The 1-silaketenyl radical (HSiCO): Ground and first excited electronic states

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The two lowest-lying (X 2A″ and A 2A′) electronic states and lowest linear stationary point (1 2Π) of the 1-silaketenyl radical (HSiCO) have been investigated systematically using ab initio electronic structure theory. The lowest linear stationary point possesses two distinct imaginary vibrational frequencies along the HSiC bending coordinates, indicating a strong Renner–Teller interaction. The ground and first excited states of HSiCO are found to have trans-planar bent structures and they are more distorted from linearity but less polar than the corresponding states of HCCO. Specifically, the X 2A″ structure features a small HSiC bond angle of 84°. With our most reliable method, cc-pVQZ CCSD(T), the classical X–A splitting has been predicted to be 35.7 kcal/mol (1.55 eV, 12500 cm⁻¹). The barriers to linearity were determined to be 53.5 kcal/mol (2.32 eV, 18700 cm⁻¹) for the X 2A″ state and 17.8 kcal/mol (0.77 eV, 6240 cm⁻¹) for the A 2A′ state. The ground state of HSiCO was found to be relatively stable thermodynamically against the two dissociation reactions HSiCO(X 2A″)→H(2S) + SiCO(X 2Σ+) and HSiCO(X 2A″)→SiH(X 2Π) + CO(X 1Σ+). Due to the large infrared (IR) intensities of some of the vibrational modes, IR spectroscopic investigation of the HSiCO radical may be feasible. HSiCO is the global minimum for these four atoms, lying energetically below SiCOH (38.5 kcal/mol), HCSiO (40.7 kcal/mol), and CSiOH (76.3 kcal/mol) at the TZ2P(f,d) configuration interaction with single and double excitations (CISD) level of theory.

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I. INTRODUCTION

The ketenyl (HCCO) radical is known to be a major product involved in the combustion of acetylene, 1–4

\[
\text{HCCH} + \text{O} \rightarrow \text{HCCO} + \text{H} \quad 80 \pm 15\%,
\]

\[
\rightarrow \text{CH}_2 + \text{CO}.
\]

For the linear configuration, HCCO possesses a lowest 2Π electronic state and displays one real and one imaginary vibrational frequency along the HCC bending (or trans π bending) coordinates. In other words, this 2Π state is subject to a Renner–Teller interaction. 5–9 The eigenvector of the imaginary vibrational frequency leads to a trans-planar bent structure for the lowest electronic state (X 2A″). The component of the 2Π state with the real bending vibrational frequency is assigned to the A 2A′(1 2Π) state. For the HCCO radical there are available a considerable number of experimental 10–18 and theoretical 19–25 studies.

In a recent study we reported the two lowest-lying electronic states of the disilaketenyl radical (HSiSiO), 26 an isovalent isomer of HCCO. The ground and first excited states of HSiSiO were predicted to be trans-planar bent structures, while the linear 1 2Π structure was found to be a saddle point with two different imaginary vibrational frequencies with respect to the HSiSi bending coordinates. The X 2A″ and A 2A′ states of HSiSiO are more distorted from linearity and more polar than the analogous states of HCCO. In particular, the HSiSiO ground state is predicted to have a peculiarly acute HSiSi bond angle of only 76°, almost suggesting an Si–Si bridging hydrogen. The present study on the HSiCO radical, an isovalent isomer of HCCO and HSiSiO, is a logical extension of our previous work. In 1992, Fan and Iwata published 27 a theoretical study on the SiNNH, HSiNN, SiCOH, and HSiCO radicals in order to identify a new free radical discovered in the envelope of the carbon star IRC +10216 by Guélin, Cernicharo, Kahana, and Gomez-Gonzalez in 1986. 28 The new free radical is linear or slightly asymmetric with the rotational constant of B [or 1/2(B + C) if asymmetric] of 5.9668 GHz. Fan and Iwata determined the geometries and harmonic vibrational frequencies of the ground state of HSiCO at the 6-31G* restricted open-shell Hartree–Fock (ROHF) and unrestricted Hartree–Fock (UHF) levels of theory. However, their predicted rotational constants suggested that the SiNNH radical is one of the best candidates for the new radical in the carbon star. To the best of our knowledge there are no experimental studies to date of the HSiCO molecule. The structures and physical properties of the two lowest-lying states as well as the lowest linear stationary point (1 2Π) of HSiCO will be reported here at the self-consistent field (SCF) and configuration interaction with single and double excitations (CISD) levels of theory. The energetics will be also discussed at the coupled cluster with single and double excitations (CCSD) and CCSD with perturbative triple excitations [CCSD(T)] levels of theory. The results will be compared with those of the isovalent HCCO and HSiSiO molecules.
II. ELECTRONIC STRUCTURE CONSIDERATIONS

