^3 \alpha_e$ (cm <sup>-1</sup> )
UHF	2.59	2.54	1.757	1.761	0.650 03	830.8	2.47	5.83
MP2	3.49	3.44	1.697	1.703	0.696 67	903.0	6.98	8.83
MP3	3.34	3.29	1.701	1.706	0.693 78	895.7	6.78	8.81
MP4DQ	3.19	3.14	1.704	1.710	0.690 95	891.8	6.49	8.64
MP4SDQ	3.32	3.27	1.704	1.710	0.691 12	910.3	7.29	8.57
PUHF	2.79	2.74	1.758	1.762	0.649 79	883.8	5.81	6.07
PMP2	3.71	3.65	1.706	1.711	0.689 42	943.8	6.97	7.72
PMP3	3.56	3.50	1.712	1.717	0.684 85	924.5	6.25	7.53
QCISD	3.66	3.60	1.722	1.726	0.676 61	966.3	6.51	6.14
QCISD(T)	3.88	3.82	1.727	1.731	0.673 09	972.6	6.00	5.68

“experimental” value) than with the full (2*d*) basis set. However, some sensitivity to the values for the exponents cannot be ruled out; this effect should decrease with increasing basis set.

Adding a set of *f* functions changes the picture dramatically, as witnessed in Table VI. The dissociation energy is increased by no less than 0.25 eV at the QCISD(T) level, whereas the bond distance is shortened by 0.006 Å. The QCISD value for  $r_e$  is in exact agreement with the “experimental” value of 1.719 Å by BROBM. However, the triples contribution again lengthens the bond by 0.005 Å. The  $D_e$  results are readily understood in terms of Dunning’s finding<sup>48</sup> (which is supported by our studies on combined bond-polarization basis sets<sup>49</sup>) that [1*d*] and [2*d* 1*f*] polarization complements are well balanced, whereas [2*d*] is not. It is possible that further expansion of the polarization complement would result in a shorter bond length; however, the CISD + (DC)/[3*d* 2*f*]  $r_e$  of BROBM is 0.004 Å longer than our CISD + DC/[1*d*] result, which is a counter-indication. In the Dunning sense, the next well-balanced basis set would have a [3*d* 2*f* 1*g*] polarization complement; however, the hardware and software available to us preclude such a large basis set. Another factor involved might be core–valence correlation. Its proper inclusion would require a basis set of at least double zeta quality in the cores, as well as (most desirably) inner-shell polarization functions. The same remarks apply here. Comparison with BL’s [2*d* 1*f*] ANO set shows that our computed  $r_e$  is much closer to the

“experimental” value. As the triple excitations significantly improve the quality of the computed  $D_e$ , their neglect does not seem warranted. Finally, the “experimental” estimate<sup>7</sup> assumes that their computed CISD + DC values<sup>7</sup> for the  $b^1\Pi$  and  $X^3\Pi$  states are in error by almost equal amounts, which implies that triple excitations and higher-order effects are similar for both states. It is easily verified from our results that this assumption does not hold for the three states considered in the present paper; upon proceeding from CCD to CCD + T(CCD) [the basis set always being MC-311G(*d*)], the  $A^3\Sigma^-$  state lengthens by 0.010 Å, whereas the  $a^1\Sigma^+$  state lengthens by no less than 0.015 Å and the  $X^3\Pi$  state even shortens by 0.003 Å. Considering the argument that the QCISD–QCISD(T) difference would be more appropriate for the latter state, we find lengthenings of 0.005, 0.011, and 0.009 Å for the  $X^3\Pi$ ,  $A^3\Sigma^-$ , and  $a^1\Sigma^+$ , respectively. It is not very likely that these differences would suddenly cease to exist upon proceeding to a larger basis set.

As we did compute spectroscopic parameters using the large basis set for the  $A^3\Sigma^-$  state (which are listed in Table VII), we could compare the computational behavior with that of the  $X^3\Pi$  state. And indeed, the effect of triple excitations is quite different in both states. Although the effect on the dissociation energy is smaller for the upper than for the lower state, the bond is lengthened by no less than 0.013 Å, compared to the 0.005 Å of the lower state. If a difference of 0.008 Å is introduced by the neglect of triple excitations, even with this rather large basis set and sophisticated elec-

TABLE VI. Computed spectroscopic constants for the  $X^3\Pi$  state [MC-311G(2*d* 1*f*)].

