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Theoretical Investigation of the Structure and Vibrational Spectrum of the Electronic Ground State $\tilde{X}(^1A')$ of HSiCl

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The transient HSiCl (monochlorosilylene) is a species for which structure and spectroscopic properties are almost unexplored by quantum chemical methods. In this work, CCSD and CCSD(T) methods in conjunction with Dunning's hierarchy of basis sets are used to investigate both aspects of this biradical. The CCSD(T)/cc-pCVTZ method using analytical second derivatives of the energy in combination with second order perturbation theory to evaluate the anharmonicity shows to be an efficient strategy to calculate its fundamental vibrational frequencies. Especially remarkable for its anharmonic nature is the calculated value for ν_1 (Si−H stretching) which is only 4 cm^{-1} bellow than the observed transition. The experimental structure is investigated by analyzing the experimental rotational constants. This latter goal was accomplished reporting high-level ab initio r_e-structures as well as empirical structural parameters using CCSD(T)/cc-pCVTZ vibrational corrections of the experimental rotational constants.

I. Introduction

Thin solid films of silicon, ranging in composition and crystallinity from amorphous hydrogenated Si to single-crystal epitaxial elemental Si are vital to modern technology,[1] finding uses in areas such as solar energy conversion[2] and microelectronics.[3] These films are routinely fabricated from gaseous precursor molecules in empirically developed chemical vapor deposition (CVD) processes.[4] A mechanistic understanding of these processes is clearly desirable from a practical point of view. Efficient optimization of film properties and growth conditions is vital in order to satisfy the demands that new technologies place on these materials. The goal of mechanistic studies is to determine which microscopic processes occur, and how they affect the macroscopic properties of the deposited films. Thus, gas-phase, gas−surface, surface, and solid-state chemical processes can all be involved, depending on the deposition conditions. Separation of gas-phase and surface reaction steps is a useful approach for both the analysis and investigation of CVD chemistry. The gas-phase chemistry determines the flux of various species to the film growth surface; the subsequent surface chemistry incorporates silicon into the film. At higher pressures in thermal systems, gas-phase unimolecular dissociation of the precursor may play an important role, which raises the question: what are the dissociation products and their chemistry? In plasma or photochemical systems, multiple dissociation channels may lead to the production of a variety of gas-phase radicals. The goal is to know what these are as well as their role in the deposition chemistry. To this end, real-time and in situ diagnostic measurements using techniques of analysis such as mass spectrometry, gas chromatography, and a number of optical techniques (infrared spectroscopy, laser Raman spectroscopy, CARS (Coherent Anti-Stokes Raman Spectroscopy), optical emission, ultraviolet UV−vis absorption, and laser-induced fluorescences (LIF), etc.) can provide direct probes of the gas-phase chemistry.[5] Nevertheless, theoretical studies of the individual molecules and elementary chemical reactions can be very helpful. In particular, quantum chemical methods can be used not only to predict accurate thermochemical (heats of formation, enthalpies, heat capacities, etc.) and kinetic data (activation energies, Arrhenius factor, etc.)[6] but also to characterize radicals and other transients that may be formed at high temperature.

Chlorinated silanes have been widely used in CVD.[7] For example, dichlorosilane (H_2SiCl_2) has been implicated as a precursor in complex processes such as atomic layer epitaxy (ALE).[8] To understand the mechanisms of film growth and develop models of silicon epitaxy from chlorinated silanes, we must be able not only to assess rates and thermodyamics of homogeneous reactions but also to identify and characterize intermediates that may play a role in them. In this sense, it is worthwhile to investigate the monochlorosilylene (HSiCl) biradical. Apart from its intrinsic interest as a biradical, the role played by this species in CVD has been a controversial subject.