The lowest electronic state of the linear HSICO radical has the degenerate electronic configurations

$$[\text{core}] (6\sigma)^2(7\sigma)^2(8\sigma)^2(9\sigma)^2(2\pi)^4(3\pi_s)^2(3\pi_o) \quad 1^2\Pi$$

and

$$[\text{core}] (6\sigma)^2(7\sigma)^2(8\sigma)^2(9\sigma)^2(2\pi)^2(3\pi_s)^2(3\pi_o) \quad 1^2\Pi,$$

where [core] denotes the seven core (Si:1s, 2s, 2p-like and C, O:1s-like) orbitals, and \(\pi_s\) and \(\pi_o\) stand for the in-plane and out-of-plane \(\pi\) molecular orbitals (MOs). The 6\(\sigma\) MO describes the CO \(\pi\) bonding, and the 7\(\sigma\) MO represents the SiC \(\pi\) bonding. The 8\(\sigma\) MO consists of a lone pair orbital on the O atom and the 9\(\sigma\) MO is the SiH \(\sigma\) bonding. The 2\(\pi\) MOs form the CO \(\pi\) bonds, whereas the 3\(\pi\) MOs describe the SiC \(\pi\) bonds. This linear configuration of HSICO presents two distinct imaginary vibrational frequencies, 965 \(\text{cm}^{-1}\) (in-plane) and 870 \(\text{cm}^{-1}\) (out-of-plane) with the TZ2P(f,d)CISD method, along the HSICO bending coordinates. According to the analysis of linear triatomic Renner–Teller molecules by Lee, Fox, Schaefer, and Pitzer, the HSICO radical is classified as a type D Renner–Teller molecule. Following the eigenvector of the in-plane imaginary bonding frequency, the \(2^2A''\) component of the \(1^2\Pi\) state is stabilized to a nonlinear equilibrium structure of the ground state (\(\tilde{X}^2A''\)).

$$[\text{core}] (7\sigma)^2(8\sigma)^2(9\sigma)^2(2\pi)^2(10\sigma)^2(11\sigma)^2$$

$$\times (12\sigma)^2(3\pi_o)^2 \quad \tilde{X}^2A'' \quad (5)$$

and following the eigenvector of the out-of-plane imaginary bonding frequency, the \(2^2A'\) component is also stabilized to a nonlinear equilibrium geometry,

$$[\text{core}] (7\sigma)^2(8\sigma)^2(9\sigma)^2(2\pi)^2(10\sigma)^2(11\sigma)^2$$

$$\times (12\sigma) \quad \tilde{A}^2A' \quad (6)$$

The \(12\sigma'\) and \(3a''\) MOs of the \(\tilde{X}^2A''\) state are depicted in Figs. 1 and 2, respectively. Since the magnitude of the imaginary bending frequency is larger for the in-plane motion, the distortion from linearity is expected to be greater for the \(\tilde{X}^2A''\) state.

