Communications to the Editor

Laser Spectroscopic Detection of the Simplest Unsaturated Silylene and Germylene

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Vinylidene, $H_2C=C$, the high-energy isomer of acetylene, has been the subject of much experimental and theoretical attention.[1] The heavy atom analogs, silylidene, $H_2C=Si$, and germylidene, $H_2C=Ge$, although of great interest, are much less well-known. Silylidene was first identified from its electronic absorption spectrum in 1979,[2] and the microwave spectrum has recently been reported,[3] but little other experimental data are available. Theoretical studies have shown that silylidene is the global minimum on the H_2CSi potential surface, with the trans-bent acetylene-like structure, $H-Si\equiv C-H$, lying ~40 kcal/mol higher.[4−7] Germylidene has not been previously reported. In the present work, we have used laser induced fluorescence (LIF) spectroscopy and *ab initio* predictions of the electronic states to determine the ground state molecular structure of $H_2C=Si$ and to detect germylidene for the first time.

Jet-cooled $H_2C=Si$ and $H_2C=Ge$ were produced by striking an electric discharge in a high-pressure argon pulse seeded with tetramethylsilane (TMS) or tetramethylgermane (TMG) vapor, using the techniques described elsewhere.[8] The corresponding deuterated compounds were obtained by using TMS-d_{12} and TMG-d_{12}, synthesized by literature methods. *Ab initio* predictions of the energies, molecular structures, and vibrational frequencies of several electronic states of $H_2C=Si$, $H_2C=Ge$, and $H_2C=Sn$ were obtained by using configuration interaction methods, including all single and double excitations, CISD, and polarized triple-ζ basis sets, TZ(2df,2pd). These theoretical predictions were used to help search for the spectra of the germanium and tin species, and to help interpret the observed spectra.

The LIF spectra of H_2CSi and D_2CSi are very intense. Each consists of 15−20 vibronic bands in the 342−300-nm region; the wavelengths of the strongest band maxima are in general agreement with the absorption spectra band head measurements reported by Leclercq and Dubois.[2] As illustrated in Figure 1, the rotational structure in these bands can be readily resolved; analysis of such spectra provides the rotational constants and moments of inertia of the combining states.

The spectrum in Figure 1 also shows that the central subband is weaker than outer ones, a necessary consequence of nuclear statistical weights if there are two equivalent hydrogen atoms. This proves that the molecule must have the silylidene, rather than the acetylene-like, structure. The rotational constants of H_2CSi and D_2CSi have been used to obtain the following ground

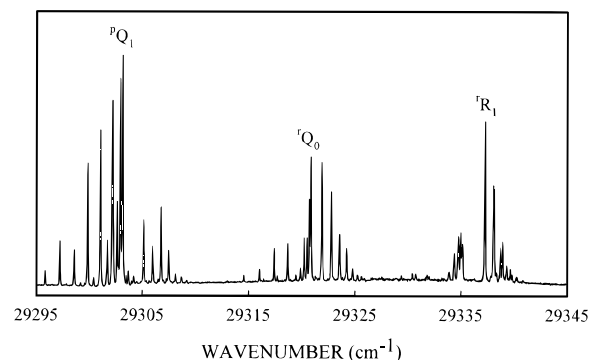**Figure 1.** High-resolution laser induced fluorescence spectrum of the $S_2 - S_0$ 0−0 band of jet-cooled $H_2C=Si$.

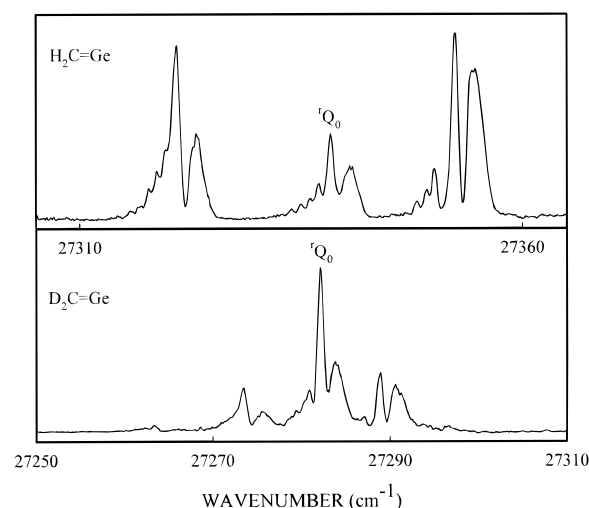**Figure 2.** Low-resolution $S_2 - S_0$ 0−0 band spectra of jet-cooled $H_2C=Ge$ and $D_2C=Ge$.

state C_{2v} partial substitution structure: $r_s(CH) = 1.099(3)$ Å, $r_s(CSi) = 1.706(5)$ Å, and $\theta_s(HCH) = 114.4(2)°$, which is in excellent accord with our theoretical prediction of $r_e(CH) = 1.083$ Å, $r_e(CSi) = 1.704$ Å, and $\theta_e(HCH) = 113.4°$. The excited state carbon−silicon stretching fundamental has a value of 701 cm^{-1}, which compares favorably with our *ab initio* harmonic frequency of 708 cm^{-1}. The excitation energy of $H_2C=Si$ is predicted to be 29 394 cm^{-1}, in excellent agreement with the observed 0−0 band origin of 29 313 cm^{-1}.