Some of the earliest in situ spectroscopic studies of chlorosilane CVD[9,10] as well as laboratory experiments with these chlorinated compounds[11] found no direct evidence of HSiCl. A few years later, Conner et al.[12] doing an experiment similar to that of ref 11 assigned emission features to monochlorosilylene (HSiCl); Ho and Breiland[13] did the first identification of HSiCl in the spectroscopic analysis of in situ chlorosilane CVD, as well as other kinetic studies with this species.[14] After these initial detection experiments and other in situ deposition investigations,[15,16] laboratory simulations of chlorosilane CVD,[17] measurements using different spectroscopic techniques[18−20] and theoretical studies of chlorosilane gas-phase decomposition[21] have been carried out. In none of the experiments was it possible to isolate HSiCl, but a series of conclusions about the existence of this biradical have been established: (a) its detection is a matter of the relative sensitivities of the detection methods,[22] the different experimental conditions and the activation energies

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for the thermal decomposition pathways; (b) although $SiCl_2$ is a major product of the decomposition of chlorosililenes, HSiCl is also possible,[23] which is expected to significantly affect the growth rate of the Si film;[16] (c) mechanisms for the homogeneous gas-phase decomposition of $HSiCl_3$, H_2SiCl_2, and H_3SiCl in hydrogen consist of unimolecular decomposition of the chlorinated silanes and secondary chemistry due to reactions where, along with other species, HSiCl is thought to play a significant role.[21]

The pioneering spectroscopic study of HSiCl was due to Herzberg and Verma,[24] who were able to resolve much of the rotational fine structure. However, they could not measure the asymmetry splittings expected at low K'_a due to spectral congestion and the rotational constants B and C could not be determined independently. However, by assuming a zero inertial defect they were able to obtain effective B and C values. For $DSi^{35}Cl$, A was based on an approximated value of B estimated from isotopic relations. On the basis of these approximations, they derived ground- and excited-state r_o-structures of HSiCl. Equilibrium geometrical parameters could not be determined because a complete set of vibration−rotation interaction constants could not be obtained. Fundamental vibrational frequencies for two of the three normal modes of the electronic ground state ($^1A'$) were also determined, ν_2 (A', HSiCl bending) = 808 cm^{-1} and ν_3 (A', Si−Cl stretching) = 522 cm^{-1}. A more recent spectroscopic analysis of HSiCl was carried out by Harper et al.,[25] who examined the ground ($^1A'$) and first singlet excited ($^1A''$) states of HSiCl and DSiCl using pulsed discharge jet and laser induced fluorescence techniques (LIF). For both electronic states, they obtained the rotational constants of the vibrational ground state of four isotopomers as well as their fundamental frequencies, except ν_2 for the ground state of $DSi^{37}Cl$. A number of anharmonicity constants were also reported for the excited state but not for the ground state. From this information they determined the r_o-structure and (using different approximations) reported values of r_o^ϵ,[26] r_s, and r_z structures. The harmonic force field of both electronic states was estimated, although the harmonic vibrational frequencies for the ground state are necessarily less reliable due to the incomplete information obtained for the ground electronic state in the LIF experiments.

The number of ab initio studies of HSiCl in the literature is relatively few. Calculations of the ground-state geometry and harmonic vibrational frequencies using the Hartree−Fock (HF) method with the 6-31G* basis set[27] and the MP2/6-31G**[28,29] treatments have been reported. The vertical excitation energy for the transition $\tilde{A}(^1A'') \leftarrow \tilde{X}(^1A')$[30] as well as the structure of the first triplet excited state ($^3A''$) at the MP2/6-31G** level of theory[28] have been also evaluated using a spin-contamined UHF function to approximate the open-shell singlet. More recently, structural parameters of the ground electronic state of HSiCl at the MP2/6-31G**, MP2/6-311+G(2df,2p), and QCISD/6-311+G(2df,2p) levels of theory have been reported.[31]

The goal of this research effort is to perform high-level quantum chemical calculations using coupled cluster theory[32] to investigate the equilibrium structure and spectroscopic properties of the singlet ground electronic state ($^1A'$) of monochlorosilylene (HSiCl). Recent advances that allow second derivatives of the energy to be calculated analytically at highly correlated levels of theory[33] have been exploited to predict properties of this closed-shell biradical species. In addition, cubic and semidiagonal quartic force constants calculated by numerical differentiation of analytic second derivatives are used to estimate spectroscopic properties that depend in part on the cubic potential constants (rotation−vibration constants), and the quartic force field (anharmonicity constants). Finally, in conjunction with equilibrium structural parameters determined by high level quantum mechanical methods, an *empirical* equilibrium structure[34−38] of HSiCl has been determined.

