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# The ground state energy levels and molecular structure of jet-cooled HGeCl and DGeCl from single vibronic level emission spectroscopy

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Single vibronic level dispersed fluorescence spectra of jet-cooled HGeCl and DGeCl have been recorded by laser excitation of selected bands of the  $\tilde{A}^1A''-\tilde{X}^1A'$  electronic transition. Twenty-six ground state vibrational levels of HGeCl and 42 of DGeCl were measured, assigned, and fitted to standard anharmonicity expressions, which allowed all the harmonic frequencies to be determined for both isotopomers. A normal coordinate least squares analysis obtained by fitting the harmonic frequencies yielded reliable values for five of the six force constants. The ground state effective rotational constants and force field data were combined to calculate average ( $r_z$ ) and approximate equilibrium ( $r_e^z$ ) structures, with  $r_e^z(\text{GeH})=1.586(1)$  Å,  $r_e^z(\text{GeCl})=2.171(2)$  Å, and the bond angle fixed at our CCSD(T)/aug-cc-pVTZ *ab initio* value of 93.9°. Comparisons show that the derived bond lengths are consistent with those of the appropriate diatomic molecules in their ground electronic states and the bond angle is similar to that of germylene ( $\text{GeH}_2$ ). A Franck-Condon simulation of the vibrational intensities in the  $0_0^0$  band emission spectrum of HGeCl using *ab initio* force field data shows good agreement with experiment, lending credence to the vibrational analysis of the observed spectra. © 2006 American Institute of Physics. [DOI: 10.1063/1.2181142]

## I. INTRODUCTION

Divalent compounds involving the group 14 elements, such as the carbenes and their heavier congeners (the silylenes and germynes), are typically short-lived, reactive intermediates, although some thermally stable compounds have been synthesized.<sup>1-4</sup> A great deal of spectroscopic information is available for the simplest transient silylenes<sup>4-10</sup> ( $\text{SiH}_2$ ,  $\text{SiHX}$ ;  $X=\text{F,Cl,Br,I}$ ) but the corresponding germynes are less well known. In the present work we report studies of the ground state vibrational energy levels and the molecular structure of monochlorogermylene, HGeCl, and its deuterated isotopomer, DGeCl.

Isabel and Guillory<sup>11</sup> were the first to report the spectroscopic detection of HGeCl. The authors photolyzed  $\text{H}_3\text{GeCl}$  in an argon matrix and used infrared absorption spectroscopy to detect  $\text{GeH}_2\text{Cl}$  and a weak infrared absorption band at  $1862\text{ cm}^{-1}$  which was tentatively assigned as due to HGeCl. Patel and Stewart<sup>12</sup> reported the electronic emission spectra of HGeCl and DGeCl obtained by dispersing the chemiluminescence generated by the reaction of germane with chlorine gas. From these studies, HGeCl ground state fundamental vibrational frequencies of  $\nu_2'=706.45\text{ cm}^{-1}$  and  $\nu_3'=439.17\text{ cm}^{-1}$  were obtained and the  $0_0^0$  band was assigned to a feature at  $4643.1$  Å. Ito *et al.*<sup>13</sup> studied the laser induced fluorescence (LIF) spectra of uncooled HGeCl produced by the reaction of germane with chlorine atoms. At a resolution of  $0.04\text{ cm}^{-1}$ , they were able to resolve the  $K$  structure of the

$0_0^0$ ,  $2_0^1$ , and  $2_0^2$  bands of HGeCl and determined  $A-\bar{B}$  and  $D_k$  for the upper and lower states of each band. Using H-Ge and Ge-Cl bond lengths transferred from other molecules, they estimated the ground state bond angle to be approximately  $110^\circ$ .

In 1998 we reported<sup>14</sup> a detailed LIF study of the  $\tilde{A}^1A''-\tilde{X}^1A'$  band systems of jet-cooled HGeCl and DGeCl. The analysis yielded monochlorogermylene ground and excited state molecular structures of  $r_0''(\text{Ge-Cl})=2.171(2)$  Å,  $r_0''(\text{H-Ge})=1.592(1)$  Å,  $\theta_0''(\text{HGeCl})=94.3^\circ$ ,  $r_0'(\text{Ge-Cl})=2.146(15)$  Å,  $r_0'(\text{H-Ge})=1.613(2)$  Å,  $\theta_0'(\text{HGeCl})=114.5^\circ$ , and the frequencies of the three excited state vibrational fundamentals. The geometry determinations were hindered by a strong correlation between the bond angle and the Ge-H bond length, due to the fact that the  $a$  axis is almost coincident with the Ge-Cl bond, necessitating that the bond angle be fixed at an *ab initio* value. The radiative lifetime of the  $\tilde{A}$  state of HGeCl was measured to be  $548\pm 19$  ns.

