

THEORETICAL STUDY OF SILICON DICARBIDE

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ABSTRACT

The ground state of silicon dicarbide is predicted from self-consistent field (SCF) calculations to be linear SiCC with a closed-shell $^1\Sigma^+$ electronic structure, confirming previous experimental analyses. A number of low-lying electronic states are predicted from SCF and limited configuration interaction (CI) calculations to have vertical excitation energies in the range of ~ 1.5 to 3 eV. Although the assignment of the observed optical transition near 2.5 eV as $^1\Sigma^+ - ^1\Pi$ is supported, it is suggested that the upper state may be strongly perturbed.

Subject heading: molecular processes

I. INTRODUCTION

Although silicon is isovalent with carbon, the two have remarkably different chemical properties. Because silicon compounds are often refractory, very little has been learned experimentally about their gas phase molecular structures, nor have there been many theoretical studies. Reported here are ab initio calculations for silicon dicarbide.

Silicon dicarbide was first observed in 1926 in spectra of cool carbon stars. It was not until 30 years later, however, that the carrier of these bands around 5000 Å was tentatively identified as SiC₂ by Kleman (1956) who produced similar spectra by inserting silicon into the graphite tube of a King furnace heated to over 2500 K. This identification rested somewhat tenuously on the circumstances of production of the spectra and on the fact that a possible vibrational assignment was consistent with a carbon-carbon stretching frequency. This identification was strengthened by subsequent mass spectral studies that showed SiC₂ as a major molecular component of vaporized silicon carbide (Drowart, DeMaria, and Inghram 1958). Subsequently, Weltner and McLeod (1964) trapped these vapors in cryogenic neon and argon matrices and obtained optical and infrared spectra which supported the identification of SiC₂ as carrier of the stellar bands, but which led to a somewhat different vibrational assignment than that of Kleman. Most recently Verma and Nagaraj (1974) have obtained improved gas phase optical spectra using flash discharge techniques and have analyzed the vibrational structure in terms of a $^1\Sigma^+ - ^1\Pi$ transition in a linear SiCC molecule. Because of some difficulties in the assignment, however, they concluded that "the question is

still open and can be answered definitely only after the rotational structure of these bands is unraveled."

The present calculations were initiated in an attempt to understand more recent astronomical observations of unidentified lines in the millimeter-wave region of the spectrum. Radioastronomical observations of the molecular envelope of the evolved carbon star IRC +10216 have led to the identification of several interesting species including the C₂H, C₃N, and C₄H radicals whose spectra had not previously been observed in the laboratory (e.g., Green 1981). The chemistry in IRC +10216 appears to be quite different from that in other standard astrophysical sources, being dominated by carbon, rather than oxygen, and having a relatively high abundance of the refractory SiO and especially SiS. The species observed in this source are generally consistent with thermodynamic equilibrium models of the chemistry in the atmospheres of carbon stars (e.g., Fujita 1970), and these models predict substantial abundances of SiC and SiC₂. There are currently several relatively strong unidentified lines in this source which are not seen in other radio objects. These lines are not harmonically related, as would be the case for rotational transitions in linear molecules, but have a pattern reminiscent of *b*-type transitions in a bent symmetric structure, such as might be postulated for CSiC.

SiC₂ is isovalent with C₃; the latter is known to have a closed-shell ground state, to be linear but with a very low frequency bending mode, and to have a low-lying $^1\Pi$ state with similar geometry (see, e.g., Liskow, Bender, and Schaefer 1972; Perić-Radić *et al.* 1977). Silicon dicarbide might be expected to have a similar structure, although it is not *a priori* obvious whether the symmetric, CSiC, or asymmetric, SiCC, should be more stable.

The present calculations were designed to determine the ground state equilibrium structure and to obtain vibrational and rotational constants. Calculations were also performed to estimate the positions and structure of low-lying electronic states.

II. GROUND ELECTRONIC STATE

SCF calculations were performed assuming a closed-shell electronic structure analogous to that in C_3 . Calculations were done for symmetric, CSiC, and asymmetric, SiCC, forms, including nonlinear geometries for both. From these it appeared that the stable form is linear SiCC.

