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Single vibronic level emission spectroscopic studies of the ground state energy levels and molecular structures of jet-cooled HGeBr, DGeBr, HGeI, and DGeI

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Single vibronic level dispersed fluorescence spectra of jet-cooled HGeBr, DGeBr, HGeI, and DGeI have been obtained by laser excitation of selected bands of the $\tilde{A}^1A''-\tilde{X}^1A'$ electronic transition. The measured ground state vibrational intervals were assigned and fitted to anharmonicity expressions, which allowed the harmonic frequencies to be determined for both isotopomers. In some cases, lack of a suitable range of emission data necessitated that some of the anharmonicity constants and vibrational frequencies be estimated from those of HGeCl/DGeCl and the corresponding silylenes (HSiX). Harmonic force fields were obtained for both molecules, although only four of the six force constants could be determined. The ground state effective rotational constants and force field data were combined to calculate average (r_e) and approximate equilibrium (r_e^z) structures. For HGeBr $r_e^z(\text{GeH})=1.593(9)$ Å, $r_e^z(\text{GeBr})=2.325(21)$ Å, and the bond angle was fixed at our CCSD(T)/aug-cc-pVTZ *ab initio* value of 93.6°. For HGeI we obtained $r_e^z(\text{GeH})=1.589(1)$ Å, $r_e^z(\text{GeI})=2.525(5)$ Å, and bond angle=93.2°. Franck-Condon simulations of the emission spectra using *ab initio* Cartesian displacement coordinates reproduce the observed intensity distributions satisfactorily. The trends in structural parameters in the halogermynes and halosilylenes can be readily understood based on the electronegativity of the halogen substituent.
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I. INTRODUCTION

The germynes ($XY\text{Ge}$) are thought to play an important role as intermediates in semiconductor growth processes for the production of germanium thin films, so the development of spectroscopic methods for detecting and quantifying them in the gas phase has many practical applications. The study of these reactive molecules is also of fundamental interest, as the carbenes, silylenes, and germynes are involved in a wide variety of chemical reactions and their structures, chemical kinetics, energetics, and physical properties have been extensively studied in the last few decades.

For several years, we have been engaged in studies of the electronic spectra of the carbenes and their heavier analogs in our laboratory. The monohalogermynes have been of particular interest, as very little was known about their spectra prior to our work. HGeBr was first reported by Isabel and Gillory,¹ as a product of the photolysis of H_3GeBr in an argon matrix. The authors observed all of the ground state vibrational fundamentals of HGeBr and DGeBr by infrared absorption spectroscopy and determined a simple valence force field. Ito *et al.*² studied the laser-induced fluorescence spectra of HGeBr produced by the reaction of germane

(GeH_4) with bromine atoms and were able to resolve the K structure in the low-lying bands, which yielded approximate values for $A-\bar{B}$ and D_K for the combining states. By transferring the Ge–H and Ge–Br bond lengths from other molecules, the authors derived ground and excited state bond angles from their data. No experimental data were available for HGeI or DGeI at the beginning of our studies.

The monohalogermynes have been the subject of a very small number of *ab initio* studies.^{3–5} For spectroscopic purposes, the most useful are the multireference singles and doubles configuration interaction (MRSDCI) calculations of Benavides-Garcia and Balasubramaniam³ which predicted the geometries, term values, and dipole moments of the three lowest lying electronic states of HGeX ($X=\text{Cl}, \text{Br}, \text{I}$).

In 1998 we reported the laser-induced fluorescence (LIF) spectra^{6,7} of jet-cooled HGeCl, HGeBr, and HGeI, which allowed us to refine our understanding of the ground and first excited singlet states of these species. In each case, we were able to obtain rotational constants of modest accuracy and molecular structures were derived from these constants. Due to the near coincidence of the a axis with the Ge– X bond and correlations between the bond angle and Ge–H bond length, we were forced to constrain the bond angle to an *ab initio* value in the structure determinations. These studies did not give much information about the ground state vibra-

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tional energy levels, although a few hot bands were detected. Recently, we have reported⁸ single vibronic level emission spectra of jet-cooled HGeCl and DGeCl, which allowed us to determine the ground state harmonic force field and obtain a good estimate of the equilibrium molecular structure. In the present work we report similar studies of HGeBr and HGeI and their deuterated isotopomers.

