

# An *ab initio* anharmonic force field of SiHCl<sub>3</sub>

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(Received 6 November 2002; accepted 13 December 2002)

An *ab initio* quartic force field of SiHCl<sub>3</sub> is derived using the second-order Møller–Plesset perturbation theory and Dunning’s correlation consistent triple-zeta basis set. After a minor empirical adjustment for the six diagonal quadratic force constants, most fundamentals of SiHCl<sub>3</sub> and SiDCl<sub>3</sub> agree with the experimental values within 1 cm<sup>-1</sup>. Additionally the observed overtones, combinations and hot band centres can also be well reproduced. Vibrational analysis based on the second-order perturbation theory is carried out with the calculated force constants. Two sets of spectroscopic constants are predicted for <sup>28</sup>SiH<sup>35</sup>Cl<sub>3</sub> and <sup>28</sup>SiD<sup>35</sup>Cl<sub>3</sub>, respectively.

## 1. Introduction

Spectra of SiHCl<sub>3</sub> in the fundamental and from the fifth through eighth Si–H stretching overtone regions were studied in earlier years [1–3]. Recently overtone spectra of the SiH chromophore in SiHCl<sub>3</sub> have been investigated experimentally in the 1000–13 000 cm<sup>-1</sup> region [4]. An *ab initio* calculation of the Si–H stretching–bending overtones has also been reported in [5], where potential energy and dipole moment surfaces of the SiH chromophore were given. Due to the small rotational constants, only some J-structure can be recognized [4] and the K-structure has been very hard to resolve until now. Very few rovibrational spectroscopy parameters were determined and only the experimental harmonic force field was obtained [1]. Meanwhile, having a high quality anharmonic force field is of great importance in the studies of rotation–vibration spectroscopy, and thermodynamic and dynamic properties of small molecules. At this moment it is impossible to derive the experimental anharmonic force field of SiHCl<sub>3</sub>, so in this work we investigate the anharmonic force field theoretically.

*Ab initio* calculation offers an alternative way to derive the force field and to predict molecular properties. An *ab initio* full dimensional potential energy surface including all the internal coordinates would be attractive for studying the intramolecular interactions of SiHCl<sub>3</sub>. In this article, an accurate *ab initio* potential energy surface up to fourth-order force constants is determined for SiHCl<sub>3</sub> using the second-order Møller–Plesset (MP2) perturbation theory [6]. This method has been successfully applied to derive the anharmonic force

field of SiHF<sub>3</sub> [7] and CHCl<sub>3</sub> [8]. Due to a lack of experimental data for other isotopomers, we focus on the two isotopomers with C<sub>3v</sub> symmetry: <sup>28</sup>SiH<sup>35</sup>Cl<sub>3</sub> and <sup>28</sup>SiD<sup>35</sup>Cl<sub>3</sub>.

## 2. Computational details

All the electronic structure calculations were carried out at the correlated level of MP2 theory in conjunction with Dunning’s correlation consistent polarized valence triple zeta basis sets (cc-pVTZ) [9, 10]. The Gaussian 98 [11] package was used in the *ab initio* calculation. Taking into account core polarization effects in the case of second-row atoms as suggested by Martin and Uzan [12], a special basis set (denoted as VTZ+1) was employed, which is derived from the triple-zeta cc-pVTZ [9, 10] basis by including an additional high exponent d function for Si and Cl atoms whose exponent equals the highest d exponent in the corresponding cc-pV5Z basis [13]. Because the chosen basis sets are not ideally suited to the description of the inner-shell contribution to the electron correlation [7], and also to decrease the calculation expense, the frozen core approximation of Si and Cl atoms was adopted in all the *ab initio* calculations. In this case, the Si and Cl 1s2s2p-like core molecular orbitals were required to remain doubly occupied.

The central difference formulas were applied to derive all the force constants. Displacements were set up in symmetry internal coordinates and a step size of 0.01 Å or 0.5° was applied for stretching or bending coordinates, respectively. The geometry and all the force constants were calculated with cc-pVTZ+1 for Si and Cl atoms, and cc-pVTZ for the H atom. All the MP2 energies were converged to 10<sup>-12</sup> hartree. The criteria

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for geometry optimization were that the rms displacement was converged to  $4.0 \times 10^{-6}$ , the rms force to  $1.0 \times 10^{-6}$  au (atomic units), and the predicted changes in energy to less than  $10^{-12}$  hartree.