To determine the sensitivity of computed spectral and structural parameters to the level of approximation, several atomic basis sets were used, and equilibrium structures and force constants were obtained in different ways. (1) Using a standard minimum Gaussian STO-3G basis, the (linear) geometry was optimized with analytic gradient techniques, and force constants were obtained from numerical differences of the gradients. (2) A double-zeta Gaussian basis (GTO-DZ) was constructed with silicon functions from the Pacansky and Hermann (1978) SiO_2 calculations and with the Dunning (1970) contraction for carbon; geometry and force constants were obtained by (a) fitting polynomials to 16 linear geometries around the minimum, and (b) analytic gradient methods. (3) A Slater-type (STO) basis was constructed from the Clementi (1965) DZ atomic functions, and structural constants were obtained by fitting a polynomial to 13 linear geometries. (4) The above basis was augmented with polarization functions—Si $3d(2.303)$ and C $3d(2.65)$ —and constants were obtained with this STO-DZP basis by fitting 13 linear geometries around the minimum to a polynomial.

Near the completion of this study it was realized that the Si GTO basis in Pacansky and Hermann (1978) contains typographical errors that affect the inner p

orbital. Calculations near the SiCC ground state equilibrium geometry with the corrected GTO-DZ basis suggested that the main effect of this error (besides giving a much poorer total energy) was to predict SiC bond lengths several percent too large; stretching and bending force constants were not significantly different. Because use of the incorrect basis is not thought to alter any of the conclusions presented here, it was not deemed worthwhile to repeat all the affected calculations; where appropriate the incorrect basis set is referred to below as GTO-DZ-X.

a) Equilibrium Structure

Results for the equilibrium structure obtained from these calculations are presented in Table 1. It is seen that gradient techniques lead to the same structure as local polynomial fits to points around the minimum, with cubic fits being more satisfactory if enough points are available. As usual, the minimal STO-3G basis predicts short bond lengths. The most accurate bond lengths are generally predicted (within the SCF approximation) by double-zeta basis sets. For small hydrocarbons, STO-DZ and GTO-DZ bases generally predict similar bond lengths; these agree here within their expected accuracy of $\sim 1\%$. As usual, addition of polarization functions to the DZ basis predicts slightly shorter bond lengths. The best estimate for the equilibrium rotational constant is given by the STO-DZ and GTO-DZ calculations which agree on a value near $B_e = 6.35$ GHz.

All of the calculations lead to the same qualitative description of the bonding which is readily ascertained from the molecular orbital vectors and the Mulliken population analysis. The SiC bond is highly ionic, with essentially one electron transferred from silicon to carbon. There is a single SiC σ bond and effectively no overlap between the Si and C π electrons. The carbons are triple bonded, although the π electrons are strongly polarized by the positive charge on Si so that they are

TABLE 1
EQUILIBRIUM STRUCTURAL PROPERTIES OF SiCC $X^1\Sigma^+$
FROM SCF CALCULATIONS^a

Basis Set	Method	$r_e(\text{SiC})$	$r_e(\text{CC})$	E_{\min}	B_e
STO-3G	gradient	3.085	2.371	-360.18953	6.70
GTO-DZ	gradient	3.181	2.427	-364.35478	6.34
	quadratic fit	3.186	2.430	-364.35482	...
	cubic fit	3.182	2.427	-364.35478	...
STO-DZ	cubic fit	3.187	2.403	-364.46777	6.37
STO-DZP ...	quadratic fit	3.148	2.383	-364.51347	...
	cubic fit	3.150	2.381	-364.51367	6.51

^aSee text for details of computational method. Distances in a_0 ; energy in hartrees; rotation constant, B_e , in GHz.

centered mostly near the central carbon. The CC bond is slightly longer than a typical CC triple bond, but is definitely shorter than a double bond.

b) Vibrational Frequencies

Vibrational frequencies were obtained by diagonalizing the mass-weighted second derivative matrix:

$$F_{ij} = (m_i m_j)^{-1/2} (\partial^2 V / \partial q_i \partial q_j).$$

In the calculations that employed analytic gradients, the second derivatives were obtained by numerical difference from displacing each atomic x , y , and z coordinate successively by $10^{-2} a_0$, resulting in a 9×9 F matrix. In the calculations that fitted polynomials, energies for a set of linear geometries (with all atoms on the x -axis) were fitted to the valence force field form