Method	$D_e$ (eV)	$D_0$ (eV)	$r_e$ (Å)	$r_0$ (Å)	$B_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$10^3 \alpha_e$ (cm <sup>-1</sup> )
UHF	2.66	2.61	1.757	1.761	0.649 93	826.0	2.90	5.94
MP2	3.72	3.66	1.690	1.695	0.703 01	909.0	8.51	9.28
MP3	3.58	3.53	1.694	1.700	0.699 57	899.1	8.22	9.26
MP4DQ	3.38	3.32	1.698	1.704	0.696 06	893.1	7.74	9.05
MP4SDQ	3.56	3.51	1.698	1.704	0.695 91	915.6	8.49	8.92
PUHF	2.86	2.80	1.758	1.763	0.649 15	879.0	5.88	6.14
PMP2	3.93	3.87	1.701	1.706	0.694 15	946.9	7.96	8.11
PMP3	3.80	3.74	1.707	1.712	0.689 03	923.8	7.12	7.91
QCISD	3.89	3.83	1.719	1.723	0.679 51	971.6	6.94	6.18
QCISD(T)	4.13	4.07	1.724	1.728	0.675 02	978.7	6.24	5.63

TABLE VII. Computed spectroscopic constants for the  $A^3\Sigma^-$  state [MC-311G(2df)].

Method	$D_e$ (eV)	$D_0$ (eV)	$r_e$ (Å)	$r_0$ (Å)	$B_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$10^3 \alpha_e$ (cm <sup>-1</sup> )
UHF	2.05	1.99	1.763	1.766	0.645 75	1005.8	4.47	4.04
MP2	3.70	3.64	1.805	1.809	0.616 00	871.2	5.52	5.33
MP3	3.61	3.56	1.804	1.807	0.616 99	883.4	4.77	4.95
MP4DQ	3.39	3.34	1.799	1.802	0.620 26	900.2	4.45	4.70
MP4SDQ	3.52	3.46	1.803	1.807	0.617 45	886.9	4.64	4.87
PUHF	1.99	1.93	1.763	1.765	0.646 04	1007.0	4.47	4.03
PMP2	3.66	3.61	1.805	1.809	0.616 22	872.1	5.51	5.32
PMP3	3.60	3.55	1.804	1.807	0.617 12	883.9	4.77	4.95
QCISD	3.47	3.42	1.802	1.806	0.617 89	888.6	4.70	4.87
QCISD(T)	3.66	3.61	1.815	1.818	0.609 68	854.6	4.75	5.17

tron correlation model, it is not very unlikely that the relative bond lengths determined by BROBM with a somewhat larger basis set using size-consistency corrected CI are in error by a similar amount.

We attempted calculations on the  $^1\Pi$  state using the MC-311G(*d*) basis set. However, this open-shell singlet resulted in a heavily contaminated wave function ( $\langle S^2 \rangle \approx 1.0$ ), for which SCF convergence could only be obtained by using the quadratically convergent self-consistent field (QCSCF)<sup>50</sup> option in the program. For the spin-projected UHF and MP energies, the Dunham analysis was even divergent. The QCISD calculations result in an unrealistically small (about 1800 cm<sup>-1</sup>) value for  $T_e$  (BROBM found 7259 cm<sup>-1</sup>). Apparently, this is due to the neglect of some “repulsive” cluster terms involving  $T_1$  in a QCISD calculation (Bartlett already pointed out in his review article<sup>51</sup> that these terms could be important for a pathological reference wave function which results in very high  $T_1$  amplitudes; such a case is definitely at hand here). For what it is worth, the bond length increases by 0.009 Å upon incorporating triple excitations; at the same level of theory, the effect on the  $X^3\Pi$  state is only 0.005 Å. This picture might well change completely when a restricted open-shell wave function could be used, but it does indicate again that the assumption of BROBM about constant bond length errors in their calculations is not valid.

At this point, we prefer to think of the 1.719 Å “best estimate” as a lower bound, with our own value of 1.725 Å as an upper bound for  $r_e(X^3\Pi)$ . So until the  $X-A$  transition has been resolved experimentally, we propose preliminary  $r_e$  and  $r_0$  values of  $1.722 \pm 0.003$  and  $1.726 \pm 0.003$  Å, respectively.

Finally, the addition of diffuse functions results in a small increase (about 0.02 eV) in binding energy, but has a negligible effect on the other spectroscopic constants. It is therefore not considered further.

Assuming additivity of corrections between the diffuse functions and the additional polarization functions, this results in a direct  $D_e$  of 4.15 eV. Applying the G1 theory<sup>36</sup> would then result in a basis set incompleteness correction of 0.16 eV. As the G1 theory has a general level of accuracy of  $\pm 0.1$  eV, this results in a best estimate of  $4.31 \pm 0.10$  eV for the dissociation energy  $D_e$  of SiC. This is about 0.1 eV lower than the best previous determination by BL, who suggested

4.4 eV based on an empirical correction for the errors in  $C_2$  and  $Si_2$ . It is remarked here that the G1 theory does not correct for inner-shell effects, being developed for first-row compounds. However, the effect of this on the dissociation energy of a mixed first-second row molecule should be negligible. Further improvement of the basis set (particularly the addition of *g* functions) could also slightly increase the computed  $D_e$ , but for the philosophy behind G1 theory to remain valid, this should also imply improvements in the basis set used to calculate the correction terms, which will lower them. However, the addition of an *sp* bond function to the  $[2d\ 1f]$  polarization space should increase the direct dissociation energy by about 0.1 eV and the computed dissociation energy with isogyric correction by about 0.05 eV.<sup>49</sup> It is possible that a further small increase would result from the addition of a *d*-type bond function. Our determination of 4.31 eV is then perhaps best considered as a lower limit; the BL estimate of 4.4 eV as an upper limit. The actual  $D_e$  is probably somewhere in between, so we recommend a preliminary value of  $4.36 \pm 0.05$  eV.