The symmetry internal coordinates of SiHCl<sub>3</sub> are defined as follows:

$$S_1(A_1) = r, \quad (1)$$

$$S_2(A_1) = \frac{1}{3^{1/2}}(R_1 + R_2 + R_3), \quad (2)$$

$$S_3(A_1) = \frac{1}{[3(1 + K^2)]^{1/2}} \times (K\alpha_{12} + K\alpha_{13} + K\alpha_{23} - \beta_1 - \beta_2 - \beta_3), \quad (3)$$

$$S_{4a}(E) = \frac{1}{6^{1/2}}(2\beta_1 - \beta_2 - \beta_3), \quad (4)$$

$$S_{5a}(E) = \frac{1}{6^{1/2}}(2R_1 - R_2 - R_3), \quad (5)$$

$$S_{6a}(E) = \frac{1}{6^{1/2}}(2\alpha_{23} - \alpha_{12} - \alpha_{13}), \quad (6)$$

$$S_{4b}(E) = \frac{1}{2^{1/2}}(\beta_2 - \beta_3), \quad (7)$$

$$S_{5b}(E) = \frac{1}{2^{1/2}}(R_2 - R_3), \quad (8)$$

$$S_{6b}(E) = \frac{1}{2^{1/2}}(\alpha_{13} - \alpha_{12}). \quad (9)$$

where  $r$  is the displacement of the SiH bond length,  $R_i$  are the displacements of SiCl<sub>*i*</sub> bond lengths,  $\alpha_{ij}$  are the displacements of Cl<sub>*i*</sub>SiCl<sub>*j*</sub> bond angles and  $\beta_i$  are the displacements of Cl<sub>*i*</sub>SiH bond angles. The angle redundancy has been removed in  $S_3$  by setting  $\Delta\alpha = -K\Delta\beta$  [14] with  $K = -3 \sin \beta \cos \beta / \sin \alpha$ .  $S_{ta}$  and  $S_{tb}$  ( $t=4-6$ ) are symmetric and antisymmetric with regard to the plane containing the atoms H, Si and Cl<sub>1</sub>. According to point group theory there are 12 ( $6A_1A_1$ ,  $6EE$ ) quadratic, 38 cubic ( $10A_1A_1A_1$ ,  $18A_1EE$ ,  $10EEE$ ) and 102 quartic ( $15A_1A_1A_1A_1$ ,  $36A_1A_1EE$ ,  $30A_1EEE$ ,  $21EEEE$ ) independent constants for the SiHCl<sub>3</sub> molecule. The dependent constants can be derived from relations given elsewhere [15]. The potential energy function can be expanded in these symmetry internal coordinates:

$$V = V_0 + \frac{1}{2} \sum_{i,j} F_{ij} S_i S_j + \frac{1}{6} \sum_{i,j,k} F_{ijk} S_i S_j S_k + \frac{1}{24} \sum_{i,j,k,l} F_{ijkl} S_i S_j S_k S_l \quad (10)$$

Then all the force constants in symmetry internal coordinates are transformed to those in normal coordinates through the  $L$  tensor [16]. Spectroscopic constants are obtained based on the second-order perturbation

theory by using the SPECTRO [17] program. Fermi resonances and Coriolis interactions are taken into account.

### 3. Results and discussion

#### 3.1. Geometry and harmonic frequencies

The optimized and experimental geometry is listed in table 1. Bürger and Ruoff [1] derived the equilibrium geometry of SiHCl<sub>3</sub> from far infrared spectra of SiHCl<sub>3</sub> and SiDCl<sub>3</sub> in 1970. Later, the molecular structure was obtained from microwave spectra by Takeo and Matsumura [18] in 1977. The differences of the Si–H and Si–Cl bond lengths between the two sets of experimental geometries are less than 0.01 Å, but the difference for bond angle HSiCl is considerably larger, which is 1.2°. Our result agrees with that computed by the CCSD (T) (coupled cluster with all single and double substitutions (CCSD) supplemented with a quasi-perturbative estimate of the contribution of the connected triple excitations) method in conjunction with cc-pVQZ + 1 basis set [5]. Both computed equilibrium distances show minor deviations from experimental values, a little shorter for Si–H and a little longer for Si–Cl (as listed in table 1).