$$V = V_0 + \frac{1}{2} \sum_{ij} k_{ij} \Delta r_i \Delta r_j + \frac{1}{6} \sum_{ijk} k_{ijk} \Delta r_i \Delta r_j \Delta r_k + \dots,$$

where Δr_1 is the displacement of SiC from its equilibrium position and Δr_2 is the displacement of CC; displacements of up to $\sim 0.1 a_0$ were used. Then

$$k_{ij} = \partial^2 V / \partial \Delta r_i \partial \Delta r_j,$$

$$k_{ijk} = \partial^3 V / \partial \Delta r_i \partial \Delta r_j \partial \Delta r_k;$$

the connection with the Cartesian coordinates used in

the analytic gradient method can be given as

$$\partial^2 V / \partial \Delta r_1^2 = \partial^2 V / \partial x_1^2,$$

$$\partial^2 V / \partial \Delta r_2^2 = \partial^2 V / \partial x_3^2,$$

$$\partial^2 V / \partial \Delta r_1 \partial \Delta r_2 = -\partial^2 V / \partial x_1 \partial x_3,$$

where the numbering starts at silicon. In these calculations a 3×3 F matrix, consisting of only components along the x -axis, was used. Force constants and vibrational frequencies from the different calculations are in Table 2.

Despite variations due to basis set and method of extracting force constants, certain points are clear. Except for the minimal STO-3G basis, the various calculations give reasonable ($\sim 10\%$) agreement on the harmonic constants. The off-diagonal force constants are all small; i.e., the valence force field model provides an adequate picture. On the other hand, the harmonic approximation may not be so good since the cubic constants are substantial.

It is often found that the SCF method overestimates vibrational frequencies by 10%–20% (Steele, Person, and Brown 1981; Blom and Altona 1977; Botschwina 1974). In particular, it is generally assumed that SCF calculations overestimate bond stretching force constants owing to the fact that bonds often dissociate improperly to excited states in this formalism. Comparison of theory and experiment for SiCC is not very consistent with this picture. The calculated CC stretch, k_{22} , is some 60%

TABLE 2
STRETCHING FORCE CONSTANTS AND VIBRATIONAL FREQUENCIES OF SiCC $X^1\Sigma^+$ FROM SCF CALCULATIONS^a

Basis Set	Method	k_{11}	k_{22}	k_{12}	k_{111}	k_{222}	k_{112}	k_{122}	ν_1	ν_2	ν_3
STO-3G	gradient	0.536	1.006	+0.047	2232	192	982
GTO-DZ	gradient	0.424	0.805	-0.005	2050	275	852
	quadratic fit	0.396	0.884	-0.005	2110	...	841
	cubic fit	0.420	0.821	-0.005	-1.044	-2.506	0.003	-0.003	2055	...	857
STO-DZ	cubic fit	0.392	0.803	-0.004	-0.584	-2.528	0.057	0.045	2023	...	831
STO-DZP	quadratic fit	0.358	0.747	-0.012	1960	...	791
	cubic fit	0.429	0.811	-0.013	-0.905	-1.786	-0.006	-0.009	2059	...	859
experiment	b	0.477 ^c	0.514 ^c	1742	147	852
	d	1742	300	853
	e	1742	...	591

^aSee text for details of computational method. Force constants are in atomic units, i.e., k_{ij} in h/a_0^2 , k_{ijk} in h/a_0^3 ; vibrational frequencies, ν_i , are in cm^{-1} .

^bVerma and Nagaraj 1974.

^cCalculated from ν_1 and ν_3 assuming a purely harmonic valence force field and choosing the more reasonable of two possible solutions (see Weltner and McLeod 1964).

^dWeltner and McLeod 1964.

^eKleman 1956.

higher than experiment, compared with the expected 10%–20%. The SiC stretch, k_{11} , on the other hand, is predicted to be less than the experimental value. The bending force constant, which is related only to the bending frequency, ν_2 , is predicted to be $\sim 35\%$ larger than experiment. The prediction for ν_1 is $\sim 15\%$ high, as expected; this frequency has often been associated with the CC stretch, but the mass combinations are such that it has more the character of an “asymmetric” stretch. The SiC (or “symmetric”) stretching frequency, ν_3 , is predicted to be somewhat smaller than experiment.