II. EXPERIMENT

The monohalogenmylenes (HGeBr, DGeBr, HGeI, or DGeI) were produced by seeding the vapor of the appropriate cooled (from -40 °C up to room temperature depending on the strength of the signal) monohalogermane (H_3GeX or D_3GeX ; $X=\text{Br}$ or I) 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,^{9,10} produced a variety of products, including substantial quantities of the germanylenes (HGeX or DGeX) and diatomic GeX species. 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) or a low-resolution (4 cm^{-1}) optical parametric oscillator (GWU VisIR2-ULD) 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, depending 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.

Bromogermane (H_3GeBr) and iodogermane (H_3GeI) were synthesized by condensing a slight molar excess of hydrogen bromide or hydrogen iodide onto degassed phenylgermane at liquid nitrogen temperature.^{6,7} 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 the halogermane, benzene, and small quantities of 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. The deuterated halogermanes (D_3GeBr and D_3GeI) were prepared in a similar fashion using phenylgermane- d_3 and DBr or DI. Phenylgermane and phenylgermane- d_3 were prepared by the lithium aluminum hydride (or deuteride) reduction of phenyltrichlorogermane (Gelest).¹¹ The hydrogen bromide (Matheson) and deuterium bromide (Cambridge Isotope Labs) were obtained commercially. Hydrogen iodide and deuterium iodide were synthesized by the reaction of H_2O or D_2O with a mixture of red phosphorus and iodine.¹²

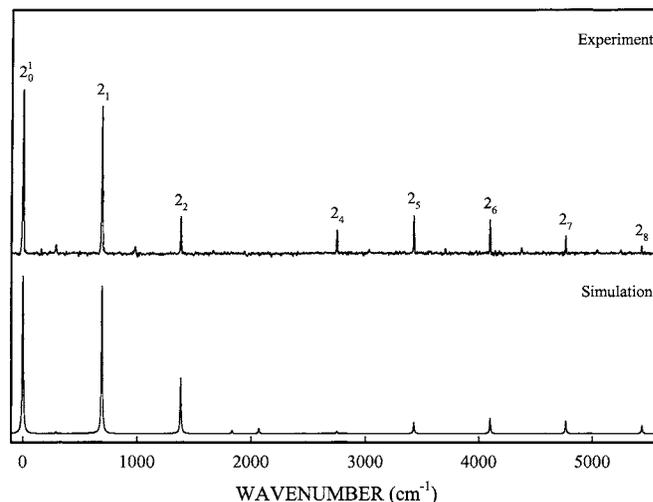


FIG. 1. An example of a dispersed emission spectrum of HGeBr. The $\tilde{A}-\tilde{X}$ vibronic transition pumped by the excitation laser is given in bold of the experimental trace and the lower state vibrational level assignments are indicated. The wave number scale is displacement from the excitation laser, giving a direct measure of the ground state vibrational energy. The lower trace is a 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 two combining states.

III. RESULTS AND ANALYSIS

Both HGeBr and HGeI are bent molecules of C_s symmetry with three a' vibrational modes conventionally labeled as ν_1 (Ge–H stretch), ν_2 (bend), and ν_3 (Ge–X stretch). The $\tilde{A}^1A''-\tilde{X}^1A'$ electronic transition involves electron promotion from a doubly occupied, nonbonding (σ_{nb}) lone pair orbital on germanium to an out-of-plane germanium p orbital and results in absorption bands following c -type selection rules. Although the molecules of interest have several naturally abundant isotopomers, 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 isotopic species. Although it makes little difference in the final analysis, we prefer this approximation over the use of atomic weights, since we usually excite a Q -branch maximum in the LIF spectrum which preferentially excites the predominant isotopomer to some extent.

A. HGeBr and DGeBr

We were able to obtain quite extensive SVL emission spectra of the monobromogermanylenes, following excitation of the 0_0^0 , 2_0^1 , 3_0^1 , and 1_0^1 bands of HGeBr and the 0_0^0 , 2_0^1 , 1_0^1 , $1_0^1 3_0^1$, and $2_0^1 3_0^1$ bands of DGeBr. Interferences from GeBr $A-X$ emission¹³ excited simultaneously by the laser were somewhat of a problem, especially for the higher energy LIF bands. As a typical example of the emission spectra, we show in Fig. 1 the spectrum of HGeBr obtained by laser excitation of the 2_0^1 band. The first bending level of the excited state emits primarily down to the bending levels in the ground state, although there is a node at 2_3 , indicative of a mismatch in the phase of the vibrational wave functions which causes a minimum in the Franck-Condon factors. In a similar fashion, excitation of the 3_0^1 band leads to strong

emission down to 3_1 and combinations of ν_2'' and ν_3'' . The levels of the Ge–H stretching mode (ν_1'') are first evident on excitation of the 1_0^0 band. The gas phase fundamentals of 1835, 694, and 291 cm^{-1} are in accord with the matrix values¹ of 1858, 701, and 283 cm^{-1} , respectively.