Recently, Lin *et al.*<sup>15</sup> reported a Fourier transform microwave study of nine isotopomers of HGeCl in natural abundance in which they were able to resolve the hyperfine structure of the  $1_{01}-0_{00}$  and  $2_{02}-1_{01}$  ( $J_{K_aK_c}$ ) transitions. Effective rotational constants,  $[(B+C)/2]$ , the chlorine and  $^{73}\text{Ge}$  nuclear quadrupole coupling constants, and the chlorine nuclear spin-rotation coupling constants were determined. The effective  $\text{H}^{74}\text{Ge}^{35}\text{Cl}$  rotational constant of  $4416.7799(4)$  MHz reported in the microwave work validates the much less precise value [ $4414(2)$  MHz] from previous LIF work, lending credence to the derived molecular structure.<sup>14</sup>

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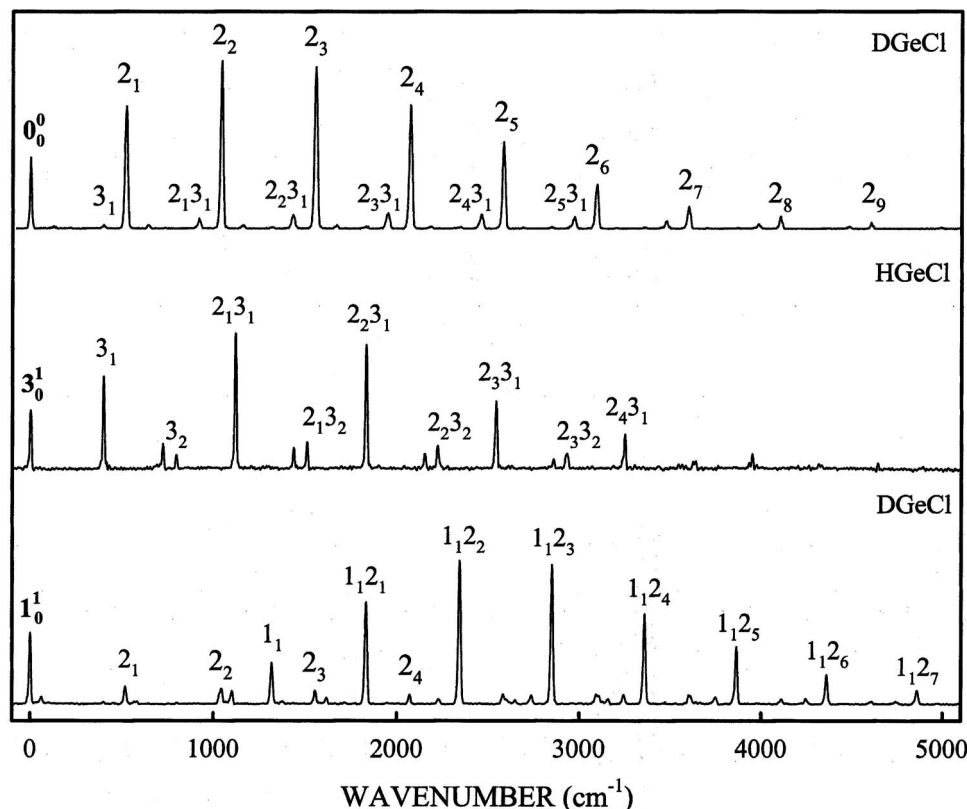


FIG. 1. Examples of the dispersed emission spectra of DGeCl and HGeCl. The  $\tilde{A}-\tilde{X}$  vibronic transition pumped by the excitation laser is given in bold at the left of each trace and the lower state vibrational level assignments are indicated. The wave number scale is the displacement from the excitation laser, giving a direct measure of the ground state vibrational energy. In each case, the resonance fluorescence feature at  $0.0\text{ cm}^{-1}$  is obscured somewhat by scattered laser light.

A very limited number of theoretical studies have been reported for HGeCl.<sup>16–20</sup> The most extensive of these are the MRSDCI calculations of Benavides-Garcia and Balasubramaniam<sup>17</sup> which predicted the geometries, term values, and dipole moments of the three lowest lying electronic states of HGeX ( $X=\text{Cl}, \text{Br}, \text{I}$ ).