The vibrational assignments differ significantly among the three available spectroscopic analyses, although the most recent study, which has access to more extensive data, seems likely to be correct. Because the differences between theoretical and experimental vibrational frequencies appear somewhat unusual, however, it is important to determine whether the inconsistencies are large enough to suggest an incorrect analysis of the data. In this context it is better to compare theory and experiment for species that are similar to SiCC than to rely on generalizations extracted from a wide variety of systems. The closest system for which good experimental and theoretical values are available appears to be OCS (Steele, Person, and Brown 1981). There the CO stretch force constant is predicted to be 20% high, the SC stretch constant 20% low, and the bending constant only a few percent high. The discrepancy in the SC stretch is very similar to that found for SiC, which is particularly comforting since the sense is opposite than usually encountered. The differences between theory and experiment for the CO (CC) stretch and the bend are in the same sense for both molecules, but much larger for SiCC than for OCS. Considering the variation in reliability of SCF calculations found for different systems and potential errors introduced by the harmonic assumption in reducing the experimental data, the present calculations can be considered consistent with the current experimental assignment (Verma and Nagaraj 1974).

c) Dipole Moment Function

The dipole moment was calculated with the STO-DZ and STO-DZP basis sets. These agree within a few percent, but the STO-DZP values should be more reliable. The equilibrium dipole moment, which determines rotational line strengths, is predicted to be

$$\mu = 4.8 \text{ debye.}$$

The variation with bond length, which determines the infrared line strengths, is found to be well described by a function linear in both bond displacements (at least for the small bond displacements of less than $\sim 0.1 \text{ \AA}$ used here). The dipole derivatives are

$$\partial\mu/\partial r_{\text{SiC}} = 7.6 \text{ debye } \text{\AA}^{-1},$$

$$\partial\mu/\partial r_{\text{CC}} = -8.2 \text{ debye } \text{\AA}^{-1}.$$

The SCF dipole moment is probably too large (owing to lack of correlation corrections) by ~ 0.5 debye (Green 1974). The dipole derivatives are also probably overestimated by $\sim 20\%$.

d) Symmetric (CSiC) Structures

Calculations constrained to linear symmetric $D_{\infty h}$ structures using the GTO-DZ-X basis set located a minimum at $r_{\text{SiC}} \approx 3.4a_0$; however, this structure was found to be unstable to bending. Calculations constrained to C_{2v} symmetry located a minimum energy structure that is nearly an equilateral triangle, $r_{\text{SiC}} = 3.60a_0$ and CSiC angle of $58^\circ 3'$, with energy $\sim 7.7 \text{ eV}$ above the equilibrium SiCC structure (and $\sim 1.5 \text{ eV}$ below linear CSiC).

During the course of these calculations it became evident that a closed-shell electronic structure is not the lowest state for the symmetric geometries. This appeared as instability in the SCF convergence and, when calculations were performed without imposing C_{2v} symmetry on the electronic wavefunction, convergence on molecular orbitals that did not possess the same symmetry as the nuclear configuration. An analogous result for C_3 was noted by Liskow, Bender, and Schaefer (1972). A few open-shell SCF (Bagus 1972) calculations were done for linear configurations at $r_{\text{SiC}} = 3.4a_0$ using the STO-DZ basis. These indicated that both the $^3\Sigma_u^+$ and the $^3\Delta$ states arising from the $2\pi_u^3 1\pi_g$ configuration are lower than the $2\pi_u^4 1\Sigma_g^+$ state (by less than $\sim 1 \text{ eV}$). States arising from $2\pi_u^2 1\pi_g^2$ or $4\sigma_u 1\pi_g$ were found to lie higher in energy than the closed-shell configuration. This behavior is consistent with the inability to form SiC double bonds; rather the carbon p electrons prefer to remain unpaired in a carbene-like arrangement. Because the energies of all the symmetric CSiC structures were found to be so much above the equilibrium SiCC, they were not considered any further.