The computed  $T_e$  value for the  $X^3\Pi - A^3\Sigma^-$  transition is 3790 cm<sup>-1</sup> at the highest level of theory used, in perfect agreement with the 3781 cm<sup>-1</sup> value of BL. Neglecting the effect of triple excitations leads to a value of 3390 cm<sup>-1</sup>, which again underscores their importance. Apparently, the multireference CI treatment by BL does include some, but of course not all, of the dominant triple excitation effects.

### Thermochemistry

The data employed in setting up the partition functions have been summarized in Table VIII. Table IX presents the thermodynamic functions for SiC over a 100–6000 K temperature range in increments of 100 K. For the two lowest-lying states, our own QCISD(T)/MC-311G(2df) data were used. For the less prominent  $a^1\Sigma^+$  state, we thought the data at the QCISD(T)/MC-311G(*d*) level to be accurate enough. For the three next states, a mixture of data from several other publications was employed; as these states are much less prominent in the total partition function, errors in these spectroscopic constants should not have too severe consequences (*vide infra*).

Some spectroscopic constants were still missing. These were then estimated from the available data using some well-

TABLE VIII. Spectroscopic constants used in thermochemistry for SiC.

State	$g_i$	$T_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$10^3 \alpha_e$ (cm <sup>-1</sup> )
$X^3\Pi_2$	2	-37.3 <sup>j</sup>	979 <sup>a</sup>	6.24 <sup>a</sup>	0.675 02 <sup>a</sup>	5.63 <sup>a</sup>
$X^3\Pi_1$	2	0	979 <sup>a</sup>	6.24 <sup>a</sup>	0.675 02 <sup>a</sup>	5.63 <sup>a</sup>
$X^3\Pi_0$	2	37.3 <sup>j</sup>	979 <sup>a</sup>	6.24 <sup>a</sup>	0.675 02 <sup>a</sup>	5.63 <sup>a</sup>
$A^3\Sigma^-$	3	3831 <sup>a</sup>	855 <sup>a</sup>	4.75 <sup>a</sup>	0.609 68 <sup>a</sup>	5.17 <sup>a</sup>
$a^1\Sigma^+$	1	4355 <sup>b</sup>	1053 <sup>b</sup>	7.36 <sup>b</sup>	0.722 99 <sup>b</sup>	6.02 <sup>b</sup>
$b^1\Pi$	2	7259 <sup>c</sup>	963 <sup>c</sup>	8.31 <sup>i</sup>	0.674 66 <sup>d</sup>	9.32 <sup>c</sup>
$c^1\Delta$	2	9306 <sup>e</sup>	855 <sup>f</sup>	7.07 <sup>i</sup>	0.605 35 <sup>c</sup>	10.57 <sup>c</sup>
$d^1\Sigma^+$	1	11614 <sup>h</sup>	980 <sup>e</sup>	10.19 <sup>i</sup>	0.620 83 <sup>d</sup>	2.76 <sup>c</sup>

$$D_e(X^3\Pi) = 4.36 \pm 0.05 \text{ eV} = 35\,167 \pm 400 \text{ cm}^{-1}.$$

<sup>a</sup>This work, QCISD(T)/MC-311G(2df).

<sup>b</sup>This work, QCISD(T)/MC-311G(d).

<sup>c</sup>BROBM (Ref. 7), *ab initio*.

<sup>d</sup>Calculated using experimental  $B_0$  and *ab initio*  $\alpha_e$  from BROBM.

<sup>e</sup>Estimated from experimental  $D_0$  and  $B_0$  values and computed  $\alpha_e$ , all from BROBM.

<sup>f</sup>MRD-CI value from Bruna *et al.* (Ref.9).

<sup>g</sup> $c^1\Delta$ - $A^3\Sigma^-$  separation from BROBM (*ab initio*);  $X^3\Pi$ - $A^3\Sigma^-$  separation from this work.

<sup>h</sup> $d^1\Sigma^+$ - $a^1\Sigma^+$  separation from BROBM (observed);  $X^3\Pi$ - $a^1\Sigma^+$  separation from this work.

<sup>i</sup> $\omega_e x_e$  estimated from the linear Birge-Sponer relationship.