## II. EXPERIMENT

Monochlorogermylene (HGeCl or DGeCl) was produced by seeding the vapor of cooled (from  $-40^\circ\text{C}$  up to room temperature depending on the strength of the signal) monochlorogermene ( $\text{H}_3\text{GeCl}$  or  $\text{D}_3\text{GeCl}$ ) into 40 psi of argon, injecting pulses of this gas mixture into a flow channel, and striking an electric discharge through each gas pulse prior to expansion of the products into a vacuum chamber. This pulsed discharge source, described in detail elsewhere,<sup>14,21</sup> produced a variety of products, including substantial quantities of HGeCl or DGeCl and GeCl. The reactive intermediates were rotationally and vibrationally cooled by free jet expansion into vacuum at the exit of the pulsed discharge apparatus.

Single vibronic level (SVL) emission spectra were obtained by fixing the wavelength of a 355 nm pumped tunable dye laser (Lumonics HD-500) on the  $^pQ_1$  branch of a band in the LIF spectrum and imaging the resulting fluorescence with  $f/1.5$  optics onto the entrance slit of a 0.50 m scanning monochromator (Spex 500M). The wavelength resolved fluorescence signals were detected with a cooled, red-sensitive photomultiplier (RCA C31034A), amplified with a gain of 800, processed using a gated integrator, and recorded digitally. A 1800 lines/mm grating blazed at 400 nm was employed in this work, with a bandpass of 0.2–0.4 nm, de-

pending on the signal intensity. The monochromator scan was calibrated to an estimated accuracy of  $\pm 2\text{ cm}^{-1}$  using known emission lines from argon and neon lamps.

Chlorogermene ( $\text{H}_3\text{GeCl}$ ) was synthesized by condensing a slight molar excess of hydrogen chloride (HCl) onto degassed phenylgermane at liquid nitrogen temperature.<sup>14</sup> The reaction mixture was sealed in a Pyrex vessel, cooled with dry ice, and allowed to warm slowly overnight to room temperature. The resulting mixture of  $\text{H}_3\text{GeCl}$ , benzene, and small quantities of  $\text{GeH}_4$  was purified by trap-to-trap distillation in vacuum to isolate the desired product, whose purity was established by gas phase infrared spectroscopy.  $\text{D}_3\text{GeCl}$  was prepared in a similar fashion using phenylgermane- $d_3$  and DCl. Phenylgermane and phenylgermane- $d_3$  were prepared by the lithium aluminum hydride (or deuteride) reduction of phenyltrichlorogermene (Gelest).<sup>22</sup>

## III. RESULTS AND ANALYSIS

Monochlorogermylene is a bent molecule of  $C_s$  symmetry with three  $a'$  vibrational modes conventionally labeled as  $\nu_1$  (Ge–H stretch),  $\nu_2$  (bend), and  $\nu_3$  (Ge–Cl stretch). The  $\tilde{A}^1A''-\tilde{X}^1A'$  electronic transition involves electron promotion from a nonbonding  $\sigma$  orbital to an out-of-plane  $p$  orbital primarily localized on the germanium atom and results in absorption bands following  $c$ -type selection rules. Although HGeCl and DGeCl each consists of ten isotopomers with significant natural abundances, in most cases the isotope splittings were not resolved in the LIF or emission spectra, so in all calculations involving isotopic masses we have assumed that we are dealing with the most abundant species,  $\text{H } ^{74}\text{Ge } ^{35}\text{Cl}$  and  $\text{D } ^{74}\text{Ge } ^{35}\text{Cl}$ .

TABLE I. Vibrational assignments, ground state vibrational energies, and residuals (in  $\text{cm}^{-1}$ ) from the single vibronic level emission spectra of HGeCl and DGeCl.