III. EXCITED ELECTRONIC STATES

The highest occupied σ and π orbitals in the closed-shell $^1\Sigma^+$ ground state are found to have comparable SCF orbital energies. However, the lowest unoccupied π orbital is much more stable than the lowest unoccupied σ orbital. This suggests that the low-lying excited electronic states will correspond to $9\sigma \rightarrow 3\pi$ or $2\pi \rightarrow 3\pi$ excitations. In order to estimate the relative energies of these states, two sets of calculations were performed. The first were limited CI using ground-state SCF virtual orbitals and including single excitations for all the term types which arise from either $9\sigma 3\pi$ or $2\pi^3 3\pi$ configurations; for $^1\Sigma^+$ all single excitations from the ground state were included. These calculations employed the STO-DZP basis set and a geometry near the ground-state equilibrium ($r_{\text{SiC}} = 3.292a_0$ and $r_{\text{CC}} = 2.426a_0$); excitations out of the core orbitals were found to be unim-

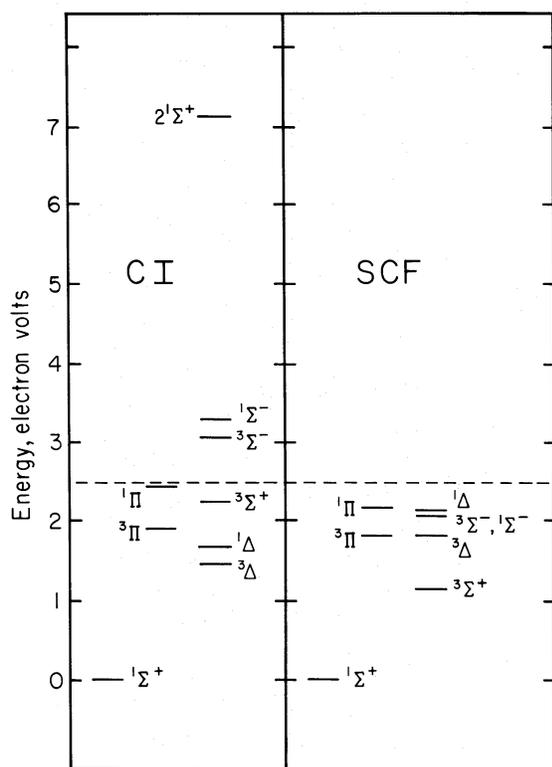


FIG. 1.—Excitation energy of electronic states of SiCC corresponding to excitations $9\sigma \rightarrow 3\pi$ and $2\pi \rightarrow 3\pi$ from the closed-shell $X^1\Sigma^+$ ground state. Details of the limited CI and open-shell SCF calculations are given in the text. Dashed line at 2.5 eV corresponds to T_0 of the observed optical spectrum.

portant and were excluded. The second calculations were open-shell SCF (Bagus 1972) using the same basis set and internuclear distances as the CI.

Results from both the CI and SCF calculations are presented in Figure 1. These calculations confirm that the closed-shell $1\Sigma^+$ is the ground state. The observed excitation energy of $T_0 = 2.5$ eV is seen to be closest to the 1Π energy in both calculations, lending confidence to the assignment of the observed spectra to a $1\Sigma^+ - 1\Pi$ transition. On the other hand, it is seen that there are several states of comparable or lower excitation energy, and this suggests that the optical spectra might suffer from strong perturbations in the upper state.

Assuming that the 1Π state is linear, the equilibrium structure was determined within the SCF approximation. Using the STO-DZP basis set, 29 points around the minimum were fitted to a cubic polynomial; resulting equilibrium bond lengths and stretching frequencies are given in Table 3. Calculations were also done with the GTO-DZ-X basis set. Here, however, a potential problem arises. The GTO calculations are done in C_{2v} symmetry, so that for the open-shell case π_x and π_y orbitals are not equivalent, and the overall electronic symmetry does not correspond to a pure Π state. It is

possible to obtain proper symmetry by putting half an electron in each of $3\pi_x$ and $3\pi_y$, and using appropriate vector coupling constants.¹ Both methods have been used here, and results are given in Table 3 as C_{2v} and $C_{\infty v}$, respectively. In the former case, 18 points were fitted to a cubic polynomial; in the latter, 19. It is seen that use of the incorrect C_{2v} symmetry introduces errors of less than 1% in the calculated equilibrium distances and stretching frequencies. The differences between bond lengths predicted by the STO and GTO basis sets are attributed to use of the incorrect GTO-DZ-X basis, as discussed above. Considering then only the STO-DZP values, it is seen that the CC bond is slightly shorter in the excited state than in the ground state and is quite typical of CC triple bonds. The SiC bond, however, is significantly longer (and weaker) in the excited state.