Table 2 shows all the harmonic and fundamental frequencies of SiHCl<sub>3</sub> and SiDCl<sub>3</sub>. The anharmonicity correction  $\omega_i - \nu_i$  values were derived from the anharmonicity constants  $x_{ij}$  and  $g_{ij}$  which have been calculated using standard formulas for perturbation theory [19]. Some interactions were considered in the calculation of the fundamental frequencies, and the details will be discussed in the next subsection. We have iteratively adjusted the six diagonal quadratic force constants such that the six computed fundamental wavenumbers of SiHCl<sub>3</sub> (values from the harmonic force field plus anharmonicity corrections) agree exactly with the experimental values. Also most experimental fundamental frequencies of SiDCl<sub>3</sub> are reproduced well (within 1 cm<sup>-1</sup>) with the same adjusted force field, except  $\nu_1$  and  $\nu_5$ . The adjusted harmonic frequency  $\omega_1$  of SiHCl<sub>3</sub> is 2340.4 cm<sup>-1</sup>, which agrees with the

Table 1. Optimized and experimental geometry (Å or degree) for SiHCl<sub>3</sub>.<sup>a</sup>

	MP2(cc-pVTZ + 1)	CCSD (T) (cc-pVQZ + 1) <sup>b</sup>	Expt. <sup>c</sup>	Expt. <sup>d</sup>
$r$ (SiH)	1.4582	1.4613	1.4655(2)	1.464
$r$ (SiCl)	2.0302	2.0306	2.0118(9)	2.020
$\angle$ HSiCl	109.4059	109.4570	108.32(25)	109.5

<sup>a</sup>Experimental substitution structures ( $r_s$ ). The value given in parentheses is one standard error in the last significant digits.

<sup>b</sup>From [5].

<sup>c</sup>From [1].

<sup>d</sup>From [18].

Table 2. Computed and experimental harmonic  $\omega_i$  and fundamental  $\nu_i$  frequencies for SiHCl<sub>3</sub> and SiDCl<sub>3</sub>. All frequencies are in cm<sup>-1</sup>.

Mode		$\omega_i$	$\omega_i$ (adjusted)	$\nu_i$ (adjusted)	$\nu_i$ (Expt.) <sup>a</sup>
SiHCl <sub>3</sub>	1(A <sub>1</sub> ) SiH str	2366.3	2340.4	2260.3	2260.3
	2(A <sub>1</sub> ) SiCl <sub>3</sub> s-str	505.5	505.6	498.6	498.6
	3(A <sub>1</sub> ) umbrella	254.8	255.4	253.7	253.7
	4(E) SiH rock	826.8	827.0	810.8	810.8
	5(E) SiCl <sub>3</sub> a-str	617.5	609.8	600.1	600.1
	6(E) SiCl <sub>3</sub> def	176.3	178.6	175.5	175.5
SiDCl <sub>3</sub>	1(A <sub>1</sub> ) SiD str	1703.2	1684.6	1643.6	1647.1
	2(A <sub>1</sub> ) SiCl <sub>3</sub> s-str	502.0	501.9	495.5	495.9
	3(A <sub>1</sub> ) umbrella	253.0	253.7	251.9	252.0
	4(E) SiD rock	642.4	642.6	633.1	633.8
	5(E) SiCl <sub>3</sub> a-str	568.6	565.4	556.8	550.0
	6(E) SiCl <sub>3</sub> def	175.4	177.7	175.2	174.5

<sup>a</sup>From [1], except  $\nu_1$  of SiHCl<sub>3</sub>, which is from [4].Table 3. Quadratic symmetry force constants  $F_{ij}$  (aJ Å<sup>-m</sup> rad<sup>-n</sup>).<sup>a</sup>

$i j$	$F_{ij}$	$F_{ij}$ (adjusted)
1 1	3.212 24	3.141 04
1 2	0.069 78	
1 3	-0.034 29	
2 2	3.601 27	3.597 07
2 3	0.150 49	
3 3	0.880 47	0.885 77
4 4	0.546 99	0.544 80
4 5	0.216 90	
4 6	-0.126 11	
5 5	3.099 41	3.018 31
5 6	-0.225 71	
6 6	0.745 67	0.763 80