The emission spectra of DGeBr were generally similar to those of HGeBr, with prominent bending progressions observed after 0_0^0 and 2_0^1 band excitations and activity in ν_1'' and ν_2'' after 1_0^1 excitation. Unfortunately, the 1_2 level could not be observed in this case so the x_{11} anharmonicity constant was not directly determinable. The 3_0^1 band proved to be too weak to obtain emission spectra, although pumping other levels involving ν_3' gave some information on the Ge–Br stretching levels in the ground state. Our gas phase values for the fundamentals (1322 , 498 , and 290 cm^{-1}) are in excellent agreement with the previous matrix values¹ of 1336 , 502 , and 281 cm^{-1} , respectively.

B. HGeI and DGeI

Obtaining good SVL emission spectra of HGeI and DGeI proved to be much more difficult, because of the limited number of LIF bands observed in the $\tilde{A}-\tilde{X}$ spectrum⁷ and strong interferences from the $A-X$ bands of GeI which occur in the same region.¹⁴ Excitation of the 0_0^0 bands of HGeI and DGeI gave strong, well-resolved emission spectra down to the ground state bending levels, as illustrated by the DGeI spectrum in Fig. 2. The $1_1 2_n$ levels were observed in the 1_0^1 band emission spectrum of HGeI, although the 1_2 level was not found, despite considerable effort. The 3_0^1 band of DGeI was sufficiently intense and free of overlap to obtain members of the $3_1 2_n$ progression. Attempts to pump other bands of HGeI and DGeI met with limited success, as they were severely contaminated by GeI emission.

C. Data analysis

The measured ground state vibrational energy levels of HGeBr, DGeBr, HGeI, and DGeI are summarized in Table I. 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 37 levels were measured for HGeBr and 45 for DGeBr, and these were all found to fit the usual anharmonic expression

$$G_0(v) = \sum_{i=1}^3 \omega_i^0 v_i + \sum_{i=1}^3 \sum_{j \geq i}^3 x_{ij}^0 v_i v_j, \quad (1)$$

to within the estimated experimental accuracy ($\pm 2\text{ cm}^{-1}$). The vibrational frequencies and anharmonicities of HGeBr were determined without constraints, whereas x_{11}^0 of DGeBr was transferred from the experimentally determined value for DGeCl.⁸ Examination of the experimentally determined anharmonicity constants for the HSiX and DSiX molecules shows that they are remarkably consistent through the series, as they are for HGeCl and HGeBr. Consequently, transferring the constants from known germynes should lead to little error. In an analogous fashion the energy levels of HGeI and DGeI were fitted to Eq. (1), but many of the anharmonicity constants and some of the vibrational frequencies were

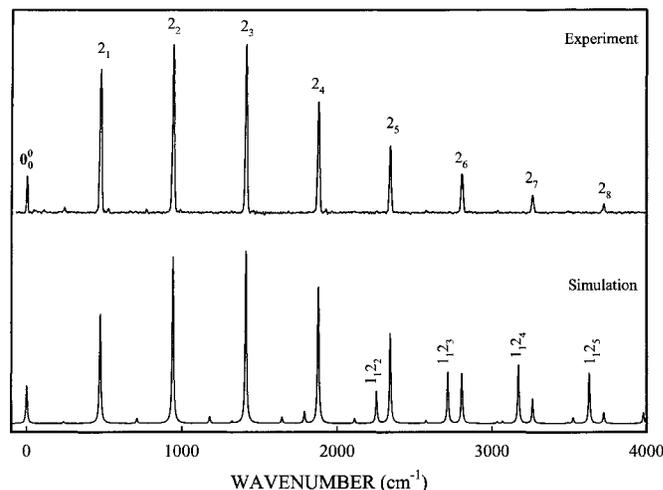


FIG. 2. An example of a dispersed emission spectrum of DGeI, obtained by single vibronic level excitation of the 0_0^0 band, with ground state vibrational assignments. The wave number scale is displacement from the excitation laser, giving a direct measure of the ground state vibrational energy. The lower trace is a 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 two combining states.

transferred or estimated from the HSiX and HGeCl species. The resulting constants are summarized in Table II. The harmonic frequencies (ω_i) were determined from the data in Table II using the relationship¹⁵

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

and are given in Table III.