<sup>j</sup>Spin-orbit coupling constant  $A = -37.3 \text{ cm}^{-1}$  from Ref. 16.

known relationships between spectroscopic constants. More specifically, the harmonic frequency for the  $d^1\Sigma^+$  state was estimated from the experimental rotational and centrifugal distortion constants

$$D_e = 4B^3/\omega_e^2, \quad (5a)$$

or approximately

$$D_0 \approx 4B_0^3/\omega_e^2 \quad (5b)$$

from which

$$\omega_e \approx \sqrt{4B_0^3/D_0}, \quad (5c)$$

whereas the anharmonicity constants for all three states were estimated from the computed dissociation and transition energies and a linear Birge-Sponer relationship

$$\omega_e x_e \approx \omega_e^2/4(D_e(X^3\Pi) - T_e). \quad (6)$$

The rotation-vibration coupling constant  $\alpha_e$  can be derived from  $r_e$ ,  $r_0$ , and either an *ab initio*  $B_e$  or an experimental  $B_0$  using the relationships

$$\alpha_e = 2B_e \left(1 - \frac{r_e^2}{r_0^2}\right) = 2B_0 \left(\frac{r_0^2}{r_e^2} - 1\right). \quad (7)$$

For the  $b^1\Pi$  and  $d^1\Sigma^+$  states, the experimental  $B_0$  from BROBM was used; for the  $c^1\Delta$  state, we employed the *ab initio*  $B_e$  from the same source.

Figure 1 presents the relative abundances for the six electronic states considered as a function of temperature. It is apparent that the ground state, being favored by its additional degeneracy entropy as a  $\Pi$  state, remains dominant even at 6000 K, where it still accounts for 76% of the total. At this same temperature, the  $A^3\Sigma^-$  state accounts for some 12%. Both states are favored against the others by their trip-

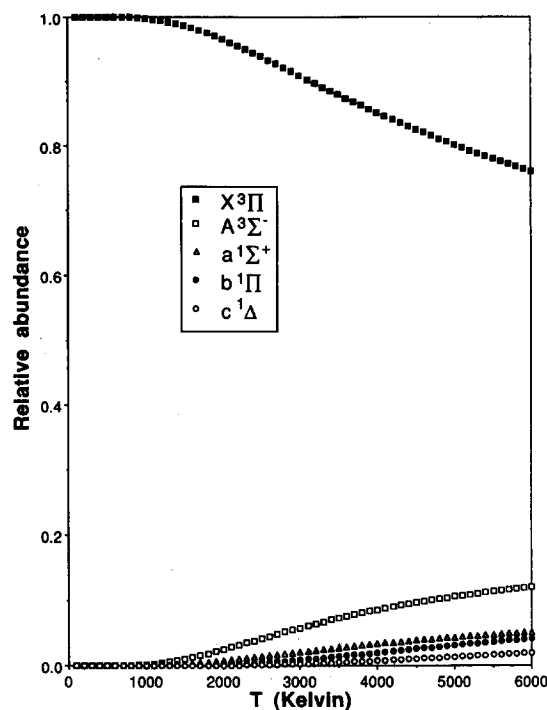


FIG. 1. Relative abundance of the five lowest states of SiC as a function of temperature.

let degeneracy entropies (at these elevated temperatures, the spin-orbit splitting levels of the  $X^3\Pi$  state are effectively degenerate). The  $a^1\Sigma^+$  state, only slightly higher in energy than the  $A^3\Pi$  state, but nondegenerate accounts for 5.1%, the  $b^1\Pi$  state (significantly higher, but having degeneracy two) for 4.2%, and the  $c^1\Delta$  state for just under 2%. The  $d^1\Sigma^+$  state fails to reach 1% of the total, so the approximation to neglect all higher states appears to be justified.

Now considering the "magical threshold" of 1% for each state, this occurs  $\sim 1500$  K for  $A^3\Sigma^-$ ,  $\sim 2200$  K for  $a^1\Sigma^+$ ,  $\sim 3200$  K for  $b^1\Pi$ , and  $\sim 4500$  K for the  $c^1\Delta$  state. For a thumbnail estimate of their effect at these temperatures on the thermodynamic functions  $C_p$ ,  $S^0$ ,  $\text{gef}(T)$ , and  $H-H_0$ , one could take their values for the individual states and interpolate linearly. [ $\text{gef}(T)$  symbolizes the Gibbs energy function  $\text{gef}(T) \equiv -(G-H_0)/T$ .] As, e.g., the four thermodynamic functions differ by only about 0.1, 2.0, 1.6 J K<sup>-1</sup> mol<sup>-1</sup>, and 0.5 kJ mol<sup>-1</sup> at 1500 K for the two lowest-lying states, neglect of a 1% contribution would result in an error of about 0.001, 0.02, 0.016, and 0.005 at this temperature. For the  $a^1\Sigma^+$  vs  $X^3\Pi$  states, errors at 2200 K will only be on the order of 0.0006, 0.012, 0.010, and 0.004. Considering the  $b^1\Pi$  state, residuals will (at 3200 K) be on the order of 0.004, 0.006, 0.003, and 0.007 when neglected. Neglect of the  $c^1\Delta$  state at 4500 K, finally, would result in errors on the order of 0.01, 0.03, 0.025, and 0.03. This magnitude of errors is certainly negligible against the other errors inherent in this treatment; however, at elevated temperatures they will become significant (see below). The thermodynamic functions  $\Delta C_p$ ,  $\Delta S^0$ ,  $\Delta \text{gef}(T)$ , and  $\Delta[H-H_0]$  for the association reaction are also tabulated in Table IX. Also given is  $-\log K_f$  for the association reaction