<sup>a</sup>For  $m$  stretching and  $n$  bending modes. 1 aJ = 10<sup>-18</sup> J.Table 4. Cubic and quartic symmetry force constants  $F_{ijk}$  and  $F_{ijkl}$  (aJ Å<sup>-m</sup> rad<sup>-n</sup>).<sup>a</sup>

$i j k$	$F_{ijk}$	$ijk/ijkl$	$F_{ijk}, F_{ijkl}$	$ijkl$	$F_{ijkl}$	$ijkl$	$F_{ijkl}$
1 1 1	-14.171 80	5 5 6	-0.218 82	1 3 6 6	0.024 56	2 5 5 5	-0.163 54
1 1 2	0.006 10	5 6 6	0.340 06	2 2 4 4	0.114 55	2 5 5 6	0.243 52
1 1 3	-0.069 69	6 6 6	-1.184 12	2 2 4 5	0.018 70	2 5 6 6	-0.293 43
1 2 2	-0.232 37	1 1 1 1	57.200 04	2 2 4 6	-0.121 64	2 6 6 6	0.032 70
1 2 3	0.120 78	1 1 1 2	0.141 66	2 2 5 5	9.787 72	3 4 4 4	-0.958 48
1 3 3	-0.060 40	1 1 1 3	-0.012 52	2 2 5 6	-0.355 95	3 4 4 5	-0.163 99
2 2 2	-9.192 31	1 1 2 2	0.000 10	2 2 6 6	0.658 53	3 4 4 6	0.563 83
2 2 3	-0.479 86	1 1 2 3	0.037 47	2 3 4 4	-0.008 20	3 4 5 5	-0.028 62
2 3 3	-0.761 70	1 1 3 3	-0.085 97	2 3 4 5	-0.085 88	3 4 5 6	0.360 83
3 3 3	-0.486 44	1 2 2 2	-0.185 32	2 3 4 6	-0.446 94	3 4 6 6	-1.014 90
1 4 4	-0.117 36	1 2 2 3	-0.112 42	2 3 5 5	0.018 73	3 5 5 5	-0.287 28
1 4 5	-0.126 83	1 2 3 3	0.085 86	2 3 5 6	-0.529 55	3 5 5 6	0.193 24
1 4 6	0.002 72	1 3 3 3	0.114 78	2 3 6 6	0.680 61	3 5 6 6	-0.270 62
1 5 5	-0.112 48	2 2 2 2	20.534 73	3 3 4 4	0.563 73	3 6 6 6	1.428 36
1 5 6	0.006 87	2 2 2 3	0.624 48	3 3 4 5	0.147 58	4 4 4 4	0.751 42
1 6 6	-0.002 86	2 2 3 3	0.429 37	3 3 4 6	-0.507 42	4 4 4 5	0.163 93
2 4 4	-0.342 92	2 3 3 3	1.328 44	3 3 5 5	0.057 28	4 4 4 6	-2.875 39
2 4 5	-0.162 55	3 3 3 3	0.976 88	3 3 5 6	-0.500 22	4 4 5 5	0.114 49
2 4 6	0.124 44	1 1 4 4	-0.114 54	3 3 6 6	1.691 42	4 4 5 6	-0.065 59
2 5 5	-8.426 74	1 1 4 5	-0.043 75	1 4 4 4	0.016 41	4 4 6 6	0.413 48
2 5 6	0.410 60	1 1 4 6	0.014 33	1 4 4 5	0.064 42	4 5 5 5	0.299 69
2 6 6	-0.865 89	1 1 5 5	-0.043 56	1 4 4 6	-0.016 43	4 5 5 6	0.014 32
3 4 4	0.053 47	1 1 5 6	0.012 50	1 4 5 5	0.043 72	4 5 6 6	0.311 60
3 4 5	0.197 37	1 1 6 6	-0.057 20	1 4 5 6	-0.007 16	4 6 6 6	-0.413 47
3 4 6	0.482 01	1 2 4 4	0.100 16	1 4 6 6	0.016 43	5 5 5 5	28.730 93
3 5 5	0.036 47	1 2 4 5	0.168 61	1 5 5 5	-0.010 85	5 5 5 6	-1.273 95
3 5 6	0.323 96	1 2 4 6	0.053 66	1 5 5 6	-0.000 03	5 5 6 6	0.171 89
3 6 6	-1.055 21	1 2 5 5	0.098 08	1 5 6 6	0.000 03	5 6 6 6	-0.229 64
4 4 4	-0.352 29	1 2 6 6	-0.007 18	1 6 6 6	-0.000 04	6 6 6 6	5.713 45
4 4 5	-0.135 11	1 2 5 6	0.043 72	2 4 4 4	-0.032 89	4a6a5b6b	0.442 81
4 4 6	-0.184 02	1 3 4 4	-0.008 22	2 4 4 5	0.007 11	4a4a5b5b	-1.660 30
4 5 5	-0.102 92	1 3 4 5	-0.153 85	2 4 4 6	0.155 76	4a4a6b6b	0.000 01
4 5 6	-0.099 76	1 3 4 6	-0.024 60	2 4 5 5	-0.049 98	5a5a6b6b	-0.343 38
4 6 6	0.715 39	1 3 5 5	-0.056 23	2 4 5 6	0.175 33	4a4a5b6b	0.000 00
5 5 5	-5.745 93	1 3 5 6	-0.014 33	2 4 6 6	-0.434 62	4a5a6b6b	0.131 15