With the harmonic frequencies of the hydrogen and deuterium isotopomers in hand, it is possible to obtain the ground state harmonic force fields of HGeBr and HGeI. In the latter case, the many assumptions made about the vibrational constants constrains the normal coordinate analysis to the determination of an approximate set of force constants. In each case, we have used the previously derived r_0 structure^{6,7} in the analysis and varied the force constants to minimize the sum of the squares of the deviations between the observed and calculated harmonic frequencies. The force constants in internal coordinates (f_{ij}) were refined using the ASYM20PC program of Hedberg and Mills.¹⁶ The lack of centrifugal distortion constants or other data to help with the refinement limited the number of determinable force constants, so that f_{12} and f_{13} were constrained to 0.0 for both molecules. The resulting refined force constants, which reproduce the harmonic frequencies very satisfactorily to within a few tenths of cm^{-1} in each case, are presented in Table III.

The final aspect of the data analysis was to attempt to obtain reliable estimates of the equilibrium structures of HGeBr and HGeI in the ground state. The first issue was to decide how to treat the bond angle, which, as previously mentioned, is highly correlated with the Ge–H bond length. In previous work, we had fixed the bond angle at the *ab initio* MRSDCI value of Benavides-Garcia and Balasubramaniam,³ but in this work we elected to do our

TABLE I. Vibrational assignments, ground state vibrational energies, and residuals (in cm^{-1}) from the single vibronic level emission spectra of HGeBr, DGeBr, HGeI, and DGeI.

HGeBr		DGeBr		HGeI		DGeI	
Assignment	Energy	Assignment	Energy	Assignment	Energy	Assignment	Energy
1 ₁	1835(0.4)	1 ₁	1322(0.0)	1 ₁	1839(0.5)	2 ₁	473(0.7)
1 ₂	3601(-0.1)	2 ₁	498(-0.8)	2 ₁	661(1.1)	2 ₂	943(0.1)
2 ₁	694(-0.3)	2 ₂	994(-0.5)	2 ₂	1316(0.8)	2 ₃	1411(0.1)
2 ₂	1384(-0.5)	2 ₃	1489(-0.3)	2 ₃	1965(-0.8)	2 ₄	1877(-0.7)
2 ₃	2069(-0.3)	2 ₄	1982(0.2)	2 ₄	2613(0.3)	2 ₅	2341(-1.0)
2 ₄	2751(0.2)	2 ₅	2471(0.1)	2 ₅	3255(-0.6)	2 ₆	2805(0.2)
2 ₅	3428(0.2)	2 ₆	2959(0.2)	2 ₆	3895(0.2)	2 ₇	3265(-0.1)
2 ₆	4101(1.1)	2 ₇	3445(-0.2)	1 ₁ 2 ₁	2483(-0.2)	2 ₈	3724(0.8)
2 ₇	4768(0.5)	2 ₈	3929(0.2)	1 ₁ 2 ₂	3124(-0.5)	2 ₉	4180(-0.2)
2 ₈	5429(-1.4)	2 ₉	4410(-0.3)	1 ₁ 2 ₃	3761(-0.0)	2 ₁₀	4635(0.1)
3 ₁	291(0.3)	2 ₁₀	4889(-0.3)	1 ₁ 2 ₄	4394(-0.1)	3 ₁	239(-0.1)
3 ₂	579(-0.6)	3 ₁	290(-0.4)	1 ₁ 2 ₅	5023(0.4)	2 ₁ 3 ₁	710(-0.5)
1 ₁ 2 ₁	2514(-0.3)	1 ₁ 2 ₁	1813(-0.5)			2 ₂ 3 ₁	1178(-0.6)
1 ₁ 2 ₂	3189(-0.5)	1 ₁ 2 ₂	2303(-0.6)			2 ₃ 3 ₁	1646(0.5)
1 ₁ 2 ₃	3860(0.2)	1 ₁ 2 ₃	2790(-0.1)			2 ₄ 3 ₁	2110(0.7)
1 ₁ 2 ₄	4527(0.4)	1 ₁ 2 ₄	3275(0.1)			2 ₅ 3 ₁	2573(0.6)
1 ₁ 2 ₅	5188(-0.1)	1 ₁ 2 ₅	3758(-0.2)			2 ₆ 3 ₁	3035(1.2)
1 ₁ 2 ₆	5846(0.2)	1 ₁ 2 ₆	4239(-0.2)			2 ₇ 3 ₁	3491(-1.8)
1 ₁ 2 ₇	6499(0.1)	1 ₁ 2 ₇	4718(0.4)				
1 ₂ 2 ₂	4927(0.6)	1 ₁ 2 ₈	5194(-0.5)				
2 ₁ 3 ₁	983(-0.4)	1 ₁ 2 ₉	5670(1.2)				
2 ₂ 3 ₁	1671(-0.4)	1 ₁ 2 ₁₀	6142(1.4)				
2 ₃ 3 ₁	2354(-0.3)	1 ₁ 2 ₁₁	6610(-0.9)				
2 ₄ 3 ₁	3034(0.1)	1 ₁ 3 ₁	1614(0.1)				
2 ₅ 3 ₁	3709(0.2)	2 ₁ 3 ₁	787(-0.6)				
2 ₆ 3 ₁	4379(-0.1)	2 ₂ 3 ₁	1283(0.4)				
2 ₇ 3 ₁	5045(0.7)	2 ₃ 3 ₁	1775(0.0)				
2 ₁ 3 ₂	1270(0.3)	2 ₄ 3 ₁	2266(0.2)				
2 ₂ 3 ₂	1956(0.4)	2 ₅ 3 ₁	2754(0.6)				
2 ₃ 3 ₂	2638(0.6)	2 ₆ 3 ₁	3240(0.1)				
2 ₄ 3 ₂	3315(-0.1)	2 ₇ 3 ₁	3724(0.3)				
2 ₅ 3 ₂	3987(-0.5)	2 ₈ 3 ₁	4205(-0.8)				
1 ₁ 3 ₁	2126(0.8)	2 ₉ 3 ₁	4686(0.3)				
1 ₁ 2 ₁ 3 ₁	2803(-0.4)	2 ₂ 3 ₂	1566(-2.3)				
1 ₁ 2 ₂ 3 ₁	3477(0.0)	2 ₃ 3 ₂	2060(0.9)				
1 ₁ 2 ₃ 3 ₁	4145(-0.1)	2 ₄ 3 ₂	2549(1.0)				
1 ₁ 2 ₄ 3 ₁	4810(-0.4)	2 ₅ 3 ₂	3036(1.2)				
		2 ₆ 3 ₂	3518(-0.8)				
		1 ₁ 2 ₁ 3 ₁	2104(0.5)				
		1 ₁ 2 ₂ 3 ₁	2592(0.9)				
		1 ₁ 2 ₃ 3 ₁	3078(1.1)				
		1 ₁ 2 ₄ 3 ₁	3560(-0.6)				
		1 ₁ 2 ₅ 3 ₁	4040(-1.2)				
		1 ₁ 2 ₆ 3 ₁	4521(0.3)				
		1 ₁ 2 ₇ 3 ₁	4996(-1.1)				