TABLE 1: Equilibrium Structural Parameters of HSiCl on the Electronic Ground State ($^1A'$)[a]

		r(H−Si)/Å	r(Si−Cl)/Å	∠(HSiCl)/deg
CCSD				
	cc-pVDZ	1.5305	2.1133	95.389
	cc-pVTZ	1.5184	2.0829	95.426
	cc-pVQZ	1.5036	2.0745	95.286
	cc-pCVTZ	1.5158	2.0784	95.468
CCSD(T)				
	cc-pVDZ	1.5328	2.1154	95.345
	cc-pVTZ	1.5210	2.0850	95.407
	cc-pVQZ	1.5059	2.0769	95.218
	cc-pCVTZ	1.5187	2.0808	95.449
	cc-pCVQZ	1.5138	2.0697	95.302
MP2/6-31G**[b]		1.509	2.077 (2.078)[d]	95.25 (95.2)[d]
MP2/6-311+G(2df,2p)[c]		1.516	2.081	95.14
QCISD/6-311+g(2df,2p)[c]		1.520	2.087	94.41

[a] Bond lengths show a significant decrease with cc-pVQZ. To check a possible anomalous behavior of this basis set additional calculations were made with atomic natural orbital basit sets of ref 55 using two different contractions, i.e., (a) [3s2p1d]for H and [5s4p2d1f] for Cl and Si; b) [4s3p2d] for H and [6s5p3d2f] for Cl and Si. The resulting structures are (a) r(Si−Cl) = 2.0796 Å, r(Si−H) = 1.5098 Å, ∠(HSiCl) = 95.14°; (b) r(Si−Cl) = 2.0735 Å, r(Si−H) = 1.5026 Å, ∠(HSiCl) = 95.21° [b] References 28−31. [c] Reference 31. [d] Exact value reported in ref 28.

II. Theoretical Methods

We have optimized the geometry of HSiCl using the coupled-cluster singles and doubles (CCSD) approach[39] augmented by a perturbative treatment of triple excitations [CCSD(T)],[40] in conjunction with Dunning's hierarchy of correlation-consistent basis sets denoted by cc-pVXZ (X = D, T, Q)[41] with X = D [4s3p1d/1s1p], T[5s4p2d1f/3s2p1d], and Q[6s5p3d2f1g/4s3p2d1f]. Calculations with this series of three basis sets at the CCSD and CCSD(T) levels were performed to analyze the basis set convergence and the effect of connected triple excitations, respectively. While the CCSD(T)/cc-pVQZ has proved to give excellent r_e-structures, most studies have only been carried out for molecules containing first-row atoms.[36,42] The presence of two heavier atoms, i.e., Cl and Si (second-row atoms) in HSiCl and previous experience[43] led us to explore core correlation effects with the cc-pCVTZ and cc-pCVQZ basis sets[44] (correlation consistent polarized core+valence triple-ζ).

Optimizations were performed with analytic energy derivatives[45] and considered converged when the root-mean-square gradient in internal coordinates fell below 10^{-5} au, except when structures were used to calculate third and fourth derivatives of the energy where a convergence criterion of 10^{-7} au was used. Second derivatives of the energy and first derivatives of the dipole moment with respect to displacements and corresponding normal coordinates (Q_i) were calculated analytically[33] at the CCSD and CCSD(T) methods with the cc-pVTZ, cc-pCVTZ basis sets. Equilibrium rotational constants (A_e, B_e, C_e) were calculated from the corresponding optimized structures. Centrifugal distortion constants corresponding to the A-reduction Hamiltonian in the I^r representation[46] were also evaluated. Cubic and semidiagonal quartic force constants were calculated by numerical differentiation[47] of analytic second derivatives. Cubic

TABLE 2: Experimental and Empirical (emp) Structures of HSiCl ($^1A'$)[a,b,c]

	$r_e^{(emp)}$		r_o			
	cc-pVTZ	cc-pCVTZ	ref 24	ref 26	r_z[d]	(r_e^z)[e]
R(Si−Cl)/Å	2.0697	2.0724	2.064	2.0729(4)	2.0720(6)	2.067(3)
R(Si−H)/Å	1.5146	1.5140	1.56_1	1.5214(8)	1.538(1)	1.525(5)
∠(HSiCl)/deg	94.78	94.66	102.8	95.0(2)	94.7(2)	96.9(5)
rms[f]	0.0027	0.0027				