<sup>a</sup>For  $m$  stretching and  $n$  bending modes. 1 aJ = 10<sup>-18</sup> J.

experimental value  $2343.95(53)\text{cm}^{-1}$ [4]. The final adjusted quadratic force constants are given in table 3.

### 3.2. Anharmonic analysis

The MP2/cc-pVTZ+1 level cubic and quartic symmetry force constants are presented in table 4. The *ab initio* anharmonic constants of SiHCl<sub>3</sub> and SiDCl<sub>3</sub> are shown in table 5 and rotational, ro-vibrational constants in table 6, which are based on the second-order perturbation formulas for symmetric top molecules. Some computed band centres of overtones and combinations are listed in tables 7 and 8. Experimental values are also given for comparison.

As expected, the anharmonicity of the potential energy surface is found to be significant for the stretching modes, with negative cubic constants ( $F_{111}$ ,  $F_{222}$ ,  $F_{555}$  and  $F_{255}$ ) and positive quartic constants ( $F_{1111}$ ,

Table 5. *Ab initio* anharmonic constants ( $\text{cm}^{-1}$ ) for SiHCl<sub>3</sub> and SiDCl<sub>3</sub> in comparison with experimental data.<sup>a</sup>

		SiHCl <sub>3</sub>		SiDCl <sub>3</sub>	
<i>ij</i>		Calc.	Obs. <sup>b</sup>	Calc.	Obs. <sup>c</sup>
<i>x<sub>ij</sub></i>	1 1	-34.269	-34.9585(92)	-17.779	-19.0(5)
	1 2	-0.894	-1.655(87)	-0.634	~ -6.0
	1 3	-0.246	0.11(13)	-0.171	~ 0.6
	1 4	-10.713	-13.598(27)	-0.418	~ -4
	1 5	0.271	-0.429(94)	-4.171	~ -7.5
	1 6	-0.075		-0.064	~ 0.6
	2 2	-0.881	-10.027	-0.842	
	2 3	-1.479*		-1.457*	~ 0
	2 4	-0.408	-5.31(14)	-2.755	
	2 5	-3.025		-0.995	
	2 6	-0.349		0.043	
	3 3	-0.106*		-0.112*	
	3 4	0.096		-0.791	
	3 5	-0.733		0.131	
	3 6	-0.078		-0.103	
	4 4	-3.677	-2.447(42)	-1.950	
	4 5	-3.022*		-1.986	
	4 6	-2.254*		-1.889	
	5 5	-1.856	-0.19(10)	-1.658	
	5 6	-0.487*		-0.506	
<i>g<sub>ij</sub></i>	6 6	0.032		0.036	
	4 4	5.827	2.816(90)	2.399	
	4 5	-0.507*		1.758	
	4 6	-3.131*		1.666	
	5 5	1.296		1.263	
<i>R<sub>ij</sub></i>	5 6	-0.015*		1.216	
	6 6	0.041		0.023	
	4 5	-2.698		-2.433	
	4 6	-2.739		-2.137	
	5 6	0.164		-0.208	

<sup>a</sup>The anharmonic constants marked with an asterisk are corrected by removing the Fermi resonance contributions from the perturbational expressions of the respective anharmonicity constants.