At this point it may be worthwhile to discuss the instability of the reference SCF wave functions. With the linear configuration (\(1^2\Pi\)), the molecular orbital (MO) Hessian (second derivatives of the SCF energy with respect to the MO rotations) presents one zero eigenvalue. The eigenvector of this zero eigenvalue is mainly assigned to the \(3\pi_o\) rotation. This means that the interchange of the \(3\pi_i\) and \(3\pi_o\) MOs does not alter the SCF energy. The MO Hessian of the ground state (\(\tilde{X}^2A''\)) has all positive eigenvalues, indicating the stable nature of the SCF wave function. For the first excited state (\(\tilde{A}^2A'\)), the MO Hessian possesses one negative eigenvalue. The eigenvector of this negative eigenvalue is principally related to the \(3a''\) \(\rightarrow\) \(12a'\) MO rotation. Therefore, the SCF wave function is unstable and there is one lower-lying state (the \(\tilde{X}^2A''\) state, which is obtained by exchanging the \(3a''\) and \(12a'\) MOs) at the equilibrium geometry. The physical properties involving this MO rotation should be interpreted with great caution. By the same token, the magnitudes of the eigenvalues of the MO Hessian may be also utilized to analyze the instability of the SCF reference wave function.

III. THEORETICAL PROCEDURES

Nine basis sets were employed in this study. The basis set of triple-\(\zeta\) (TZ) quality for Si is derived from McLean and Chandler’s contraction33 of Huzinaga’s primitive Gaussian set and is designated (12s9p6s5p). The TZ basis sets for C, O, and H are obtained from Dunning’s triple-\(\zeta\) contraction35 of Huzinaga’s primitive Gaussian set and are designated (10s6p5s3p) for C and O, and (5s3p) for H. The orbital exponents of the polarization functions are:

$$\alpha_{d}(\text{Si}) = 1.00, 0.25, \alpha_{d}(\text{C}) = 1.50, 0.375, \alpha_{d}(\text{O}) = 1.70, 0.425, \text{and} \quad \alpha_{d}(\text{H}) = 1.50, 0.375 \text{for double polarization (TZ2P); and}$$

$$\alpha_{d}(\text{Si}) = 2.00, 0.50, 0.125, \alpha_{d}(\text{C}) = 3.00, 0.75, 0.1875, \alpha_{d}(\text{O}) = 3.40, 0.85, 0.2125, \text{and} \alpha_{d}(\text{H}) = 3.00, 0.75, 0.1875 \text{for triple polarization (TZ3P). The orbital exponents of the higher angular momentum functions are:} \alpha_{f}(\text{Si}) = 0.32, \alpha_{f}(\text{C}) = 0.80,
α_c(O) = 1.40, and α_d(H) = 1.00 for one set of higher angular momentum functions [TZ2P(f,d)]. And α_c(Si) = 0.64, 0.16, α_c(C) = 1.60, 0.40, α_c(O) = 2.80, 0.70, and α_d(H) = 2.00, 0.50 for two sets of higher angular momentum functions [TZ3P(2f,2d)]. The orbital exponents of the diffuse functions are: α_c(Si) = 0.023, 54 and α_c(Si) = 0.025, 67, α_c(C) = 0.033, 89 and α_c(C) = 0.048, 12, α_c(O) = 0.058, 40 and α_c(O) = 0.089, 93, and α_c(H) = 0.030, 16 for a single set of diffuse functions [TZ2P+diff and TZ2P(f,d)+diff]. Pure angular momentum d and f functions were used throughout.

The TZ3P(2f,2d) basis set comprises 158 contracted Gaussian functions with a contraction scheme of Si(12s9p3d2f/6s5p3d2f), C and O (10s6p3d2f5s3p3d2f), and H(5s3p2d3s3p2d). Three correlation consistent polarized valence basis sets developed by Dunning and co-worker,37,38 cc-pVDZ, cc-pVTZ, and cc-pVQZ have been also employed. The cc-pVQZ basis set consists of 199 contracted Gaussian functions with a contraction scheme of Si(16s11p3d2f5g/6s5p3d2f), C and O(12s6p3d2f5g5s4p3d2f), and H(6s3p2d1f/4s3p2d1f).