HGeCl		DGeCl			
Assignment	Energy	Assignment	Energy	Assignment	Energy
1 <sub>1</sub>	1830(−0.1)	1 <sub>1</sub>	1320(0.2)	2 <sub>1</sub> 3 <sub>1</sub>	921(0.9)
1 <sub>2</sub>	3592(0.0)	1 <sub>2</sub>	2604(−0.5)	2 <sub>2</sub> 3 <sub>1</sub>	1438(1.0)
2 <sub>1</sub>	721(−0.4)	2 <sub>1</sub>	521(−0.3)	2 <sub>3</sub> 3 <sub>1</sub>	1952(0.5)
2 <sub>2</sub>	1438(−0.4)	2 <sub>2</sub>	1040(−0.2)	2 <sub>4</sub> 3 <sub>1</sub>	2464(−0.3)
2 <sub>3</sub>	2150(−0.1)	2 <sub>3</sub>	1556(−0.5)	2 <sub>5</sub> 3 <sub>1</sub>	2974(0.2)
2 <sub>4</sub>	2859(0.5)	2 <sub>4</sub>	2070(−0.4)	2 <sub>6</sub> 3 <sub>1</sub>	3480(−1.5)
2 <sub>5</sub>	3561(0.2)	2 <sub>5</sub>	2582(−0.4)	2 <sub>7</sub> 3 <sub>1</sub>	3987(0.0)
2 <sub>6</sub>	4260(0.2)	2 <sub>6</sub>	3092(0.5)	2 <sub>8</sub> 3 <sub>1</sub>	4492(1.6)
2 <sub>7</sub>	4953(−0.7)	2 <sub>7</sub>	3599(0.0)	1 <sub>1</sub> 2 <sub>1</sub> 3 <sub>1</sub>	2228(−1.2)
3 <sub>1</sub>	400(0.1)	2 <sub>8</sub>	4104(0.2)	1 <sub>1</sub> 2 <sub>2</sub> 3 <sub>1</sub>	2739(0.4)
3 <sub>2</sub>	796(0.9)	2 <sub>9</sub>	4607(0.7)	1 <sub>1</sub> 2 <sub>3</sub> 3 <sub>1</sub>	3246(1.1)
1 <sub>1</sub> 2 <sub>1</sub>	2535(−0.3)	2 <sub>10</sub>	5106(−0.5)	1 <sub>1</sub> 2 <sub>4</sub> 3 <sub>1</sub>	3749(−0.2)
1 <sub>1</sub> 2 <sub>2</sub>	3236(0.1)	2 <sub>11</sub>	5604(−0.7)	1 <sub>1</sub> 2 <sub>5</sub> 3 <sub>1</sub>	4250(−1.0)
1 <sub>1</sub> 2 <sub>3</sub>	3932(0.3)	3 <sub>1</sub>	398(−2.2)	1 <sub>1</sub> 2 <sub>6</sub> 3 <sub>1</sub>	4751(0.2)
1 <sub>1</sub> 2 <sub>4</sub>	4623(0.2)	1 <sub>1</sub> 2 <sub>1</sub>	1833(−0.3)	1 <sub>1</sub> 2 <sub>7</sub> 3 <sub>1</sub>	5248(−0.8)
1 <sub>1</sub> 2 <sub>5</sub>	5310(0.6)	1 <sub>1</sub> 2 <sub>2</sub>	2343(−0.7)	1 <sub>1</sub> 2 <sub>8</sub> 3 <sub>1</sub>	5744(0.0)
1 <sub>1</sub> 2 <sub>6</sub>	5991(−0.8)	1 <sub>1</sub> 2 <sub>3</sub>	2852(−0.3)		
1 <sub>2</sub> 2 <sub>1</sub>	4280(0.0)	1 <sub>1</sub> 2 <sub>4</sub>	3358(−0.4)		
2 <sub>1</sub> 3 <sub>1</sub>	1118(−0.8)	1 <sub>1</sub> 2 <sub>5</sub>	3862(0.2)		
2 <sub>2</sub> 3 <sub>1</sub>	1832(−0.9)	1 <sub>1</sub> 2 <sub>6</sub>	4364(0.6)		
2 <sub>3</sub> 3 <sub>1</sub>	2543(0.1)	1 <sub>1</sub> 2 <sub>7</sub>	4863(0.3)		
2 <sub>4</sub> 3 <sub>1</sub>	3249(0.3)	1 <sub>1</sub> 2 <sub>8</sub>	5360(0.3)		
2 <sub>5</sub> 3 <sub>1</sub>	3950(1.0)	1 <sub>1</sub> 2 <sub>9</sub>	5855(0.6)		
2 <sub>6</sub> 3 <sub>1</sub>	4646(0.1)	1 <sub>1</sub> 2 <sub>10</sub>	6346(−0.4)		
2 <sub>1</sub> 3 <sub>2</sub>	1511(−0.1)	1 <sub>2</sub> 2 <sub>1</sub>	3110(0.5)		
2 <sub>3</sub> 3 <sub>2</sub>	2931(−0.8)	1 <sub>3</sub> 3 <sub>1</sub>	1719(1.5)		