own theoretical predictions using the GAUSSIAN 03 suite of programs.¹⁷ Calculations using both density functional theory (B3LYP) (Refs. 18 and 19) and coupled cluster singles and doubles with triple excitations included perturbatively [CCSD(T)] theory with Dunning's correlation consistent triple-zeta basis sets augmented by diffuse functions²⁰ (aug-cc-pVTZ) consistently gave bond angles of 0.3° – 0.5° smaller than the MRSDCI predictions, as shown in Table IV. We chose to use the CCSD(T)/aug-cc-pVTZ bond angles in

all subsequent structure refinements.

Two kinds of structures were determined. First, the average (r_2) structures were derived by adding the harmonic contributions to the vibration-rotation constants (α) obtained from the normal coordinate analysis to the previously determined $v''=0$ rotational constants^{6,7} (B_0) to obtain the average (B_2) rotational constants. The structural parameters were then refined by fitting the six average rotational constants, with the bond angles constrained to our *ab initio* values. The

TABLE II. The ground state vibrational constants of HGeBr, DGeBr, HGeI, and DGeI (in cm^{-1}).

	HGeBr	DGeBr	HGeI	DGeI
ω_1^0	1868.20(60) ^a	1339.31(44)	1872.36(53)	1341.5
ω_2^0	696.50(11)	499.60(11)	661.54(26)	473.23(16)
ω_3^0	291.81(47)	291.34(64)	240.0	239.86(54)
x_{11}^0	-33.82(30)	-16.9	-34.0	-18.0
x_{22}^0	-2.208(16)	-1.067(12)	-2.074(52)	-0.971(19)
x_{33}^0	-1.10(23)	-0.71(32)	-0.5	-0.5
x_{12}^0	-14.68(8)	-7.09(7)	-14.3	-7.0
x_{13}^0	0.47(40)	0.69(49)	0.0	0.0
x_{23}^0	-1.901(55)	-1.648(69)	-2.0	-1.67(13)