The zeroth-order descriptions of the ground and first excited states as well as the linear stationary point of HSICO were obtained by the self-consistent field (SCF) wave functions. Correlation effects were included employing the configuration interaction with single and double excitations (CISD), coupled cluster with single and double excitations (CCSD),39,40 and CCSD with perturbative triple excitations (CCSD(T))41,42 methods. In the correlated procedures employing the valence TZ-plus basis sets, the seven core (Si:1s-, 2s-, 2p-like and C, O; 1s-like) orbitals were frozen and the three highest-lying virtual (Si, C, O; 1s*-like) orbitals were deleted. For single point energy calculations using the three correlation consistent basis sets, the seven core orbitals were frozen.

In our earlier systematic studies, the calculations without the frozen core orbital approximation with the valence TZ-plus basis sets sometimes presented anomalous behavior in predicting the geometries and energies.26,43 The analytic first derivatives for the CCSD and CCSD(T) methods currently available in our laboratory are applicable only to cases without the frozen core and deleted virtual approximations. Therefore, the CCSD and CCSD(T) methods were used to only determine the total energies at the CISD optimized geometries with the frozen core and deleted virtual approximations.

The structures of the three stationary points were optimized using analytic derivative methods.44-46 Harmonic vibrational frequencies at the SCF level were evaluated analytically, while at the CISD level of theory they were obtained by finite differences of analytic gradients. Computations were carried out using the psi 2.0.8 program package47 on IBM RS/6000 workstations.

IV. RESULTS AND DISCUSSION

In Fig. 3 the optimized geometries of the linear stationary point (1\( ^2\Pi \)) are depicted at the 12 levels of theory. The predicted equilibrium structures are shown in Fig. 4 for the \( X^2\AA\) state and in Fig. 5 for the \( \tilde{X}^2\AA' \) state. Table I presents the total energies, dipole moments, and harmonic vibrational
The two lowest-lying states of HSICO are found to have trans-planar bent equilibrium structures as depicted in Figs. 4 and 5. The SiH and SiC bond distances are longer for the $\tilde{X}^2A''$ state than the $1^2I$ state, while the reverse is true for the CO bond distance. Given a basis set, the CISD method generally provides longer bond distances than the SCF method. At the TZ3P(2d,2f)SCF level, the SiH and SiC bond distances are shorter and the CO bond distances are longer for the $1^2A'$ state than for the $\tilde{X}^2A''$ state. The HSICO bond angle of this excited state is about 30° larger than that of the ground state. The 12a' MO in Eq. (5) involves SiH antibonding and C\cdot\cdot\cdotH bonding as seen in Fig. 1, while the 3a'' MO in Fig. 2) presents SiC $\pi$ bonding and CO $\pi$ antibonding. Thus, a single electron excitation,

\[
(12a')^2(3a'')\rightarrow(12a')(3a'')^2,
\]

shortens the SiH and SiC bond lengths, elongates the CO bond distance, and opens the HSICO bond angle. The first excited state of HSICO presents an HSICO bond angle of 120.8°,26 whereas the first excited state of HCCO reflects the HCC bond angle of 180°.24 The SiC bond angles of the two bent states of HSICO shift marginally from linearity.

**B. Dipole moments**

The dipole moment of the 1^2I stationary point of HSICO is predicted to be 2.89 debye at the TZ3P(2f,2d)CISD level of theory. With the same method, the dipole moments for the two equilibria are determined to be 0.38 ($\tilde{X}^2A''$) and 1.52 debye ($1^2A'$), respectively. It is seen that the HSICO radical is the most polar at the linear configuration and the deviation from linearity significantly decreases the magnitude of dipole moment. The accepted electronegativities of the four relevant atoms are H(2.1), O(2.5), O(3.4), and Si(1.8), respectively.53 The larger difference in the electronegativities of Si–O in HSICO compared to C–O in HCCO may be related to the greater dipole moment (2.89 debye) of HSICO than the dipole moment (2.04 debye) of HCCO at their respective linear configurations.