TABLE IX. Thermodynamic functions at 0.1 MPa for SiC and for the association reaction (all functions in  $\text{J K}^{-1} \text{mol}^{-1}$ , except  $H-H_0$  which is in  $\text{kJ mol}^{-1}$ , and  $\log K_f$ , which is dimensionless).

$T(K)$	$C_p$	$S^0$	$gef(T)$	$H-H_0$	$\Delta C_p$	$\Delta S^0$	$\Delta gef(T)$	$\Delta(H-H_0)$	$-\log K_f$
100	30.497	193.238	161.224	3.201	-18.796	-82.827	-345.299	-416.803	-234.743
200	29.889	214.028	183.042	6.197	-14.811	-94.556	-217.448	-418.471	-119.712
298.15	31.057	226.150	195.357	9.181	-12.302	-99.929	-177.967	-419.782	-81.980
300	31.085	226.343	195.548	9.238	-11.987	-100.001	-177.484	-419.805	-81.506
400	32.585	235.494	204.436	12.423	-9.843	-103.141	-158.538	-420.890	-62.458
500	33.819	242.904	211.412	15.746	-8.301	-105.162	-147.673	-421.793	-51.055
600	34.763	249.157	217.195	19.177	-7.189	-106.571	-140.712	-422.565	-43.468
700	35.513	254.574	222.156	22.692	-6.339	-107.613	-135.914	-423.240	-38.057
800	36.152	259.359	226.513	26.276	-5.641	-108.413	-132.428	-423.838	-34.006
900	36.731	263.651	230.405	29.921	-5.032	-109.041	-129.796	-424.370	-30.858
1000	37.274	267.549	233.928	33.621	-4.485	-109.543	-127.746	-424.847	-28.343
1100	37.790	271.126	237.149	37.375	-3.990	-109.947	-126.109	-425.269	-26.288
1200	38.282	274.435	240.120	41.179	-3.544	-110.275	-124.777	-425.645	-24.577
1300	38.747	277.518	242.880	45.030	-3.148	-110.542	-123.672	-425.980	-23.130
1400	39.184	280.406	245.458	48.927	-2.802	-110.762	-122.742	-426.276	-21.890
1500	39.593	283.124	247.879	52.866	-2.503	-110.944	-121.951	-426.542	-20.817
1600	39.973	285.691	250.163	56.845	-2.250	-111.098	-121.267	-426.778	-19.878
1700	40.324	288.125	252.325	60.860	-2.039	-111.229	-120.673	-426.993	-19.051
1800	40.648	290.439	254.379	64.909	-1.868	-111.340	-120.152	-427.187	-18.315
1900	40.946	292.645	256.335	68.989	-1.730	-111.437	-119.690	-427.367	-17.657
2000	41.220	294.753	258.204	73.098	-1.621	-111.522	-119.280	-427.534	-17.066
2100	41.471	296.770	259.993	77.233	-1.539	-111.600	-118.912	-427.691	-16.531
2200	41.702	298.705	261.709	81.391	-1.479	-111.669	-118.582	-427.843	-16.044
2300	41.913	300.563	263.358	85.573	-1.438	-111.735	-118.282	-427.988	-15.600
2400	42.108	302.351	264.946	89.774	-1.412	-111.795	-118.011	-428.130	-15.194
2500	42.286	304.074	266.476	93.994	-1.399	-111.852	-117.763	-428.271	-14.820
2600	42.450	305.736	267.955	98.231	-1.398	-111.907	-117.537	-428.410	-14.474
2700	42.601	307.341	269.384	102.484	-1.403	-111.960	-117.330	-428.549	-14.155
2800	42.740	308.893	270.767	106.751	-1.416	-112.011	-117.139	-428.691	-13.858
2900	42.870	310.395	272.108	111.032	-1.431	-112.060	-116.962	-428.832	-13.582
3000	42.991	311.850	273.409	115.325	-1.449	-112.110	-116.799	-428.976	-13.324
3100	43.104	313.262	274.672	119.630	-1.469	-112.157	-116.650	-429.123	-13.084
3200	43.211	314.632	275.899	123.946	-1.487	-112.204	-116.510	-429.271	-12.858
3300	43.312	315.964	277.093	128.273	-1.506	-112.250	-116.380	-429.419	-12.646
3400	43.410	317.258	278.255	132.609	-1.519	-112.295	-116.260	-429.570	-12.446
3500	43.504	318.518	279.388	136.955	-1.530	-112.338	-116.147	-429.723	-12.258
3600	43.596	319.745	280.492	141.310	-1.537	-112.382	-116.042	-429.876	-12.081
3700	43.687	320.941	281.569	145.675	-1.538	-112.424	-115.943	-430.029	-11.913
3800	43.778	322.107	282.621	150.048	-1.534	-112.465	-115.851	-430.182	-11.754
3900	43.870	323.245	283.648	154.431	-1.522	-112.505	-115.764	-430.335	-11.603
4000	43.962	324.357	284.652	158.823	-1.504	-112.543	-115.684	-430.486	-11.460
4100	44.056	325.444	285.633	163.224	-1.479	-112.580	-115.608	-430.635	-11.324
4200	44.152	326.507	286.594	167.635	-1.447	-112.614	-115.536	-430.781	-11.195
4300	44.252	327.547	287.534	172.055	-1.406	-112.648	-115.468	-430.924	-11.071
4400	44.354	328.566	288.455	176.486	-1.359	-112.680	-115.405	-431.062	-10.953
4500	44.459	329.564	289.358	180.926	-1.303	-112.710	-115.343	-431.195	-10.841
4600	44.568	330.542	290.242	185.378	-1.240	-112.738	-115.287	-431.322	-10.733
4700	44.680	331.502	291.110	189.840	-1.171	-112.764	-115.233	-431.443	-10.630
4800	44.796	332.444	291.962	194.314	-1.094	-112.787	-115.182	-431.556	-10.531
4900	44.915	333.369	292.797	198.800	-1.011	-112.809	-115.134	-431.661	-10.436
5000	45.038	334.277	293.618	203.298	-0.921	-112.830	-115.087	-431.758	-10.346
5100	45.164	335.170	294.424	207.808	-0.826	-112.847	-115.043	-431.844	-10.258
5200	45.292	336.049	295.216	212.331	-0.726	-112.861	-115.001	-431.922	-10.174
5300	45.423	336.913	295.994	216.867	-0.621	-112.874	-114.962	-431.989	-10.094
5400	45.556	337.763	296.760	221.416	-0.512	-112.885	-114.923	-432.046	-10.016
5500	45.690	338.600	297.513	225.978	-0.401	-112.894	-114.886	-432.092	-9.941
5600	45.826	339.425	298.254	230.554	-0.286	-112.899	-114.850	-432.126	-9.869
5700	45.962	340.237	298.984	235.144	-0.170	-112.903	-114.815	-432.148	-9.799
5800	46.098	341.037	299.702	239.747	-0.053	-112.906	-114.783	-432.159	-9.732
5900	46.233	341.827	300.409	244.363	0.064	-112.905	-114.751	-432.160	-9.667
6000	46.368	342.605	301.106	248.993	0.182	-112.903	-114.720	-432.147	-9.604