[a] CCSD(T) method was used to calculate vibration−rotation constants for $r_e^{(emp)}$. [b] All the structures from ref 25 include a Laurie correction of 0.003 Å except for r_z-structure. [c] As additional information, *inertial defects*[56] ($\Delta = I_C - I_A - I_B$) determined from the equilibrium empirical rotational constants [$A_e^{(emp)}$, $B_e^{(emp)}$, and $C_e^{(emp)}$] have the next values. cc-pVTZ: [$HSi^{35}Cl = -0.026$, $HSi^{37}Cl = 0.017$, $DSi^{35}Cl = -0.004$, and $DSi^{37}Cl = -0.006$]. cc-pCVTZ: [$HSi^{35}Cl = -0.027$; $HSi^{37}Cl = 0.017$; $DSi^{35}Cl = -0.005$; and $DSi^{37}Cl = -0.007$]. [d] Reference 25. Values in parentheses are one standard error in units of the last significant figure. [e] Reference 25. Values in parentheses are estimated uncertainties in units of the last significant figures. [f] rms: Root-mean-square deviations of the differences between empirical A, B, and C constants and those obtained from the refined least-squares structures (in units of amu Å^2).

force constants so obtained for HSiCl were then transformed to the normal coordinate representation of the four isotopomers studied by Harper et al.[25] ($HSi^{35}Cl$, $HSi^{37}Cl$, $DSi^{35}Cl$, and $DSi^{37}Cl$). Using expressions deduced by second-order perturbation theory,[48] the vibration−rotation interaction constants and anharmonicity constants were evaluated. A local version of the ACES II program system[49] was used in all the work presented here.

III. Results and Discussion

A. Structure. Equilibrium structures predicted by various levels of theory for HSiCl are presented in Table 1. Included are results from the present research as well as selected values from the literature.[29−31] It can be seen that calculated values follow the usual behavior i.e., structures are contracted by improvements in the basis set and expanded by improvement in the correlation treatment.[50] The bond angle is only slightly sensitive with respect to basis set and correlation effects.

Effects of core correlation have been examined by doing calculations with the cc-pCVTZ and cc-pCVQZ basis set. In Table 1 it can be observed that core correlation effects decrease the H−Si bond length by 0.0026 and 0.0023 Å using the CCSD and CCSD(T) methods and the cc-pCVTZ basis set, respectively; by contrast, the same effects evaluated with the CCSD(T)/cc-pCVQZ method gives an increase of 0.0079 Å for this bond length with respect to the especially short Si−H distance obtained using the cc-pVQZ basis set. The reduction of the Si−Cl bond distance is predictably more significant with corresponding values of 0.045 and 0.042 Å using the CCSD and CCSD(T) methods and the cc-pCVTZ basis set, and of 0.0072 Å with CCSD(T)/cc-pCVQZ. With both CC methods the bond angle is again not sensitive; it changes by only 0.18° in going from cc-pVQZ to the cc-pCVQZ basis set.

With respect to theoretical structures calculated by others, MP2/6-311+G(2df,2p) gives a Si−H bond distance 0.002 Å larger than our CCSD(T)/cc-pCVQZ. Similar qualitative behavior is observed in the Si−Cl distance, which is calculated at the MP2/6-311G+(2df,2p) level to be 0.011 Å larger than the CCSD(T)/cc-pCVQZ value. Although the agreement between MP2/6-311G+(2df,dp) and CCSD(T)/cc-pCVQZ is good this coincidence is fortuitous and can be attributed to a cancellation of errors. With QCISD/6-311+G(2df,2p), bond distances appear to be systematically overestimated.

In Table 2, calculated equilibrium structures are compared with experimental results obtained by Herzberg et al.[24] and Harper et al.[25] (see Table 2). As noted in ref 25, large discrepancies are observed between the r_o (effective) structure of Herzberg and that determined by Harper. The CCSD(T)/cc-pCVQZ r_e values also agree rather poorly with the effective structures. In addition, Harper et al. evaluated harmonic contributions to rotation−vibration interaction constants (α_i^{ξ})

TABLE 3: Rotational Constants (in MHz) of Four Isotopic Species of HSiCl[a,b,c,d]