In an effort to record a sufficient range of emission data to determine all of the vibrational frequencies and their anharmonicities, SVL spectra were obtained by laser excitation of the  $0_0^0$ ,  $3_0^1$ ,  $2_0^1$ , and  $1_0^1$  bands of HGeCl and the  $0_0^0$ ,  $3_0^1$ ,  $2_0^1$ ,  $1_0^1$ , and  $1_0^1 2_0^1$  bands of DGeCl. Pumping the  $^pQ_1$  branch of each band guaranteed that the emission down to each ground state vibrational level consisted of a single  $K'_a=0-K''_a=1$  subband, yielding the simplest, most intense emission spectra. There was no evidence of collisional relaxation in the excited state, so the spectra were readily interpretable as originating from a single upper state level. Some of the observed spectra obtained by excitation of the higher energy LIF bands showed spurious features with an interval of approximately  $400\text{ cm}^{-1}$  which we attributed to laser excited emission from GeCl ( $A\ ^2\Sigma^+-X\ ^2\Pi_r$ ) also produced in the discharge jet.<sup>23</sup>

Examples of the observed spectra are shown in Fig. 1. Due to the approximately  $20^\circ$  increase in the bond angle on electronic excitation, the spectra are dominated by long progressions involving  $\nu_2''$ , particularly for the  $0^0$  and  $2^1$  upper state levels. These data gave a HGeCl bending fundamental value of  $720.9\text{ cm}^{-1}$  and  $\omega_2^0=723.61(16)\text{ cm}^{-1}$ , with the latter substantially at variance with the  $689.17\text{ cm}^{-1}$  value reported from low-resolution chemiluminescence data.<sup>12</sup> Excitation of the  $3_0^1$  band of HGeCl shows a strong emission transition down to  $3_1$  and a weaker feature which can be assigned as the  $3_2^1$  band, which allowed the determination of

the  $x_{33}$  anharmonicity constant. Unfortunately, the  $3_0^1$  band emission spectrum of DGeCl did not show a band which could be unambiguously assigned as emission down to  $3_2$ , so the anharmonicity constant was not determinable. Excitation of the  $1_0^1$  bands of HGeCl and DGeCl reveals new transitions not present in the emission spectra of bands not involving  $\nu_1'$ . These new bands were readily assignable as transitions down to ground state levels involving  $\nu_1''$ , the Ge–H or Ge–D stretching vibrations. The  $1_2$  level was observed in both isotopomers, so that the  $x_{11}$  anharmonicity constant, which is of substantial magnitude, was determinable.

Table I summarizes the measured ground state vibrational energy levels of HGeCl and DGeCl. In each case, the reported values are taken from those bands in the emission spectra which were as free of overlap as possible and had the highest signal-to-noise ratio. A total of 26 levels were measured for HGeCl and 42 for DGeCl and these were all found to fit the usual anharmonic expression

$$G_0(\nu) = \sum_{i=1}^3 \omega_i^0 \nu_i + \sum_{i=1}^3 \sum_{j \geq 1}^3 x_{ij}^0 \nu_i \nu_j \quad (1)$$

to within the estimated experimental accuracy ( $\pm 2\text{ cm}^{-1}$ ). The resulting vibrational constants are reported in Table II and the harmonic frequencies ( $\omega_i$ ), determined using the relationship<sup>24</sup>

TABLE II. The ground state vibrational constants of HGeCl and DGeCl (in  $\text{cm}^{-1}$ ).

	HGeCl	DGeCl
$\omega_1^0$	1864.47(80) <sup>a</sup>	1337.51(93)
$\omega_2^0$	723.61(16)	522.27(12)
$\omega_3^0$	401.60(64)	400.23(45)
$x_{11}^0$	-34.24(42)	-17.57(52)
$x_{22}^0$	-2.273(27)	-1.164(13)
$x_{33}^0$	-2.14(32)	...
$x_{12}^0$	-16.46(12)	-8.00(8)
$x_{13}^0$	...	-2.63(51)
$x_{23}^0$	-2.294(96)	-1.691(87)

<sup>a</sup>Standard errors of  $1\sigma$  are given in parentheses.

$$\omega_i = \omega_i^0 - x_{ii}^0 - \sum_{j \neq i} \frac{1}{2} x_{ij}^0, \quad (2)$$

are given in Table III.

The ground state harmonic force field of monochlorogermylene was obtained by fitting the derived harmonic frequencies of HGeCl and DGeCl using the previously derived  $r_0$  structure.<sup>14</sup> In the least squares analysis, the harmonic frequencies were weighted equally. The normal coordinate analysis was set up using internal coordinates and the force constants were refined using the ASYM20PC program of Hedberg and Mills.<sup>25</sup> As centrifugal distortion constants were not available for inclusion in the data set, only five of the six force constants were determinable and  $f_{12}$  was constrained to a value of 0.0 in the final analysis. The force constants reproduced all of the harmonic frequencies very satisfactorily, well within their estimated errors, as shown in Table III.