(The thermodynamic functions used for Si and C atoms were reconstructed from the energy level information given in the JANAF tables.<sup>41</sup> It should be noted that the three components of the ground state of Si are mixed up as printed, and that even with an additional  $^3P$  state at  $33\,326\text{ cm}^{-1}$  as suggested, minor deviations from the JANAF tables are seen above 5500 K.) The primary qualitative information to be deduced from these tables is that SiC is apparently quite stable as a molecule, having a formation constant of the order of  $10^{9.6}$  even at 6000 K.

### Effect of various approximations

Table X lists, at temperatures from 1000 to 6000 K in increments of 1000 K, as well as at room temperature, the deviations in the thermodynamic functions introduced by a number of approximations. In the table and the subsequent discussion, all changes are incremental; i.e., we are always discussing the effect of the next approximation with respect to the previous approximate partition function, never the cumulated effect of them all.

The first one is the neglect of the isotope effect. Apparently, this effect is rather small and becomes practically un-

TABLE X. Overview of the effect of different approximations on the computed thermochemical functions.

T(K)	$\delta C_p$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\delta S^0$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\delta_{\text{gef}}(T)$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\delta(H-H_0)$ (kJ mol <sup>-1</sup> )
Neglect of isotope effects				
298.15	-0.004	-0.052	-0.051	0.000
1000	-0.002	-0.057	-0.055	-0.003
2000	0.000	-0.058	-0.056	-0.004
3000	-0.001	-0.059	-0.057	-0.005
4000	-0.001	-0.058	-0.057	-0.005
5000	0.000	-0.058	-0.057	-0.005
6000	0.000	-0.058	-0.058	-0.005
Neglect of the highest excited state ( $d\ ^1\Sigma^+$ )				
298.15	0.000	0.000	0.000	0.000
1000	0.000	0.000	0.000	0.000
2000	-0.023	-0.003	0.000	-0.006
3000	-0.143	-0.032	-0.005	-0.082
4000	-0.282	-0.094	-0.019	-0.299
5000	-0.362	-0.167	-0.042	-0.628
6000	-0.365	-0.235	-0.068	-0.997
Neglect of all but the first excited states (i.e., $a\ ^1\Sigma^+$ , $b\ ^1\Pi$ , $c\ ^1\Delta$ , and $d\ ^1\Sigma^+$ )				
298.15	0.000	0.000	0.000	0.000
1000	-0.098	-0.018	-0.002	-0.015
2000	-1.032	-0.328	-0.070	-0.516
3000	-2.118	-0.963	-0.256	-2.121
4000	-2.782	-1.673	-0.522	-4.604
5000	-3.181	-2.341	-0.820	-7.603
6000	-3.307	-2.938	-1.124	-10.877
Neglect of all excited states				
298.15	0.000	0.000	0.000	0.000
1000	-0.649	-0.140	-0.022	-0.118
2000	-2.365	-1.223	-0.331	-1.785
3000	-2.375	-2.218	-0.806	-4.238
4000	-1.948	-2.844	-1.244	-6.403
5000	-1.590	-3.237	-1.606	-8.161
6000	-1.378	-3.507	-1.901	-9.634
Neglect of spin-orbit coupling				
298.15	-0.177	0.089	1.407	-0.393
1000	-0.016	0.008	0.439	-0.430
2000	-0.004	0.002	0.222	-0.439