	A	B	C
$HSi^{35}Cl$			
B_e			
cc-pVTZ	227915.5	7292.3	7066.2
cc-pCVTZ	228654.3	7321.5	7094.4
$B^{(A)}$			
cc-pVTZ	226487.6	7270.4	7034.5
cc-pCVTZ	227178.7	7318.2	7079.9
$B^{(A)}$(exp)	227440.9	7383.3	7144.1
B_e(emp)			
cc-pVTZ	228868.9	7405.2	7175.8
cc-pCVTZ	228916.7	7386.7	7158.5
$HSi^{37}Cl$			
B_e			
cc-pVTZ	227912.7	7113.8	6898.5
cc-pCVTZ	228651.5	7142.4	6926.0
$B^{(A)}$			
cc-pVTZ	226482.2	7092.6	6867.9
cc-pCVTZ	227173.5	7139.0	6912.2
$B^{(A)}$(exp)	227465.1	7202.9	6970.8
B_e(emp)			
cc-pVTZ	228895.6	7224.1	7001.4
cc-pCVTZ	228943.5	7206.2	6984.7
$DSi^{35}Cl$			
B_e			
cc-pVTZ	118833.5	7108.6	6707.3
cc-pCVTZ	119224.2	7136.8	6733.7
$B^{(A)}$			
cc-pVTZ	118362.1	7089.1	6676.6
cc-pCVTZ	118739.4	7134.4	6718.0
$B^{(A)}$(exp)	119031.7	7202.6	6780.2
B_e(emp)			
cc-pVTZ	119503.0	7222.1	6810.9
cc-pCVTZ	119516.5	7204.9	6795.8
$DSi^{37}Cl$			
B_e			
cc-pVTZ	118829.3	6931.5	6549.5
cc-pCVTZ	119220.0	6959.0	6575.2
$B^{(A)}$			
cc-pVTZ	118356.2	6912.6	6519.8
cc-pCVTZ	118733.3	6956.6	6560.1
$B^{(A)}$(Exp)	118914.2	7024.5	6621.9
B_e(emp)			
cc-pVTZ	119387.4	7043.4	6651.5
cc-pCVTZ	119400.9	7026.7	6636.9

[a] CCSD(T) level was used for all ab initio values. [b] $B^{(A)}$, rotational constants expressed in the A-reduction. [c] $B^{(A)}$(exp) corresponds to experimental rotational constants from ref 25, [A-reduction/I^r representation Hamiltonian]. [d] $B_e(\mathrm{emp}) = [B_e - B^{(A)}]_{cal} + B^{(A)}(\mathrm{exp})$.

TABLE 4: Experimental and Calculated Harmonic Vibrational Wavenumbers (cm^{-1}) for Four Isotopomers of HSiCl along with Infrared Intensities (km/mol) Evaluated within the Double Harmonic Approximation[a]

	exptl[b]		CCSD/cc-pVTZ		CCSD/cc-pCVTZ		CCSD(T)/cc-pVTZ		CCSD(T)/cc-pCVTZ	
mode[a]	est[c]	calcd[d]	ω_i	intensity	ω_i	intensity	ω_i	intensity	ω_i	intensity
					$HSi^{35}Cl$					
ω_1	2004.3	2013.8	2066.2	271.8	2064.3	268.6	2048.5	265.0	2044.6	265.0
ω_2	807.9	808.3	832.0	52.9	833.7	53.4	820.8	49.6	821.7	50.0
ω_3	525.0	525.2	536.9	108.7	532.9	109.7	532.2	100.9	529.8	101.4
					$HSi^{37}Cl$					
ω_1	2004.2	2013.8	2066.2	269.8	2064.3	268.6	2048.5	265.0		
ω_2	807.6	808.0	831.7	53.0	833.3	53.5	820.7	49.7		
ω_3	518.6	518.7	530.3	106.0	526.3	106.9	527.6	98.4		
					$DSi^{35}Cl$					
ω_1	1452.6	1449.3	1487.5	143.2	1486.1	142.6	1474.7	140.5		
ω_2	593.6	592.1	609.5	59.3	610.3	57.7	601.8	57.3		
ω_3	520.2	519.6	531.1	83.3	527.5	86.1	528.1	75.4		
					$DSi^{37}Cl$					
ω_1	1452.6	1452.6	1487.5	143.2	1486.1	142.6	1474.7	140.5		
ω_2			608.9	57.0	609.7	56.2	601.2	55.4		
ω_3	519.6	513.7	524.6	82.4	520.9	84.9	521.7	74.8		

[a] All the fundamental belong to A′ symmetry. ω_1, ω_2, and ω_3 correspond to Si−H stretching, angle bending, and Si−Cl stretching, respectively. [b] Reference 25. [c] Approximations introduced in estimating the anharmonicities using anharmonic constants from diatomic molecules. [d] Obtained from the refinement of the harmonic force field, where two force constants were constrained to 0.0.