Using the derived force field, we were able to determine average ( $r_z$ ) and estimated equilibrium ( $r_e^z$ ) structures for HGeCl in the following fashion. First, the harmonic contributions to the vibration-rotation constants ( $\alpha$ ) obtained from the normal coordinate analysis were added to the previously determined  $\nu''=0$  rotational constants<sup>14</sup> ( $B_0$ ) of HGeCl and DGeCl to obtain the average ( $B_z$ ) rotational constants. The structural parameters of HGeCl were then refined by fitting the six average rotational constants. As in previous work, the Ge-H bond length and the bond angle were found to be

highly correlated, so we constrained the bond angle at a value of  $93.9^\circ$ . This bond angle was obtained through a series of *ab initio* optimizations of the ground state geometry using the GAUSSIAN 03 program.<sup>26</sup> Calculations using both density functional theory (B3LYP) (Refs. 27 and 28) and coupled cluster singles and doubles with triple excitations included perturbatively theory [CCSD(T)] with Dunning's correlation consistent triple-zeta basis sets augmented by diffuse functions<sup>29</sup> (aug-cc-pVTZ) gave identical  $93.9^\circ$  bond angles. The *ab initio* structures are summarized in Table IV—note that the present bond angle prediction is  $0.4^\circ$  smaller than the MRSDCI value<sup>17</sup> used in our previous  $r_0$  structure.<sup>14</sup> In the present work, allowance was made for a  $0.0036 \text{ \AA}$  Laurie contraction ( $\delta r_z$ ) of the Ge-H bond upon deuteration, determined using<sup>30-32</sup>

$$\delta r_z = \frac{3}{2} a \delta \langle u^2 \rangle - \delta K, \quad (3)$$

where the change ( $\delta$ ) in the root-mean-square amplitude ( $\langle u^2 \rangle$ ) on deuteration and the change in the perpendicular amplitude correction ( $K$ ) were obtained from the force field. The Morse anharmonicity parameter ( $a$ ) (Ref. 33) was obtained from the equation

$$a = \frac{2}{3} \pi \omega_e \sqrt{\frac{c\mu}{2hB_e^3}} \left( \alpha_e + \frac{6B_e^2}{\omega_e} \right), \quad (4)$$

where the  $\omega_e$  and  $B_e$  values are the ground state spectroscopic constants of the GeH diatomic molecule.<sup>34</sup> From the  $r_z$  structure, the ground state equilibrium bond lengths ( $r_e^z$ ) can be estimated by using the data from the appropriate diatomic molecules [GeH and GeCl (Ref. 23)] and the results of the normal coordinate analysis. The bond lengths are given by the relationship used in microwave spectroscopy,<sup>30-32</sup>

$$r_e^z = r_z - \frac{3}{2} a \langle u^2 \rangle + K, \quad (5)$$

where  $a$  is defined in Eq. (4) and the other quantities are defined above. The results are summarized in Table IV.

TABLE III. The ground state harmonic force field of HGeCl.

Parameter	HGeCl			DGeCl		
	Obs.	Calc.	% error	Obs.	Calc.	% error
$\omega_1$ ( $\text{cm}^{-1}$ )	1906.9(1.0) <sup>a</sup>	1906.8	-0.005	1360.4(1.0)	1360.6	0.01
$\omega_2$ ( $\text{cm}^{-1}$ )	735.3(1.0)	735.0	-0.04	528.3(1.0)	528.8	0.09
$\omega_3$ ( $\text{cm}^{-1}$ )	404.9(1.0)	404.3	-0.15	402.4(1.0)	403.0	0.15
$f_{11}$ ( $\text{aJ \AA}^{-2}$ )			2.1218(55) <sup>b</sup>			
$f_{22}$ ( $\text{aJ}$ )			0.7859(32)			
$f_{33}$ ( $\text{aJ \AA}^{-2}$ )			2.573(103)			
$f_{13}$ ( $\text{aJ \AA}^{-2}$ )			0.68(15)			
$f_{23}$ ( $\text{aJ \AA}^{-1}$ )			0.219(60)			

<sup>a</sup>Estimated uncertainties used in the force field refinement are given in parentheses.<sup>b</sup>Standard errors of  $1\sigma$  are given in parentheses. The internal coordinates are  $R_1 = \Delta r(\text{H-Ge})$ ,  $R_2 = \Delta \theta(\text{H-Ge-Cl})$ , and  $R_3 = \Delta r(\text{Ge-Cl})$ .



TABLE IV. Comparison of the experimental and *ab initio* structural parameters and harmonic vibrational frequencies for the ground state of monochlorogermylene.