<sup>b</sup>From [4]

<sup>c</sup>From [1].

$F_{2222}$ ,  $F_{5555}$  and  $F_{2255}$ ). All other anharmonic symmetry force constants involving bending modes are smaller in absolute value. Except for the stretching modes, the anharmonicity correction  $\omega_4-\nu_4$  of SiHCl<sub>3</sub> and SiDCl<sub>3</sub> are rather large (16.2 and 9.5  $\text{cm}^{-1}$ , respectively) due to the relatively small reduced mass of SiH(D).

By using the anharmonic constants of SiHCl<sub>3</sub> calculated from this force field, some band centres of overtones, combinations and hot bands were calculated, which agree well with the observed band centres [1, 4]. Here we will correct some errors in the assignment given in [4]. The observed band centre  $1435.0\text{cm}^{-1}$  should be

Table 6. *Ab initio* and experimental spectroscopic constants for SiHCl<sub>3</sub> and SiDCl<sub>3</sub>.

	SiHCl <sub>3</sub>		SiDCl <sub>3</sub>	
	Calc.	Obs. <sup>a</sup>	Calc.	Obs. <sup>a</sup>
$B_0/\text{cm}^{-1}$	0.081 697	0.082 427	0.080 183	0.080 868
$C_0/\text{cm}^{-1}$	0.043 825	0.044 270	0.043 825	0.044 270
$\alpha_1^B/\text{MHz}$	0.627		1.067	
$\alpha_2^B/\text{MHz}$	3.778		4.460	
$\alpha_3^B/\text{MHz}$	1.734		1.696	
$\alpha_4^B/\text{MHz}$	1.080		3.316	
$\alpha_5^B/\text{MHz}$	4.451		1.386	
$\alpha_6^B/\text{MHz}$	-2.509		-2.368	
$\alpha_1^C/\text{MHz}$	0.203		0.203	
$\alpha_2^C/\text{MHz}$	2.886		2.886	
$\alpha_3^C/\text{MHz}$	0.286		0.286	
$\alpha_4^C/\text{MHz}$	0.227		0.227	
$\alpha_5^C/\text{MHz}$	2.178		2.178	
$\alpha_6^C/\text{MHz}$	0.639		0.639	
$\zeta_{44}^z$	0.992	0.95(5)	-0.881	0.86(4)
$\zeta_{55}^z$	-0.643	0.78(7)	-0.719	0.67(5)
$\zeta_{66}^z$	-0.703	-0.87(10)	0.684	-0.66(15)
$ \zeta_{25}^y $	0.72 777		0.40 671	
$ \zeta_{36}^y $	0.44 731		0.46 817	
$q_4^+/\text{MHz}$	29.343		15.540	
$q_5^+/\text{MHz}$	3.594		9.780	
$q_6^+/\text{MHz}$	4.506		4.116	
$10^7 D_J/\text{cm}^{-1}$	0.34 334	0.47(1)	0.31 740	
$10^7 D_{JK}/\text{cm}^{-1}$	-0.58 747		-0.53 749	
$10^7 D_K/\text{cm}^{-1}$	0.27 641		0.25 238	
$10^{13} H_J/\text{cm}^{-1}$	0.37 934		0.33 085	
$10^{13} H_{JK}/\text{cm}^{-1}$	-1.48 037		-1.28 419	
$10^{13} H_{KJ}/\text{cm}^{-1}$	1.84 204		1.59 579	
$10^{13} H_K/\text{cm}^{-1}$	-0.73 640		-0.63 783	
$10^{14} h_3/\text{cm}^{-1}$	0.24 875		0.21 482	

<sup>a</sup>From [1].

Table 7. Band centres of the infrared spectrum of SiHCl<sub>3</sub> (in cm<sup>-1</sup>).