to give a r_z-structure. This r_z-structure is a rough approximation to r_e because the anharmonic contributions to the α_i^{ξ} values are omitted and, second, because the harmonic force field parameters were of an approximate nature. Their approximate r_e-structure (r_e^z) was estimated from the r_z-structure using Kuchitsu's formulas.[51−52] This experimental approximation to r_e agrees rather well with the CCSD(T)/cc-pCVQZ value for the Si−Cl distance, but both the Si−H distance and the bond angle are in less satisfactory agreement. To further investigate this issue, we have determined an empirical r_e-structure[34−38] for HSiCl. In an empirical equilibrium structure, bond lengths and bond angles are obtained from equilibrium rotational constants based on (A_o, B_o, and C_o) corrected for vibrational effects using ab initio calculations. Recently, it has been shown for molecules containing first-row atoms that empirical distances are in essentially quantitative agreement with experimental structures, when the latter are available.[36] In the present work, we have combined experimental rotational constants based on Watson's *A*-reduction Hamiltonian in the I^r representation[46] [$A^{(A)}$, $B^{(A)}$, and $C^{(A)}$] from ref 25 with centrifugal distortion and vibration−rotation constants derived from calculated harmonic and cubic force fields at the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pCVTZ levels. The resulting empirical rotational constants [$A_e^{(emp)}$, $B_e^{(emp)}$, and $C_e^{(emp)}$] as well as equilibrium rotational constants calculated with CCSD(T)/cc-pVTZ and CCSD(T)/cc-pCVTZ are reported in Table 3. Structures obtained by least-squares adjustment of atomic coordinates to moments of inertia based on the $A_e^{(emp)}$, $B_e^{(emp)}$, and $C_e^{(emp)}$ constants for four isotopomers are documented in Table 2 and denoted as $r_e^{(emp)}$. The two empirical structures agree rather well with one another, and also with the CCSD(T)/cc-pCVQZ values, whereas the discrepancies with the experimental (r_e^z) Si−H bond length persist. The Si−Cl distance, is given as 2.072, 2.070, and 2.067 Å by the empirical technique, the CCSD(T)/cc-pCVQZ method and the experimental determination, respectively, suggesting that the true value is very near 2.071 Å. The silicon−hydrogen distance is determined as 1.514 Å by both the empirical technique and pure theoretical determination, which is 0.011 Å smaller than the Si−H equilibrium distance inferred from experiment. The empirical and purely ab initio values of the bond angle are in reasonable agreement with the r_z and r_0 structures, and a value of 95.0° for this parameter might be a final estimation. The obvious discrepancies between the Si−H distance and bond angle reported here and those from experiment[25] point out the difficulties presented in determining hydrogen atom coordinates from analysis of rotational constants.

TABLE 5: Fundamental, Overtone, and Combination Vibrational Wavenumbers and Anharmonicity Corrections (in cm^{-1}) of the Ground Electronic State ($^1A'$) of $HSi^{35}Cl$

	CCSD		CCSD(T)		exptl	
	cc-pVTZ	cc-pCVTZ	cc-pVTZ	cc-pCVTZ	ref 25[a]	ref 24
ν_1	1991.97	1987.1	1972.09	1964.60	1968.7(4)	
ν_2	818.58	819.4	806.97	808.56	805.9(2)	808
ν_3	531.56	527.6	528.78	528.18	522.8(1)	522
$2\nu_1$	3915.72	3903.3	3874.05	3856.17		
$2\nu_2$	1631.81	1632.8	1608.49	1611.62		
$2\nu_3$	1058.99	1051.1	1053.41	1055.35		
$\nu_1 + \nu_2$	2797.61	2793.5	2765.68	2759.23		
$\nu_1 + \nu_3$	2524.25	2515.5	2501.66	2492.90		
$\nu_2 + \nu_3$	1346.92	1343.8	1332.46	1335.53		
$\omega_1 - \nu_1$	74.28	77.14	76.43	79.94		
$\omega_2 - \nu_2$	13.43	14.22	13.80	13.08		
$\omega_3 - \nu_3$	5.34	5.29	5.40	1.58		

[a] Values of the second column of data of Table 3, ref 25.