	Experiment			<i>Ab initio</i>		
	$r_0$	$r_z$	$r_e^z$	MRSDCI <sup>a</sup>	B3LYP <sup>b</sup>	CCSD(T) <sup>b</sup>
$r$ (GeCl) (Å)	2.171(2) <sup>c</sup>	2.174(2)	2.171(2)	2.201	2.214	2.186
$r$ (GeH) (Å)	1.592(1)	1.599(1)	1.586(1)	1.589	1.603	1.582
$\theta$ (HGeCl) (°)	94.3	93.9	93.9	94.3	93.9	93.9
$\omega_1$ (cm <sup>-1</sup> )		1906.9/1360.4 <sup>d</sup>		...	1865/1326	1955/1392
$\omega_2$ (cm <sup>-1</sup> )		735.3/528.3		...	720/517	743/543
$\omega_3$ (cm <sup>-1</sup> )		404.9/402.4		...	380/380	402/402

<sup>a</sup>From Ref. 17.<sup>b</sup>This work, using an aug-cc-pVTZ basis set.<sup>c</sup>From Ref. 14.<sup>d</sup>HGeCl/DGeCl harmonic frequencies.

#### IV. DISCUSSION

We have used *ab initio* Franck-Condon simulations of the emission spectra as a test of the validity of the analysis. The simulation program, originally developed by Yang *et al.*<sup>35</sup> and locally modified for the calculation of SVL emission spectra, requires input of the molecular structures, vibrational frequencies, and mass-weighted Cartesian displacement coordinates from the force fields of both the ground and excited states. Franck-Condon factors are then calculated in the harmonic approximation using the exact recursion relations of Doktorov *et al.*<sup>36</sup> As discussed in our previous work,<sup>14</sup> the lack of sufficient vibrational structure and irregularities in the LIF spectrum made it impossible to determine the excited state harmonic frequencies and perform a normal coordinate analysis, so for the present purposes we have relied on *ab initio* calculations to obtain the necessary data. For both states, the geometry was optimized and the vibrational frequencies and normal coordinates were calculated using

density functional theory (B3LYP/aug-cc-pVTZ). Although theory reproduced the ground state frequencies quite satisfactorily, the calculated excited state Ge-H stretching frequency was substantially larger than the experimental<sup>14</sup> one (1765 cm<sup>-1</sup> versus 1263 cm<sup>-1</sup>), suggesting that the potential is very anharmonic along the  $Q_1$  normal coordinate. Fortunately,  $\nu'_1$  is not active in the experimental  $0_0^0$  band spectrum that we attempted to simulate, so this anomaly does not affect the Franck-Condon calculations.

The Franck-Condon simulation of the emission spectrum after excitation of the zero point of HGeCl is compared to the observed spectrum in Fig. 2. The simulation reproduces the major bending progression very well. The observed much weaker  $3_1 2_n$  progression is also evident in the simulation, although the calculation predicts it to be somewhat stronger than that in the experiment. Similar anomalies are found in simulations of the emission spectra of the monohalosilylenes<sup>8-10</sup> and can be attributed to the large anhar-