**C. Harmonic vibrational frequencies**

With the TZ3P(2f,2d)CISD method, the orderings of the stretching vibrational frequencies of the three states of HSICO are

\[
2482(1^2I) > 2345(\tilde{X}^2A'') > 2147(\tilde{X}^2A''')
\]

for the SiH stretching ($\omega_1$),

\[
2143(\tilde{X}^2A'') > 2074(\tilde{X}^2A'') > 2036(1^2I)
\]

for the CO stretching ($\omega_2$), and

\[
839(1^2I) > 726(\tilde{X}^2A'') > 504(\tilde{X}^2A''')
\]

for the SiC stretching ($\omega_3$). These features are consistent with the conclusion from Badger’s rule that a shorter bond length is associated with a higher vibrational frequency (larger force constant).54,55 For example, the harmonic vibrational frequency of the SiH stretching mode ($\omega_3$) of the $1^2I$
state is considerably higher than those of the $\tilde{X}^2A''$ and $\tilde{X}^2A'$ states, due to the former's shorter SiH bond length. It is seen that the predicted SIC stretching frequencies ($\omega_1$) reflect most sensitively the changes in the SiC bond length among the three states.

The experimental harmonic vibrational frequencies for the diatomics SiH($\tilde{X}^2\Sigma^+$) and CO($\tilde{X}^1\Sigma^+$) are 2041.8 and 2169.8 cm$^{-1}$, respectively. For the three stationary points of HSiCO considered here, the predicted SiH stretching frequencies are higher and the CO stretching frequencies are lower compared to their diatomic counterparts. For the $\tilde{X}^2A''$ state of HSiCO at the SCF level of theory, the CO($\omega_2$) stretching frequency is predicted to be higher (over 100 cm$^{-1}$) than the SiH($\omega_1$) stretching frequency. However, these two stretching frequencies are determined to be much closer (within 25 cm$^{-1}$) with the CISD method. This feature may be due to the considerably elongated CO bond distances at the CISD level of theory (see Fig. 4). In Table III the SCF torsional ($\omega_3$) frequency and its IR intensity may not be entirely reliable due to the possible instability of the SCF wave function discussed in Sec. II, although they appear to be quite reasonable.

### D. Infrared (IR) intensities

The IR intensity of the CO stretching ($\omega_2$) mode is markedly large for both the ground and first excited states. The intensity of the SiH stretching ($\omega_1$) mode is significantly larger for the ground state than for the first excited state. The closer vibrational frequencies and resultant strong interaction between the SiH and CO stretching modes for the ground state may be attributed to this feature. This strong ground-state interaction between SiH and CO stretches also explains the substantial variation in the CISD IR intensities as a function of basis set. For the $\tilde{X}^2A'$ state, we note that the SiH and CO stretching frequencies are well separated, by nearly 300 cm$^{-1}$. Since the IR intensities of some of the vibrational modes are relatively large, it may be possible to investigate this radical using IR spectroscopic techniques.

### E. Energetics

In Table IV the total CISD, CCSD, and CCSD(T) energies for the $\tilde{X}^2A''$, $\tilde{A}^2A'$, and $\tilde{1}^2\Pi$ states of HSiCO at the CISD optimized geometries are presented with the same TZ-plus basis sets. The correlated energies with the three corre-
relation consistent basis sets were determined at the TZ3P(2,2d)CISD optimized geometries. Table V provides the relative energies among the three states at the 33 levels of theory.

1. \(^2A^\prime\) – \(^2A^\prime\) splitting

With the TZ3P(2,2d) basis set, the classical \(\tilde{X} - \tilde{A}\) splitting was predicted to be 39.2 (SCF), 37.7 (CISD), 36.9 (CCSD), and 35.8 kcal/mol [CCSD (T)]. It is seen that an improved treatment of correlation effects and an increase of the basis set size diminish the energy separation. The cc-pVDZ basis set provides the largest energy separation among the nine basis sets employed at the three correlated levels of theory. The cc-pVTZ basis set presents similar energetics as the TZ2P(f,d) + diff basis set, while the cc-pVQZ basis set shows similar energetics as the TZ3P(2,2d) basis set. With our most reliable method, cc-pVQZ CCSD(T), the \(\tilde{X} - \tilde{A}\) energy separation is determined to be 35.7 kcal/mol (1.55 eV, 12 500 cm\(^{-1}\)). The \(\tilde{X} - \tilde{A}\) splitting (35.7 kcal/mol) of HSiCO is very similar to that (36.3 kcal/mol) of HSiSiO\(^2\) and it is noticeably larger than that (1.84 kcal/mol) predicted for HCCO.\(^2\)