Considering both the purely ab initio and empirical structures, allows us to provide a recommended equilibrium structure of HSiCl: $r_e(Si-H) = 1.514 \pm 0.001$ Å, $r_e(Si-Cl) = 2.071 \pm 0.001$ Å, and $\angle(HSiCl) = 95.0 \pm 0.5°$.

B. Vibrational Frequencies. Harmonic vibrational frequencies and infrared intensities predicted for four isotopomers of HSiCl at the CCSD and CCSD(T) levels using the cc-pVTZ and cc-pCVTZ basis sets are presented in Table 4, where harmonic vibrational frequencies deduced from the experimental work of Harper et al.[26] may also be found. Fundamental frequencies evaluated from the anharmonic force field were calculated for $HSi^{35}Cl$ at the CCSD and CCSD(T) levels with the cc-pVTZ and cc-pCVTZ basis sets; the results are shown in Table 5. For the three remaining isotopic species i.e., $HSi^{37}Cl$, $DSi^{35}Cl$, and $DSi^{37}Cl$, fundamental frequencies were calculated at the CCSD/cc-pVTZ level and are listed in Table 6. Tables 5 and 6 also contain wavenumbers for transitions associated with selected overtone and combination bands as well as anharmonicity corrections to the vibrational frequencies of

TABLE 6: Fundamental, Overtone and Combination Vibrational Wavenumbers and Anharmonicity Corrections (in cm^1) of the Ground Electronic State ($^1A'$) of the Isotopic Species of HSiCl Calculated at the CCSD/cc-pVTZ Level[a]

	HSi^{37}Cl		DSi^{35}Cl		DSi^{37}Cl	
	calcd	obs	calcd	obs	calcd	obs
ν_1	1991.96	1968.7(3)	1449.45	1434.4(1)	1449.44	1434.4(2)
ν_2	818.26	805.6(1)	602.46	592.3(3)	601.90	
ν_3	525.08	516.3(2)	525.98	518.1(2)	519.55	511.6(4)
$2\ \nu_1$	3915.70		2863.59		2863.57	
$2\ \nu_2$	1631.16		1201.52		1200.43	
$2\ \nu_3$	1046.12		1048.07		1035.30	
$\nu_1 + \nu_2$	2797.28		2046.84		2046.18	
$\nu_1 + \nu_3$	2517.84		1975.03		1968.66	
$\nu_2 + \nu_3$	1340.15		1126.29		1119.33	
$\omega_1 - \nu_1$	74.29		38.04		38.05	
$\omega_2 - \nu_2$	13.41		7.02		7.01	
$\nu_3 - \nu_3$	5.23		5.15		5.02	

[a] Observed values of the second column of data of Table 3, ref 25. The values in parentheses are standard errors 1σ.

each isotopomer. A list of anhamonicity constants and quadratic, cubic, and semidiagonal quartic force fields in terms of normal coordinates and (curvilinear) valence internal coordinates, as well as centrifugal distortion constants in the *A*-reduction, are provided in the Supporting Information.

Correlation effects to anharmonicities when triple excitations are considered in the CC approach [via CCSD(T)] have only been tested for the normal species. In this case, differences are small. Improvement of the electron correlation treatment by means of the approximation of triple excitations plays a more important role in predicting harmonic frequencies. At the CCSD(T)/cc-pVTZ level, ω_1, ω_2, and ω_3 are 17.7, 11.2, and 4.7 cm^{-1}, respectively, smaller than CCSD/cc-pVTZ values. Comparing results between CCSD/cc-pCVTZ and CCSD(T)/cc-pCVTZ for HSi^{35}Cl, the first method gives values of 2064, 834, and 533 cm^{-1} for ω_1, ω_2, and ω_3 transitions, respectively, whereas the latter gives 2049, 821, and 532 cm^{-1}, respectively. With respect to infrared intensities, core−electron correlation effects again do not play as important a role as does improvement of the electron correlation treatment.

The harmonic frequencies of Harper et al.[25] (denoted as "est" in Table 4) represent estimates based on anharmonicity data from diatomic molecules. Comparing Harper's values with our CCSD(T)/cc-pCVTZ harmonic frequencies for HSi^{35}Cl, the largest deviation corresponds to that normal mode expected to be the most anharmonic i.e., the Si−H stretching displacement. For this vibration they deduce a value of 2004.3 cm^{-1}, which is 40.6 cm^{-1} below our value. ω_2(H−Si−Cl bend) and ω_3 (Si−Cl stretch) were estimated at only 13.8 and 4.8 cm^{-1} below our best calculations. Harper et al. also calculated the harmonic frequencies from the refinement of a harmonic force field, and reported a second set of harmonic frequencies, which is denoted as "calcd" in Table 4.