To determine whether the equilibrium structure of the 1Π state is linear, calculations were done with the GTO-DZ-X basis set and small bending displacements from near the minimum energy in the linear structure. The 1Π state splits on bending into $1A'$ and $1A''$ states. For the latter, the SCF energy increases on bending. It is not possible to obtain meaningful SCF results for the $1A'$ state that correlates with the 1Π since it is not the lowest state of this symmetry; the ground state also correlates with a $1A'$ state on bending. However, the $1A'$ state is expected to lie higher than the $1A''$ state on bending, owing to unfavorable overlap of the π electrons, suggesting that the 1Π state does, indeed, have a linear equilibrium structure. Although a proper calculation has not been done for the bending frequency, ν_2 , in the 1Π state, from the energy increases on bending of the $1A''$ state it appears that the frequency in the excited state is comparable to or slightly higher than that in the ground state.

The bonding in the 1Π state is less ionic than in the ground state since an electron has been transferred from the 9σ orbital, which is essentially a nonbonding lobe pointing away from the end carbon, to the 3π orbital, which is essentially a Si $3p\pi$ orbital. This charge shift is partially compensated since the CC π bond is much less polarized toward the center carbon atom than in the ground state. Mulliken population analysis indicates partial charges of +0.5 on silicon and -0.5 on the center carbon. This shift of charge is reflected in a much smaller dipole moment in the 1Π state; from the STO-DZP calculations,

$$\mu = 0.43 \text{ debye,}$$

and the dipole derivatives are

$$\partial\mu/\partial r_{\text{SiC}} = 6.4 \text{ debye } \text{\AA}^{-1},$$

$$\partial\mu/\partial r_{\text{CC}} = 1.1 \text{ debye } \text{\AA}^{-1}.$$

¹For a 1Π state in C_{2v} symmetry arising from the configuration $\sigma\pi_x^{1/2}\pi_y^{1/2}$, the nonzero coupling coefficients are $k_{\sigma x} = k_{\sigma y} = +3$, $k_{xx} = k_{yy} = -1$, and $j_{xy} = k_{xy} = +1$ (see Bagus 1972).

TABLE 3
 PROPERTIES OF SiCC ¹Π FROM SCF CALCULATIONS^a

Basis Set	$r_e(\text{SiC})$	$r_e(\text{CC})$	E_{\min}	k_{11}	k_{22}	k_{12}	ν_1^b	ν_3^b
STO-DZP(C _{∞v}).....	3.535	2.256	-364.44972	0.173	1.180	0.011	2313	585
GTO-DZ-X(C _{2v}) ...	3.738	2.302	-358.38597	0.120	1.088	-0.006	2226	487
GTO-DZ-X(C _{∞v}) ...	3.751	2.299	-358.38479	0.123	1.100	-0.013	2246	491

^aAll values are in atomic units except frequencies, ν_i , in cm^{-1} .

^bExperimental value for ν_1 is 1464 cm^{-1} ; for ν_3 the value is given as 499 cm^{-1} in Verma and Nagaraj 1974, 1015 cm^{-1} in Weltner and McLeod 1964, and 456 cm^{-1} in Kleman 1956.

The SiC bond in the ¹Π state is not only longer and less ionic than that in the ground state, but also has a much smaller valence force field stretching constant, k_{11} . As might be expected for the shorter CC bond in the excited state, its stretching constant k_{22} is somewhat larger than in the ground state. These changes predict a small increase in ν_1 and a decrease in ν_3 on going from the ground to the excited state. As in the ground state, the predicted ν_3 is in good accord with the (gas phase) experimental value. However, the prediction that ν_1 increases on going from ground to excited state is contrary to the experimental finding. Because the experimental value for ν_1 seems secure and because theory is expected to correctly predict at least relative values, it seems likely that this discrepancy reflects perturbations in the ¹Π state. That is, the theory used here ignores vibrational-electronic interactions that would mix the ¹Π state with states of other symmetry, whereas the observed levels most likely correspond to such an admixture.

IV. CONCLUSIONS

The ground state of silicon dicarbide is found to be linear SiCC with a closed-shell ¹Σ⁺ electronic structure, as had been inferred from previous experimental studies. The bond lengths are predicted to be $r_e(\text{SiC}) = 1.68 \text{ \AA}$ and $r_e(\text{CC}) = 1.28 \text{ \AA}$, with an estimated uncertainty of 1%. Calculated vibrational frequencies are in harmony with the most recent analysis of the optical spectral data (Verma and Nagaraj 1974). Predicted values for the dipole moment and dipole derivatives are given that should be useful for determining microwave and infrared line strengths, respectively.