2. Barriers to linearity

With the TZ3P(2,2d) basis set, the barrier to linearity for the ground state is predicted to be 66.9 (SCF), 59.5 (CISD), 56.7 (CCSD), and 53.8 kcal/mol [CCSD(T)]. At the highest level of theory, cc-pVQZ CCSD(T), the \(\tilde{X}^2A^\prime\) – \(^1\)\(\tilde{I}\)I energy separation was predicted to be 53.5 kcal/mol (2.32 eV, 18 700 cm\(^{-1}\)), whereas the \(\tilde{A}^2A^\prime\) – \(^1\)\(\tilde{I}\)I energy separation was determined to be 17.8 kcal/mol (6240 cm\(^{-1}\)). The barriers to linearity of the two states decrease with increase of the basis set size and advanced treatment of correlation effects. It is seen that the \(^1\)\(\tilde{I}\)I state of HSiCO is preferentially stabilized by correlation effects, probably due to enforced multiple bonds of the linear configuration. The three relative energies presented in Table V are clearly convergent in terms of the basis set expansion and level of correlation effects.

3. Dissociation energies

In order to examine the stability of the HSiCO radical, the following two dissociation reactions were investigated:

\[
\text{HSiCO} (\tilde{X}^2A^\prime) \rightarrow \text{H}^2(S) + \text{SiCO} (\tilde{X}^3\Sigma^\text{-}) \tag{11}
\]

and

\[
\text{HSiCO} (\tilde{X}^2A^\prime) \rightarrow \text{SiH} (\tilde{X}^2\text{II}) + \text{CO} (\tilde{X}^1\Sigma^\text{+}). \tag{12}
\]

Employing the cc-pVQZ CCSD(T) methods, the total energies of HSiCO(\(\tilde{X}^2A^\prime\)) and SiCO(\(\tilde{X}^3\Sigma^\text{-}\)) were determined to be \(-402.787\,038\) hartree (this study) and \(-402.175\,016\) hartree (Ref. 43) at the respective TZ3P(2,2d)CISD geometries. The SCF energy of H\(^2\)(S) with the cc-pVQZ basis set is known to be \(-0.499\,946\) hartree. Thus, the dissociation

\[
\text{TABLE IV. Total CISD, CCSD, and CCSD(T) energies in hartrees for the } \tilde{X}^2A^\prime, \tilde{A}^2A^\prime, \text{ and } ^1\text{III} \text{ states of HSiCO at the CISD optimized geometries.}
\]

<table>
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<tr>
<th>Electronic state</th>
<th>Level of theory</th>
<th>(\tilde{X}^2A^\prime) trans</th>
<th>(\tilde{A}^2A^\prime) trans</th>
<th>(^1)(\tilde{I})I linear</th>
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energy for the reaction (11) becomes \( D_e = 70.3 \text{ kcal/mol} \) due to the CISD zero-point vibrational energy (ZPVE) correction, the quantum mechanical dissociation energy becomes \( D_0 = 66.2 \text{ kcal/mol} \).

The cc-pVQZ CCSD(T) total energies of SiH\( (\tilde{X}^2 \Pi) \) and CO\( (\tilde{X}^2 \Sigma^+) \) were determined to be \(-289.553 \pm 626 \) and \(-113.187 \pm 617 \) hartrees at their respective TZ3P(2\( f,2d \)) CISD optimized geometries. Accordingly, the classical dissociation energy for the reaction (12) becomes \( D_e = 28.7 \text{ kcal/mol} \). Using the CISD ZPVE correction, the quantum mechanical dissociation energy becomes \( D_0 = 25.9 \text{ kcal/mol} \). It is seen that the ground state of HSICO is relatively thermodynamically stable against the two dissociation reactions.