^aStandard errors of 1σ are given in parentheses. Values without errors are transferred from similar molecules and fixed in the least squares analysis.

average structure differs from the equilibrium structure solely because of the anharmonicity of the vibrations. In the structure determination, allowance was made for a 0.0035 Å Laurie contraction (δr_z) of the Ge–H bond upon deuteration, determined using^{21–23}

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

where the change (δ) 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. 24) 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 ω_e and B_e values are the ground state spectroscopic constants of the GeH diatomic molecule.²⁵

The ground state equilibrium bond lengths (r_e^z) can be estimated from the r_z structure using anharmonicity data from the appropriate diatomic molecules^{14,25,26} (GeI, GeH, and GeBr) and the results of the normal coordinate analysis. The bond lengths are given by the relationship most often used in the analysis of microwave data,^{21–23}

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

where a is defined in Eq. (4) and the other quantities are defined above. The results are summarized in Table IV. All the evidence suggests that r_e^z structures derived in this fashion are good approximations to the equilibrium structure. For example, direct comparisons of the r_e and r_e^z structures of HSiF show excellent agreement,²⁷ as do the experimentally derived r_e^z structure of HSiCl and the best estimated r_e structure, obtained from experimental B_0 constants and *ab initio* rotation-vibration (α) parameters.^{28,29}

IV. DISCUSSION

In this work we have obtained SVL emission spectra from the \tilde{A}^1A'' electronic states of HGeBr, DGeBr, HGeI, and DGeI and used the data to refine the ground state harmonic force fields and molecular structures. We have used Franck-Condon simulations of the emission spectra as a check on the validity of the assignments. Ideally, these would be generated from the force fields of the ground and excited states, as we have done previously for the HSiX molecules,²⁸ but insufficient data were available from the LIF spectra of the HGeX species to determine the excited state harmonic frequencies, so we have resorted to *ab initio* theory. Using the B3LYP/aug-cc-pVTZ method and basis set, we calculated the ground and excited state molecular structures, vibrational frequencies, and mass-weighted Cartesian displacement coordinates, which were used as input to the simulation program originally developed by Yang *et al.*³⁰ and locally modified for the calculation of SVL emission spectra. The Franck-Condon factors were calculated in the harmonic approximation and the appropriate frequency factors ($I \propto \nu^4$) were applied prior to convolution over a suitable line shape function with a full width half maximum of 10 cm^{-1} . Although theory reproduced the ν'_2 and ν'_3 frequencies quite well, ν'_1 was always substantially larger than experiment, suggesting that the true potential is very anharmonic along the Q_1 normal coordinate. This anomaly had little effect on the Franck-Condon simulations as the Ge–H stretch is inactive in most of the experimental emission spectra.

Figure 1 shows the Franck-Condon simulation for the 2_0^1 band emission spectrum of HGeBr and the comparison with

TABLE III. The ground state harmonic force fields of HGeBr and HGeI.

Parameter	HGeBr		DGeBr		HGeI		DGeI	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
ω_1 (cm^{-1})	1909.1(1.0) ^a	1909.0	1359.4(1.0)	1359.5	1913.6(1.0)	1913.7	1363.0(1.0)	1362.8
ω_2 (cm^{-1})	707.0(1.0)	706.8	505.0(1.0)	505.3	671.7(1.0)	671.7	478.5(1.0)	478.6
ω_3 (cm^{-1})	293.6(1.0)	293.2	292.5(1.0)	292.9	241.5(1.0)	241.4	241.2(1.0)	241.3
f_{11} ($\text{aJ } \text{Å}^{-2}$)		2.1349(9) ^{b,c}			2.1454(4)			
f_{22} (aJ)		0.7418(18)			0.6698(8)			
f_{33} ($\text{aJ } \text{Å}^{-2}$)		1.967(20)			1.676(38)			
f_{23} ($\text{aJ } \text{Å}^{-2}$)		0.154(60)			0.220(60)			

^aEstimated uncertainties used in the force field refinement are given in parentheses.

^bStandard errors of 1σ are given in parentheses.

^cThe internal coordinates are $R_1 = \Delta r(\text{H-Ge})$, $R_2 = \Delta \theta(\text{H-Ge-X})$, and $R_3 = \Delta r(\text{Ge-X})$.