3000	-0.001	0.001	0.148	-0.441
4000	-0.001	0.000	0.112	-0.442
5000	-0.001	0.000	0.089	-0.443
6000	0.000	0.001	0.074	-0.444
RRHO approximation ( $\omega_0 = \omega_e - 2\omega_e x_e$ )				
298.15	-0.038	-0.059	-0.045	-0.004
1000	-0.314	-0.233	-0.109	-0.125
2000	-0.732	-0.577	-0.255	-0.644
3000	-1.230	-0.964	-0.425	-1.615
4000	-1.903	-1.404	-0.614	-3.162
5000	-2.911	-1.930	-0.823	-5.536
6000	-4.311	-2.580	-1.060	-9.119

TABLE X. (continued).

T(K)	$\delta C_p$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\delta S^0$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\delta \text{gef}(T)$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\delta(H-H_0)$ (kJ mol <sup>-1</sup> )
Effect of a + 100 cm <sup>-1</sup> error in $T_e(X^3\Pi \rightarrow A^3\Sigma^-)$				
298.15	0.000	0.000	0.000	0.000
1000	-0.057	-0.016	-0.003	-0.013
2000	-0.035	-0.060	-0.022	-0.076
3000	0.028	-0.061	-0.036	-0.075
4000	0.047	-0.049	-0.041	-0.034
5000	0.047	-0.038	-0.042	0.013
6000	0.041	-0.030	-0.040	0.057
Effect of a + 10 cm <sup>-1</sup> error in $\omega_e$ for the ground state				
298.15	-0.049	-0.018	-0.004	-0.005
1000	-0.028	-0.076	-0.041	-0.036
2000	-0.018	-0.091	-0.063	-0.056
3000	-0.027	-0.100	-0.073	-0.078
4000	-0.048	-0.109	-0.082	-0.114
5000	-0.087	-0.124	-0.088	-0.180
6000	-0.123	-0.144	-0.096	-0.287
Effect of a + 0.005 cm <sup>-1</sup> error in $B_e$ on ditto				
298.15	0.000	-0.062	-0.062	0.000
1000	-0.002	-0.063	-0.063	-0.001
2000	-0.004	-0.065	-0.064	-0.003
3000	-0.008	-0.068	-0.064	-0.010
4000	-0.013	-0.070	-0.066	-0.020
5000	-0.024	-0.074	-0.067	-0.038
6000	-0.043	-0.081	-0.069	-0.070
Effect of a + 2 cm <sup>-1</sup> error in $\omega_e x_e$ on ditto				
298.15	0.021	0.007	0.002	0.001
1000	0.062	0.053	0.022	0.030
2000	0.156	0.121	0.054	0.135
3000	0.347	0.215	0.091	0.373
4000	0.733	0.364	0.139	0.897
5000	1.102	0.571	0.204	1.836
6000	0.993	0.772	0.283	2.937
Effect of a + 0.002 cm <sup>-1</sup> error in $\alpha_e$ on ditto				
298.15	0.006	0.014	0.013	0.000
1000	0.040	0.038	0.021	0.016
2000	0.097	0.082	0.040	0.084
3000	0.183	0.136	0.063	0.221
4000	0.365	0.211	0.090	0.482
5000	0.758	0.330	0.125	1.023
6000	1.301	0.515	0.173	2.051

noticeable for  $C_p$  and  $H - H_0$  at practical temperatures. The effect on  $S^0$  and  $\text{gef}(T)$  is basically constant at these temperatures. It mainly comes from the translation terms.

The second approximation considered is the neglect of the  $d^1\Sigma^+$  state, which should give some indication of the effect of neglecting higher excited states. Apparently, the effect on the free energy function is negligible, that on the entropy somewhat less so, whereas the enthalpy might change by about 1 kJ mol<sup>-1</sup> at 6000 K, where  $C_p$  changes by 0.37 J K<sup>-1</sup> mol<sup>-1</sup>. These effects drop sharply with temperature.