Assignment <sup>a</sup>	Expt. <sup>b</sup>	Cal.	Δ(c-e)
*ν <sub>6</sub>	175.5	175.5	0.0
*ν <sub>3</sub>	253.7	253.7	0.0
*ν <sub>2</sub>	498.6	498.6	0.0
*ν <sub>4</sub> -ν <sub>3</sub>	558	557.1	-0.9
*ν <sub>5</sub>	600.1	600.1	0.0
*ν <sub>4</sub>	810.8	810.8	0.0
*ν <sub>3</sub> +ν <sub>5</sub>	855	853.7	-1.3
*ν <sub>3</sub> +ν <sub>4</sub>	1065	1064.6	-0.4
*ν <sub>2</sub> +ν <sub>5</sub>	1101	1095.7	-5.3
*ν <sub>2</sub> +ν <sub>4</sub>	1310	1309.0	-1.0
ν <sub>2</sub> +ν <sub>5</sub> +ν <sub>6</sub>	1263.7	1270.4	6.7
ν <sub>2</sub> +ν <sub>4</sub>	1302.0	1309.0	7.0
2ν <sub>4</sub> -ν <sub>3</sub>	1346.3	1348.9	2.6
ν <sub>4</sub> +ν <sub>5</sub>	1405.3	1407.4	2.1
ν <sub>1</sub> -ν <sub>4</sub>	1451.3	1449.5	-1.8
2ν <sub>4</sub>	1606.1	1602.6	-3.5
ν <sub>3</sub> +ν <sub>4</sub> +ν <sub>5</sub>	1657.5	1660.4	2.9
ν <sub>1</sub> -ν <sub>2</sub>	1751.3	1761.7	10.4
3ν <sub>5</sub> +ν <sub>2</sub> -ν <sub>2</sub>	1787.3	1777.5	-9.8
3ν <sub>5</sub>	1799.5	1786.6	-12.9
3ν <sub>4</sub> -ν <sub>2</sub>	1901.5	1900.1	-1.4
ν <sub>1</sub> -ν <sub>3</sub>	2006.5	2006.6	0.1
ν <sub>2</sub> +2ν <sub>4</sub>	2094.4	2100.4	6.0
ν <sub>1</sub> +ν <sub>4</sub> -ν <sub>4</sub>	2248.0	2249.6	1.6
ν <sub>1</sub>	2260.3	2260.3	0.0
3ν <sub>4</sub>	2406.3	2398.7	-7.6
ν <sub>1</sub> +ν <sub>6</sub>	2435.5	2435.7	0.2
ν <sub>1</sub> +ν <sub>3</sub>	2514.6	2513.7	-0.9
ν <sub>1</sub> +ν <sub>2</sub>	2757.0	2758.0	1.0
ν <sub>1</sub> +ν <sub>5</sub>	2854.0	2860.7	6.7
ν <sub>1</sub> +ν <sub>4</sub>	3054.5	3060.4	5.9
ν <sub>1</sub> +2ν <sub>2</sub>	3231.4	3254.0	22.6
ν <sub>1</sub> +2ν <sub>4</sub>	3842.0	3841.5	-0.5
2ν <sub>1</sub> +ν <sub>4</sub> -ν <sub>4</sub>	4425.2	4430.6	5.4
2ν <sub>1</sub>	4450.4	4452.0	1.6

<sup>a</sup>For the degenerate overtone and combination bands only the lowest angle momentum quantum number  $l_i$  is considered.

<sup>b</sup>From reference [4] except that marked with an asterisk which is from [1].

the  $2\nu_4^0 - \nu_6^{\pm 1}$  hot band (the calculated value is  $1427.1 \text{ cm}^{-1}$ ) instead of the  $3\nu_2$  band. The calculated  $3\nu_2$  band centre locates at  $1490.6 \text{ cm}^{-1}$ , but it is not observed. The band at  $2964.3 \text{ cm}^{-1}$  should not be assigned as  $\nu_1 + \nu_2 + \nu_4^{\pm 1}$ , since the calculated band centre of  $\nu_1 + \nu_2 + \nu_4^{\pm 1}$  is  $3557.7 \text{ cm}^{-1}$ . From tables 7 and 8, most band centres can be reproduced well by these two sets of anharmonic constants. The anharmonic constants corresponding with SiH(D) chromophore vibrational modes,  $x_{11}$ ,  $x_{14}$  and  $x_{44}$  agree with those fitted from experimental band centres [4]. However others have large discrepancy, even with opposite sign. Fuss and Weizbauer [20] obtained some anharmonic constants from FTIR spectra, many constants of which are also different from those of this work and of [4]. Maybe the difference comes from the limited number of

Table 8. Band centres of the infrared spectrum of SiDCl<sub>3</sub> (in cm<sup>-1</sup>).