F. Comparisons among HCCO, HSICO, and HSiSO

In Table VI the structures and energetics of ketenyl, mono- and di-silaketenyl radicals, HCCO, HSICO, and HSiSiO are compared. The HSi bond angles of the two lowest equilibrium HSICO electronic states are significantly smaller than the corresponding states of HCCO, as was the case for HSISO. The deviation from linearity is larger for the ground state of HSICO compared to the ground state of HCCO. According to Kutzelnigg’s argument,\(^56\) the \( s \) and \( p \) valence atomic orbitals (AOs) of first row atoms are localized in roughly the same region of space, while the valence (AOs) of second or higher row atoms are much more extended in space. Consequently, single bonds between first row elements are weak and multiple bonds are strong, whereas for the higher row elements single bonds are strong and multiple bonds are weak. Furthermore, ideal hybridization is realized if \( s \) and \( p \) valence AOs are localized in the same region of space and hence have comparable bonding and overlapping power. This is the case only for first row atoms, and particularly for carbon. In elements of the higher rows the actual valence configurations differ considerably from the ideal hybrids. They are, in fact, somewhere between the ground configurations and ideal valence configurations.\(^57\)

The structural features of HCCO, HSICO, and HSiSiO in Table VI are consistent with Kutzelnigg’s analysis.\(^56,57\)

The dipole moments of the \( \tilde{X}^2 A'' \) and \( \tilde{A}^2 A' \) states of the three ketenyl radicals are in order of

\[
\mu_e(\text{HSiSiO}) > \mu_e(\text{HCCO}) > \mu_e(\text{HSICO}).
\]
It is seen that the HSiSiO molecule is the most polar and HSiCO is the least polar. Ignoring other factors, the dipole moments suggest that HSiSiO may be the easiest to observe by microwave spectroscopy.

While the $\tilde{X}-\tilde{A}$ splitting of HSICO is about the same as that of HSiSiO, it is significantly larger than the energy separation of HCCO. The $\tilde{X}^2A'$ and $\tilde{A}^2A'$ states of HSICO present the largest barriers to linearity among the three isovalent radicals. For the ground state of the HSICO and HSiSiO radicals, the presence of a $\cdots$H interaction (in HSICO) and a Si·H interaction (in HSiSiO) may be one of the main reasons for the larger (compared to HCCO) barriers to linearity.

V. CONCLUDING REMARKS

The two lowest-lying states of the HSICO radical, an isovalent isomer of HCCO and HSiSiO, have been investigated at the SCF, CISD, CCSD, and CCSD(T) levels of theory with a wide range of basis sets. The $\tilde{X}^2A'$ and $\tilde{A}^2A'$ states of the HSICO molecule were found to be more distorted from linearity than the corresponding states of HCCO. The ground state of HSICO is specifically characterized by a small HSIC bond angle of 84°. While the $\tilde{X}-\tilde{A}$ splitting of 35.7 kcal/mol (1.55 eV, 12,500 cm$^{-1}$) is quite similar to the $\tilde{X}-\tilde{A}$ energy separation (36.3 kcal/mol, 1.57 eV, 12,700 cm$^{-1}$) of HSiSiO, this energy separation is significantly larger than that for HCCO. The ground state of HSICO is predicted to be reasonably stable against the dissociation reactions. Due to the relatively large IR intensities of some of the vibrational modes, it should be feasible to investigate this radical using IR spectroscopic techniques. The ground state of the SiCO radical is predicted to be the global minimum for these four atoms, lying energetically below SiCOH (38.5 kcal/mol), HCSI0 (40.7 kcal/mol), and CSiOH (76.3 kcal/mol) with the TZ2P$(f,d)$CISD method at the TZ2P$(f,d)$CISD optimized geometries.

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