The search for the spectrum of $H_2C=Ge$ was greatly aided by *ab initio* predictions of the electronic excitation energy, which suggested that the onset of the spectrum should occur about 30 nm lower than that of silylidene. With use of TMG and TMG-d_{12} precursors, weak spectra of $H_2C=Ge$ and $D_2C=Ge$ were obtained in the 366−345-nm regions. The 0−0 bands have rotational profiles similar to those of the silylidenes and also show the intensity alternation expected for a molecule with two equivalent hydrogens, as illustrated in Figure 2. High-resolution spectra of the 0−0 band of $H_2C=Ge$, although incompletely resolved due to the presence of five germanium isotopes in natural abundance, show clear evidence of ^{70}Ge, ^{72}Ge, and ^{74}Ge isotope splittings. The experimental 0−0 band energy (27 331 cm^{-1}) and excited state C−Ge stretching frequency (548 cm^{-1}) are also in good agreement with the *ab initio* values of 27 303 and 588 cm^{-1}, respectively. The ground state structure is predicted to be similar to that of silylidene, with $r(CH) = 1.082$ Å, $r(CGe) = 1.794$ Å, and $\theta(HCH) = 114.2°$. All of the

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evidence leaves no doubt that the observed spectrum is that of germylidene, a species hitherto unknown.

Our *ab initio* studies of stannylidene predict the $S_2 - S_0$ excitation energy to be 23 472 cm^{-1} (426 nm), slightly lower in energy than germylidene. Experiments with tetramethylstannane were unsuccessful; we were unable to locate any LIF signals in the 445−355-nm region that could be attributed to $H_2C{=}Sn$. The ground state geometry of H_2CSn predicted by theory is similar to those of H_2CSi and H_2CGe, except for the longer carbon−tin bond length: $r(CSn) = 2.015$Å, $r(CH) = 1.084$ Å, and $\theta(HCH) = 113.1°$.

The spectroscopic data and the results of our *ab initio* studies make it clear that it is the $S_2 - S_0$ electronic transition—involving promotion of an electron from the nonbonding or lone pair orbital of a_1 symmetry on the heteroatom to the in-plane heteroatom p orbital of b_2 symmetry—that we are monitoring in each case. Our observation of fluorescence from the second excited singlet state (S_2) in these polyatomic molecules is unusual, and constitutes another of the rare exceptions to Kasha's empirical rule[9] that emission of light or photochemical reactions occur from the lowest excited electronic state of a given multiplicity. Other well-known examples include azulene and several thiocarbonyl compounds,[10] which share an energy level structure similar to that of silylidene and germylidene. In each case, the $S_1 - S_0$ energy gap is approximately equal to the $S_2 - S_1$ energy gap, so that efficient internal conversion from S_2 to S_1 does not occur. In contrast, the majority of organic molecules have relatively small $S_2 - S_1$ energy gaps, which accounts for the success of Kasha's rule.

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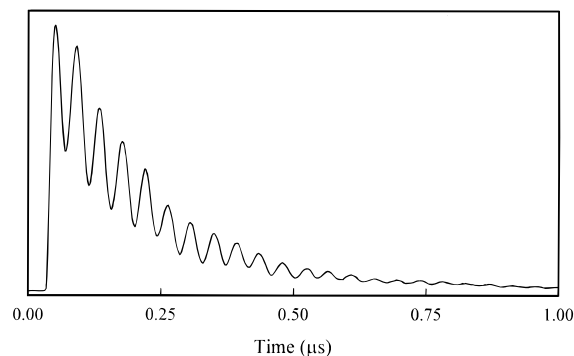
Figure 3. Quantum beats in the fluorescence decay of S_2 $D_2C{=}Si$ excited at 29 243.467 cm^{-1}.

Silylidene also shows evidence of intensity anomalies in the LIF spectra, suggesting interesting excited state decay dynamics. Of even more interest is our observation that both silylidene and germylidene exhibit quantum beats[11] in their collision-free fluorescence decays, as illustrated in Figure 3. Almost all of the excited state rovibronic levels have oscillatory decays, and the beat patterns vary dramatically from level to level. Density of state arguments indicate that the perturbing state is predominantly the ground state. Further LIF and quantum beat studies of both intermediates are in progress.

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