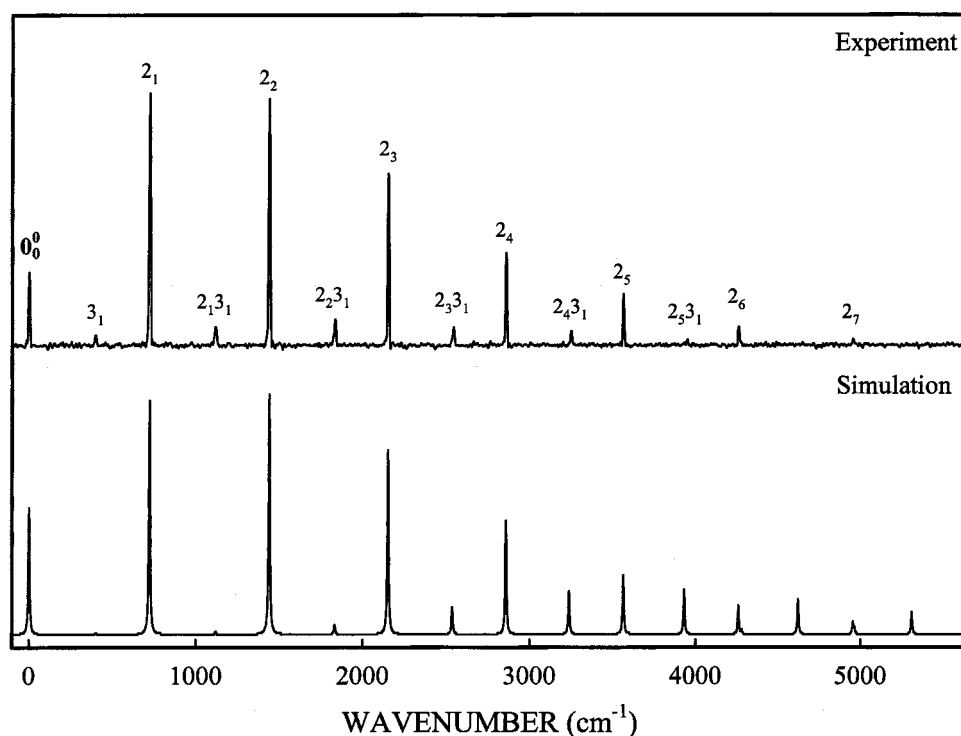


FIG. 2. Top: the emission spectrum obtained by single vibronic level excitation of the  $0_0^0$  band of HGeCl, with vibrational assignments. Bottom: the Franck-Condon simulation of the emission spectrum in the harmonic approximation, obtained using *ab initio* (B3LYP/aug-cc-pVTZ) geometries and force fields for the combining states.

nicities in the excited state and the use of the purely harmonic approximation in the calculations. Despite these deficiencies, it is apparent that *ab initio* theory predicts the intensity distribution in the emission spectra with reasonable fidelity and supports the assignments made in our analysis of the experimental data.

In this work we have obtained the first complete set of ground state vibrational frequencies of HGeCl and DGeCl. The validity of the derived harmonic frequencies was tested by applying the Redlich-Teller product rule<sup>37</sup> for *HXY* molecules of  $C_s$  symmetry:

$$\frac{\omega_1^* \omega_2^* \omega_3^*}{\omega_1 \omega_2 \omega_3} = \sqrt{\left(\frac{C}{C^*}\right) \left(\frac{M^*}{M}\right)^2 \left(\frac{m_H}{m_D}\right)^2}. \quad (6)$$

The experimental harmonic ratio (0.509) is in reasonable agreement with the theoretical ratio (0.511), lending credibility to the derived frequencies. As expected, deuteration substantially decreases  $\omega_1$  and  $\omega_2$ , while  $\omega_3$  is essentially unaffected. Our *ab initio* predictions of the harmonic frequencies (Table IV) are also in excellent accord with the experimental values. The HGeCl/DGeCl stretching frequencies (1906.9/1360.4 and 404.9/402.4  $\text{cm}^{-1}$ ) and diagonal anharmonicities ( $|x_{11}|=34.24/17.57$  and  $|x_{33}|=2.14$ ) are almost identical with the harmonic frequencies ( $\omega_e$ ) and anharmonicities ( $\omega_e x_e$ ) of the corresponding diatomic molecules:<sup>23,34,38</sup> GeH=1900.382 and 33.502  $\text{cm}^{-1}$ , GeD=1353.317 and 16.759  $\text{cm}^{-1}$ , and GeCl=405.2 and 1.26  $\text{cm}^{-1}$ . It is apparent that the stretching potential curves must be very similar for HGeCl and its diatomic fragments.

Finally, we can compare the structural parameters of HGeCl to those of similar molecules. The  $r_e$  Ge–H bond length of 1.586(1) Å is very close to the germanium hydride ground state equilibrium bond length<sup>34</sup> of 1.5872 Å and very similar to experimental<sup>39</sup> (1.588 Å) and *ab initio*/nonrigid bender<sup>40</sup> (1.591 Å) estimates of the equilibrium bond length of ground state GeH<sub>2</sub>. The Ge–Cl bond length of 2.171 Å is not in particularly good agreement with the experimental<sup>23</sup> GeCl value of 2.144 Å, but the latter was calculated based on a previously published<sup>41</sup> value of  $\alpha_e$ , which may be in error. In this regard we note that our *ab initio* CCSD(T)/aug-cc-pVTZ prediction of the bond length of GeCl of 2.178 Å is in very good agreement with the experimentally derived HGeCl value. The *ab initio* bond angle for HGeCl (93.9°) used in the present work is only slightly larger than the experimental<sup>39</sup> (91.22°) and theoretical<sup>40</sup> (91.4°) estimates for GeH<sub>2</sub> and the trend follows that of HSiCl, whose equilibrium bond angle<sup>10</sup> is 3.0° larger than that of SiH<sub>2</sub>. All lines of evidence suggest that the derived HGeCl geometric parameters are reasonable and follow expectations based on the molecular structures of the corresponding silylenes.<sup>10</sup>

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