Assignment <sup>a</sup>	Expt. <sup>b</sup>	Cal.	Δ(c-e)
ν <sub>6</sub>	174.5	175.2	0.7
ν <sub>3</sub>	252.0	251.9	-0.1
ν <sub>2</sub>	495.9	495.5	-0.4
ν <sub>5</sub>	555.0	556.8	1.8
ν <sub>4</sub>	633.8	633.1	-0.7
ν <sub>2</sub> +ν <sub>3</sub>	748.0	745.9	-2.1
ν <sub>1</sub> -ν <sub>4</sub>	1015.5	1010.5	-5.0
ν <sub>2</sub> +ν <sub>4</sub>	1129	1125.8	-3.2
ν <sub>4</sub> +ν <sub>5</sub>	1178.5	1189.4	10.9
2ν <sub>4</sub>	1264	1257.5	-6.5
ν <sub>1</sub> -ν <sub>6</sub>	1472.9	1468.4	-4.5
2ν <sub>1</sub> -ν <sub>1</sub>	1608.7	1608.1	-0.6
ν <sub>1</sub> +ν <sub>2</sub> -ν <sub>2</sub>	1637.5	1643.0	5.5
ν <sub>1</sub> +ν <sub>5</sub> -ν <sub>5</sub>	1637.5	1639.2	1.7
ν <sub>1</sub>	1647.1	1643.6	-3.5
ν <sub>1</sub> +ν <sub>6</sub>	1822.2	1818.7	-3.5
ν <sub>1</sub> +ν <sub>3</sub>	1899.7	1895.4	-4.3
ν <sub>1</sub> +ν <sub>2</sub>	2137	2138.5	1.5
ν <sub>1</sub> +ν <sub>5</sub>	2197	2196.0	1.0
ν <sub>1</sub> +ν <sub>4</sub>	2277	2276.3	-0.7
2ν <sub>1</sub>	3256.2	3251.7	-4.5

<sup>a</sup>For the degenerate overtone and combination bands only the lowest angle momentum quantum number  $l_i$  is considered.

<sup>b</sup>From [1].

observed band centres included in the fitting and also some misassignments.

The Coriolis coefficients,  $H_{22}$  diagonal  $\alpha$  constants and rotational  $l$ -type doubling constants  $q_l^+$  are listed in table 6. The Coriolis interactions of  $\nu_2$ ,  $\nu_5$  and  $\nu_3$ ,  $\nu_6$  are considered. Effective rotational constants (in which distortion due to the quartic centrifugal distortion constants is included), quartic and sextic centrifugal distortion constants are also listed in the same table. The Fermi resonances, the  $(\nu_2, 2\nu_3)$ ,  $(\nu_4^{\pm 1}, \nu_5^{\pm 1} + \nu_6^{\pm 1})$ ,  $(\nu_4^{\pm 1}, \nu_3 + \nu_5^{\pm 1})$  for SiHCl<sub>3</sub>, and the  $(\nu_2, 2\nu_3)$  for SiDCl<sub>3</sub>, have been treated explicitly so that the corresponding anharmonic constants were corrected by removing their contributions from the perturbational expressions of the respective anharmonicity constants. Since Ding *et al.* [4] pointed out that the Fermi resonance between the SiH stretching and bending modes is not significant, we do not treat this resonance interaction explicitly, but include it perturbationally. As a result the  $\nu_1$  and  $2\nu_4$  band centres still agree with the experimental values well without this resonance. Because very high resolution spectra of SiHCl<sub>3</sub> have not been obtained, we lack values for these constants.

#### 4. Conclusion

An accurate quartic force field of SiHCl<sub>3</sub> has been obtained using the MP2 theory and cc-pVTZ+1 basis

set under the frozen core approximation. An optimized geometry is also given. From this *ab initio* and a minor empirical adjustment force field, fundamentals for SiHCl<sub>3</sub> and SiDCl<sub>3</sub> are derived based on second-order perturbation theory and the predicted band centres agree well with the experimental results. The spectroscopic constants of SiHCl<sub>3</sub> and SiDCl<sub>3</sub> are predicted, although some of them cannot agree with the values fitted from the limited available experimental results. To determine these spectroscopic constants, high resolution spectra need to be recorded.

This work was jointly supported by the National Natural Science Foundation of China (Grant No: 20103007), by the National Project for the Development of Key Fundamental Sciences in China, and by the Chinese Academy of Science.

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