Symmetric CSiC structures, including cyclic structures, are found to lie at very high energies. Although a metastable isomeric structure has not been located in the present study, neither has the possible existence of such a structure been excluded. However, if such a metastable isomer exists, it is predicted to be an open-shell electronic state and to be at least several eV above the stable form; it is unlikely that such a species can account for unidentified microwave lines observed in interstellar sources.

Several low-lying electronic states, with vertical excitation energies in the range of ~ 1.5 to 3 eV , are predicted to arise from configurations corresponding to $9\sigma \rightarrow 3\pi$ and $2\pi \rightarrow 3\pi$ excitations from the ground state. Of these, the ¹Π is predicted to be closest to the observed optical excitation at $\sim 2.5 \text{ eV}$, lending support to the experimental assignment. Of course, this is also the only one of the states with a dipole allowed transition to the ground state. Calculations for the ¹Π state indicate that its equilibrium structure is linear, with the SiC bond $\sim 0.2 \text{ \AA}$ longer and the CC bond $\sim 0.1 \text{ \AA}$ shorter than in the ground state. The most significant discrepancy between the present calculations and the experimental analysis is for ν_1 in the ¹Π state. Whereas the data indicate a lower frequency in the excited state, the calculations predict a higher frequency. It is suggested that perturbation of the ¹Π state by other low-lying electronic states is responsible for this discrepancy and may also be responsible for some of the other difficulties in the analysis noted by Verma and Nagaraj (1974).

Note added in manuscript.—After completing this work, a new experimental study has appeared (Bondybey 1982) that suggests a large increase in the value of ν_3 in the excited state, in significantly poorer agreement with theory.

Several computer programs were used in this study. Calculations employing analytic gradients were performed with HONDO; I thank the National Resource for Computation in Chemistry, and especially M. Dupuis, for providing this program. Other SCF calculations using STO and GTO basis sets were done with the ALCHEMY and the joint MOLECULE-ALCHEMY programs, respectively; I thank the IBM theoretical chemistry group, P. S. Bagus, B. Liu, A. D. McLean, P. Siegbahn, and M. Yoshimine, for providing these programs. Finally, I thank R. D. Verma for helpful comments on an early version of the manuscript and F. Wm. Chickering for post-prandial editorial assistance.

REFERENCES

- Bagus, P. S. 1972, IBM Research Rept. RJ1077.
Blom, C. E., and Altona, C. 1977, *Molec. Phys.*, **33**, 875.
Bondeybey, V. E. 1982, *J. Phys. Chem.*, **86**, 3396.
Botschwina, P. 1974, *Chem. Phys. Letters*, **29**, 580.
Clementi, E. 1965, *IBM J. Res. Development*, **9**, 2.
Drowart, J., DeMaria, G., and Inghram, M. G. 1958, *J. Chem. Phys.*, **29**, 1015.
Dunning, T. H. 1970, *J. Chem. Phys.*, **53**, 2823.
Fujita, Y. 1970, *Interpretation of Spectra and Atmospheric Structure in Cool Stars* (Tokyo: University of Tokyo Press).
Green, S. 1974, *Adv. Chem. Phys.*, **25**, 173.
Green, S. 1981, *Ann. Rev. Phys. Chem.*, **32**, 103.
Kleman, B. 1956, *Ap. J.*, **123**, 162.
Liskow, D. H., Bender, C. F., and Schaefer, H. F. 1972, *J. Chem. Phys.*, **56**, 5075.
Pacansky, J., and Hermann, K. 1978, *J. Chem. Phys.*, **69**, 963.
Perić-Radić, J., Römelt, J., Peyerimhoff, S. D., and Buenker, R. J. 1977, *Chem. Phys. Letters*, **50**, 344.
Steele, D., Person, W. B., and Brown, K. G. 1981, *J. Phys. Chem.*, **85**, 2007.
Verma, R. D., and Nagaraj, S. 1974, *Canadian J. Phys.*, **52**, 1938.
Weltner, W., and McLeod, D. 1964, *J. Chem. Phys.*, **41**, 235.

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