The third one is the neglect of all excited states but the first (i.e.,  $a^1\Sigma^+$ ,  $b^1\Pi$ ,  $c^1\Delta$ , and  $d^1\Sigma^+$ ). It is hardly noticeable at lower temperatures, but at 6000 K, the effect on

$H - H_0$  may increase to as much as 11 kJ mol<sup>-1</sup>. The effect on entropy is just under 3 J K<sup>-1</sup> mol<sup>-1</sup>, whereas that on the free energy function is about 1.1 J K<sup>-1</sup> mol<sup>-1</sup>.

The effects of also neglecting the first excited state  $A^3\Sigma^-$  are similar, except that the heat capacity is affected markedly less.

The effect of neglecting spin-orbit coupling in the ground state is apparently only felt at room or lower temperatures. It may safely be ignored at temperatures of interest for high-temperature chemistry. The enthalpy effect, which has an asymptote at the spin-orbit coupling constant of 37.3 cm<sup>-1</sup>, may basically be seen as the consequence of equal population in the three spin-orbit levels. The effect on the free energy function at these temperatures is readily ex-

plained: since  $\delta S^0$  is very small,  $\delta \text{gef} \approx -\delta(H - H_0)/T$ .

Finally, the RRHO approximation does result in an error of about  $8 \text{ kJ mol}^{-1}$  on the enthalpy, and of grossly 4, 2, and  $1 \text{ J K}^{-1} \text{ mol}^{-1}$  on the molar heat, entropy, and free energy function, respectively, at 6000 K. Given the drastic nature of this approximation, this relatively low magnitude of errors is quite surprising. The errors in  $C_p$  and  $H - H_0$  sink drastically with temperature: those in  $S^0$  and  $\text{gef}(T)$  appear to decrease linearly.

In order now to assess the effect of errors in our computed spectroscopic constants, we evaluated the partition function for the ground state using small perturbations in the constants.

The effect considered of a  $+100 \text{ cm}^{-1}$  error on the  $X^3\Pi \rightarrow A^3\Sigma^-$  transition energy (neglecting all other states) is found to be surprisingly small: only of the order of  $0.05 \text{ J K}^{-1} \text{ mol}^{-1}$  on  $C_p$ ,  $S^0$ , and  $\text{gef}(T)$ , and  $0.05 \text{ kJ mol}^{-1}$  on  $H - H_0$ . This implies that the electronic transition energies determined in this work should normally be accurate enough. Note that the error changes sign for  $C_p$  and  $H - H_0$ , and that it appears to pass through a maximum (in absolute value) at different temperatures for all spectroscopic constants.

Increasing the harmonic frequency by  $10 \text{ cm}^{-1}$  appears to result in only minor effects (less than  $0.3 \text{ kJ mol}^{-1}$  on the enthalpy, about  $0.1 \text{ J K}^{-1} \text{ mol}^{-1}$  on the other constants). For the excited state contributions, the effects of such errors would then certainly become negligible. This means that our *ab initio* frequencies are certainly accurate enough for the present purpose.

Next, the effect of changing the ground-state rotational constant by  $0.005 \text{ cm}^{-1}$  (which would imply a large error in the bond distance of about  $0.006 \text{ \AA}$ ) would result in only petty effects (on the order of  $0.05$  to  $0.08 \text{ J K}^{-1} \text{ mol}^{-1}$ ), which are almost constant with temperature, on  $S^0$  and  $\text{gef}(T)$ . For the other two functions, the effect rises with temperature, but can still be safely ignored at 6000 K.

Oddly enough, the partition functions are rather sensitive to the values used for the anharmonicity constant, however, a perturbation of  $+2 \text{ cm}^{-1}$  (which would imply a relative error of 33%) is necessary to produce an enthalpy effect which is about  $3 \text{ kJ mol}^{-1}$  at 6000 K, but which does not exceed  $1.2 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $C_p$  and  $S^0$ , and  $0.4 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $\text{gef}(T)$ . Furthermore, the effects drop with temperature. This suggests that some care should be taken in evaluating them for the ground state, but that highly approximate values can safely be used for the excited states. Similar considerations apply for a  $0.002 \text{ cm}^{-1}$  perturbation (relative error of 40%) on the rotation-vibration coupling constant. Here the effect drops steeply with decreasing temperature, so that it becomes quite harmless even at 3000 K.

All this means that the spectroscopic constants computed *ab initio* in this work should be quite good enough for the construction of the partition functions even to very high temperatures. If higher accuracy in the partition functions is required, the most desirable step would be to find some approximate parameters for the higher excited states. Even crude SCF values would suffice, given that the electronic transition energy be evaluated at some modest correlated

level. However, to make these improvements sensible, it would be even more imperative to obtain a more accurate estimate for the binding energy.

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