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

	Expt.			<i>Ab initio</i>		
	r_0	r_z	r_e^z	MRSDCI ^a	B3LYP ^b	CCSD(T) ^b
HGeBr						
$r(\text{GeBr}) \text{ \AA}$	2.329(12) ^c	2.327(21)	2.325(21)	2.388	2.370	2.337
$r(\text{GeH}) \text{ \AA}$	1.598(6) ^c	1.606(9)	1.593(9)	1.572	1.600	1.582
$\theta(\text{HGeBr})^\circ$	93.9 ^c	93.6	93.6	93.9	93.5	93.6
$\omega_1(\text{cm}^{-1})^d$		1909.1/1359.4		...	1872/1334	1953/1391
$\omega_2(\text{cm}^{-1})^d$		707.0/505.0		...	693/495	713/510
$\omega_3(\text{cm}^{-1})^d$		293.6/292.5		...	275/275	293/292
HGeI						
$r(\text{GeI}) \text{ \AA}$	2.525(10) ^e	2.527(5)	2.525(5)	2.580	2.602	2.590
$r(\text{GeH}) \text{ \AA}$	1.593(15) ^e	1.601(1)	1.589(1)	1.575	1.599	1.580
$\theta(\text{HGeI})^\circ$	93.5 ^e	93.2	93.2	93.5	93.0	93.2
$\omega_1(\text{cm}^{-1})^f$		1913.6/1363.0		...	1889/1346	1947/1387
$\omega_2(\text{cm}^{-1})^f$		671.7/478.5		...	669/477	692/494
$\omega_3(\text{cm}^{-1})^f$		241.5/241.2		...	228/227	234/233

^aFrom Ref. 3.^bThis work, using an aug-cc-pVTZ basis set. A 6-311G** basis set was used for the HGeI calculations.^cFrom Ref. 6.^dHGeBr/DGeBr harmonic frequencies.^eFrom Ref. 7.^fHGeI/DGeI harmonic frequencies.

experiment. The simulation reproduces the overall pattern of activity in the bending mode quite satisfactorily, including the minimum in intensity for the 2_3 level, but underestimates the intensity of the higher members of the 2_n^1 progression. Since the experimental spectrum is uncorrected for the often substantial effects of the wavelength dependent sensitivity of the detection system and the lesser time-dependent variations in the discharge efficiency, the agreement is quite satisfactory. Figure 2 compares the experimental 0_0^0 band emission spectrum of DGeI and the simulation, which again reproduces the bending progression with high fidelity. In this case there is an extraneous $1_1^{0,2,0}$ progression predicted theoretically which is not observed experimentally. We attribute this discrepancy, which is also apparent in Franck-Condon simulations of the HSiX species,^{27,28} to the substantial vibrational anharmonicities in the excited state. A proper treatment would necessitate explicitly accounting for anharmonic effects in the Franck-Condon calculations. Nevertheless, the simulations provide convincing evidence that the assignments are reliable.

As a further test of the derived harmonic frequencies, we applied the Redlich-Teller product rule³¹ for HXY molecules of C_s symmetry, using the rotational constants from our LIF studies,^{6,7}

$$\frac{\omega_1^* \omega_2^* \omega_3^*}{\omega_1 \omega_2 \omega_3} = \sqrt{\left(\frac{C}{C^*}\right) \left(\frac{M^*}{M}\right)^2 \left(\frac{m_{\text{H}}}{m_{\text{D}}}\right)^2}. \quad (6)$$

The experimental harmonic ratios (0.5067 for HGeBr and 0.5068 for HGeI) are in reasonable agreement with the theoretical ratios (0.5085 and 0.5075, respectively), suggesting that the transfer of frequencies and anharmonicities from related molecules does not lead to significant errors in determining the harmonic frequencies. We also note that the

Ge–H and Ge–D harmonic stretching frequencies (Table III) are very similar for monobromogermylene and monoiodogermylene and differ only slightly from the frequencies of HGeCl/DGeCl (1906.9/1360.4 cm^{-1}) (Ref. 8) and GeH/GeD (1900.382/1353.317 cm^{-1}).²⁵ Similarly, the germanium-halogen stretching frequencies of the germynes (Table III) are very similar to $\omega_e''=295.4$ and 240.0 cm^{-1} for GeBr (Ref. 26) and GeI.¹⁴ There can be little doubt that our approximate anharmonicity analysis and the derivation of the harmonic frequencies must be substantially correct.