Our best calculated harmonic frequencies for HSi^{37}Cl, DSi^{35}Cl, and DSi^{37}Cl are those obtained at the CCSD(T)/cc-pVTZ level. The comparison of these values with the experimental estimations (est and calcd) of Harper et al.[25] shows roughly the same level of agreement as the normal isotopomer.

An excellent agreement is observed for HSi^{35}Cl between our best calculated fundamental frequencies, i.e., those at the CCSD(T)/cc-pCVTZ level, and experimental values from refs 24 and 25, (Table 5). ν_1 (Si−H stretch) shows a difference between experiment and theory of only 4 cm^{-1}. ν_2 and ν_3 transitions calculated with CCSD(T)/cc-pCVTZ differ only by three and five cm^{-1}, respectively, from the observed values. These excellent predictions demonstrate the effectiveness of, first, using analytic second derivatives of the energy together with high-level correlation methods in calculating a reliable near-equilibrium PES and, second, that a perturbational treatment of anharmonicity can be a good approach for the type of system here studied (two-third-row atoms), which exhibit a degree of anharmonicity of the order of half that found in molecules as HOCl[53] and HOBr.[54]

For HSi^{37}Cl, DSi^{35}Cl, and DSi^{37}Cl, agreement between experimental and calculated frequencies at the CCSD/cc-pVTZ level follows similar behavior to that discussed for the normal species. Overtone and combination bands for the four isotopomers are also reported in Tables 5 and 6 and could be used to guide future experiments.

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Supporting Information Available: Table 1S. Anharmonicity constants, x_{ij} (in cm^{-1}), of the electronic ground state ($^1A'$) of HSi^{35}Cl. Table 2S. Anharmonicity constants, x_{ij} (in cm^{-1}), of the electronic ground state ($^1A'$) of the isotopic species of HSiCl calculated at the CCSD/cc-pVTZ level of theory. Table 3S. Centrifugal distortion constants corresponding to the *A*-reduction Hamiltonian in the I^r representation of HSiCl. Table 4S. Cubic (ϕ_{ijk}) and semidiagonal quartic (ϕ_{iikl}) force constants (in cm^{-1}) of HSi^{35}Cl in dimensionless normal coordinates. Table 5S. Cubic (ϕ_{ijk}) and semidiagonal quartic (ϕ_{iikl}) force constants (in cm^{-1}) of HSi^{37}Cl, DSi^{35}Cl, and DSi^{37}Cl, in dimensionless normal coordinates. Table 6S. Quadratic and cubic force constants in curvilinear internal coordinates of HSiCl ($^1A'$). This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) HSiCl has only been detected in CVD using laser-induced fluorescence spectroscopy (LIF). It is known that LIF is one of the most sensitive techniques available for the detection of atoms and molecules and it has proved its ability to provide unambiguous species identification (ref 5).

(23) $SiCl_2$ is the thermodynamically favored product by 32.6 kcal/mol; the activation energy for the elimination of HCl from dichlorosilane yielding HSiCl was estimated form theoretical considerations to be only 13.0 kcal/mol higher than for the elimination of H_2 (at 1000° a difference of 5 kcal/mol). According to ref 13 in Kruppa et al.'s paper (ref 15), the activation energies for the elimination of HCl form dichlorosilane were calculated assuming that the difference in reactivity in the reverse insertion reaction is caused by a difference in activation energy due to the difference in siglet-triplet splittings in the series, SiH_2, HSiCl, and $SiCl_2$. Calculations at the GVB-DCCI//MP2/6-31G** level show that the singlet−triplet splitting in $SiCl_2$ is 34.1 kcal/mol greater than SiH_2 and HSiCl has a singlet−triplet splitting 14.5 kcal/mol greater than SiH_2 (ref 29). For HSiCl and $SiCl_2$ formation from dichlorosilane, the difference in singlet−triplet splitting between HSiCl and SiH_2 was added to the reaction endothermicity to obtain the activation energy.

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