In Table V we have collected together a comparison of the ground state structures and vibrational frequencies of the monohalogenmylenes and germane. Unfortunately, there is no experimental data for HGeF, as it has never been observed, although we have tried to obtain the LIF spectrum in the past.⁶ For completeness, we have calculated the properties of HGeF using coupled cluster theory and it is these predictions that are included in Table V. The data suggest that the Ge–H bond lengths are virtually invariant to halogen substitution, contrary to the trend in the HSiX species where there is a slight increase in the SiH bond length with increasing electronegativity of the halogen.³² However, it is likely that the bond length variations are obscured by fixing the bond angle in the structure determinations, as the experimentally derived ω_1 vibrational frequencies and f_{11} stretching force constants do increase monotonically from HGeCl to HGeI. The germanium-halogen bond lengths are comparable to the available diatomic ground state values^{35–37} (GeF = 1.750 \AA , GeCl = 2.144 \AA , and GeBr = 2.308 \AA) and similar to the bond lengths of the dihalogenmylenes^{38–41} (GeF₂ = 1.745 \AA , GeCl₂ = 2.183 \AA , GeBr₂ = 2.359 \AA , and GeI₂ = 2.540 \AA). The dihalogenmylene symmetric stretching frequencies^{42–45} [GeF₂ = 692 cm^{-1} , GeCl₂ = 391.2 cm^{-1} ,

TABLE V. A comparison of the ground state structural parameters and vibrational frequencies of the germlylenes.

	GeH ₂ ^a	HGeF ^b	HGeCl ^c	HGeBr ^d	HGeI ^d
$r(\text{GeH}) \text{ \AA}$	1.588(1)	1.587 ^b	1.586(1)	1.593(9)	1.589(1)
$r(\text{GeX}) \text{ \AA}$...	1.754	2.171(2)	2.325(21)	2.525(5)
$\theta(\text{HGeX})^\circ$	91.22(4)	94.3	93.9	93.6	93.2
$\omega_1(\text{cm}^{-1})^e$	1856/1335	1939/1381	1906.9/1360.4	1909.1/1359.4	1913.6/1363.0
$\omega_2(\text{cm}^{-1})^e$	916/657	782/568	735.3/528.3	707.0/505.0	671.7/478.5
$\omega_3(\text{cm}^{-1})^e$	1866/1352 ^f	669/672	404.9/402.4	293.6/292.5	241.5/241.2

^aReference 33.^bStructure and frequencies from CCSD(T)/aug-cc-pVTZ calculations of this work.^cReference 8.^dThis work.^eGeH₂/GeD₂ or HGeX/DGeX frequencies.^fHarmonic frequencies from a fitted *ab initio* potential surface, Ref. 34.

GeBr₂=286 cm⁻¹ (Ar matrix), and GeI₂=230 cm⁻¹ (Ar matrix)] are also very similar to the ω_3 values in Table V. The data indicate that the derived HGeX bond lengths and stretching frequencies are entirely consistent with those of similar molecules and with trends observed for the HSiX species.

The HGeX bond angles decrease with increasing size of the substituted halogen, a trend which is somewhat counter-intuitive, but is exactly the same as was found for the monohalosilylenes,³² so it can hardly be accidental. As argued previously,²⁸ the electronegativity of the halogen substituent can be used to account for this effect. In the HGeX series, we note that the calculated charge on the central germanium atom increases with increasing substituent electronegativity (HGeI=0.28, HGeBr=0.28, HGeCl=0.51, and HGeF=0.70), consistent with the conclusion from theoretical studies on the silylenes⁴⁶ that electronegative substituents *X* induce a transfer of charge from the lone pair σ_{nb} orbital on Si to the Si–*X* bond. Thus, in the present case, more electron withdrawing substituents decrease the spatial extent of the lone pair orbital, allowing the HGeX bond angle to increase. The bond angle in GeH₂ is 2°–3° smaller, as there is no unbalanced inductive effect.

This work completes our series of studies of the SVL emission spectra of the jet-cooled halosilylenes and germlylenes. A consistent picture emerges from the derived ground state structures and vibrational frequencies of both families of molecules. As a general rule, the halogen substituted silylenes and germlylenes can be thought of as minor modifications of the parent silylene (SiH₂) or germlylene (GeH₂), with slight increases in the bond angle with increasing halogen electronegativity. The SiH and GeH bond lengths of HSiX and HGeX are very similar to those of the parent molecules, but are slightly elongated in the fluorinated species, due to inductive effects. The Si–*X* and Ge–*X* bond lengths and vibrational frequencies can be also be predicted with high fidelity from those of the corresponding diatomic molecules. In the absence of extensive microwave or infrared data, our derived r_e^z structures are probably the best approximations to the equilibrium structures of these molecules that can be experimentally obtained at this time.

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