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LABORATORY INVESTIGATIONS ON THE INFRARED ABSORPTIONS OF GERMANIUM-BEARING MOLECULES—DIRECTING THE IDENTIFICATION OF ORGANO-GERMANIUM MOLECULES IN THE ATMOSPHERES OF JUPITER AND SATURN

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ABSTRACT

Germanium-bearing molecules of the formula Ge_2H_x ($x = 2$–6) are plausible candidates for organometallic molecules present in the atmospheres of Jupiter and Saturn. Combining low-temperature spectroscopy with computed vibrational spectra of these molecules, we have observed strong fundamentals of seven germanium-bearing molecules GeH_3 (germyl radical), Ge_2H_6 (digermane), Ge_2H_5 (digermyl radical), H_2GeGeH_2 (digermene), $HGeGeH_3$ (digermanylidene), $HGeGeH_2$ (digermenyl radical), and GeH_2Ge (di-μ-hydrodigermanium) via infrared spectroscopy in the laboratory. These bands were confirmed in D4-germane matrices. Our data can guide the search for hydrogen-deficient germanium-carrying molecules in the atmospheres of Jupiter and Saturn, where the germane (GeH_4) precursor molecule is present.

Subject headings: molecular data — planets and satellites: individual (Jupiter, Saturn)

Online material: color figure

1. INTRODUCTION

During the last decades, the chemical composition of the giant gas planets Jupiter and Saturn has received ever-increasing attention (Barbieri et al. 1997; Marov et al. 1997; Yung & DeMore 1999; Bakich 2000; de Pater & Lissauer 2001; Taylor 2001). Simple, saturated hydrides in particular represent significant chemical constituents both in the Jovian and Saturn's atmosphere (Encrenaz et al. 1996; Yung & DeMore 1999; Kunde et al. 2004; Atreya et al. 2003; Brown et al. 2003; Atreya & Wong 2005). Here, the *Voyager* missions, star occultations, and terrestrial based telescopes identified methane (CH_4) in the atmospheres of Jupiter (Moreno et al. 1991; Molina & Moreno 1992; Ortiz et al. 1992; Satoh & Kawabata 1992; Encrenaz et al. 1995; Maillard et al. 1995; Sada et al. 1998) and Saturn (Ortiz et al. 1993; Table 1). Phosphine (PH_3; Noll & Larson 1991; Griffith et al. 1992; Weisstein & Serabyn 1994; Borunov et al. 1995; Encrenaz et al. 1996; Davis et al. 1997; Edgington et al. 1998; Lara et al. 1998; Orton et al. 2000) and water (H_2O; Dowling & Ingersoll 1989; Delgenio & McGrattan 1990; Joiner et al. 1992; Gibbard et al. 1995; Noll et al. 1995; Degraauw et al. 1997; Roos-Serote et al. 1998; Bergin et al. 2000; Simon-Miller et al. 2000) are present on both giant planets as well. Hydrogen sulfide (H_2S) has only been detected on Jupiter (Yung & DeMore 1999), but upper limits have been derived for Saturn (Deboer & Steffes 1994). So far, silane (SiH_4) has never been discovered in the atmosphere of any solar system planet. Only upper abundance limits of 4×10^{-9} relative to hydrogen have been suggested for the atmosphere of Saturn (Yung & DeMore 1999). Germane (GeH_4), arsine (AsH_3), and ammonia (NH_3) have also been found on Jupiter (Noll & Larson 1991; Ferris et al. 1992; Griffith et al. 1992; Molina & Moreno 1992; Nava et al. 1993; Davis et al. 1997; Edgington et al. 1998, 1999; Folkner et al. 1998; Roos-Serote et al. 1998; Lara et al. 1998; Fouchet et al. 2000a; de Pater et al. 2001) and Saturn (Chen et al. 1991; Nava et al. 1993).

Although the presence of the germane molecule (GeH_4), a potential precursor to complex germanium-bearing species, has been observed spectroscopically on Jupiter and Saturn with abundances of 7×10^{-10} and 4×10^{-10} relative to hydrogen, respectively, little is known about the chemistry of the germane molecule in these environments (Fink et al. 1978; Drossart et al. 1982; Kunde et al. 1982; Noll et al. 1988; Noll & Larson 1991; Atreya 2004; Encrenaz 2004). Guillemin et al. (1995) suggested that the germane chemistry is initiated by solar photons, leading preferentially to the germyl radical (GeH_3) plus atomic hydrogen; the germyl species could react then with unsaturated hydrocarbons or was proposed to react with a second germyl radical to form digermane (Ge_2H_6) in the atmospheres of Jupiter and Saturn. Cook et al. (2001) examined the response of germane to Lyα photons (121.6 nm) and found that the initially formed germyl radical can decompose via atomic hydrogen elimination to germylene [$GeH_2(X\,^1A_1)$]. In addition, suprathermal hydrogen atoms holding kinetic energies up to a few electron volts were recommended to react with germane molecule via hydrogen abstraction, yielding molecular hydrogen and the germyl radical (GeH_3). Summarized, all previous examinations imply that the germane molecule can be degraded initially either to the germyl radical and/or the germylene molecule. Therefore, a rich germane chemistry can be driven—in a similar matter as the methane chemistry—by a photolysis of germane in the atmospheres of Jupiter and Saturn. Here, the germyl radicals, for instance, could recombine in the gas phase to internally excited digermane molecules, which can be either stabilized by a third body collision or undergo unimolecular decomposition to smaller Ge_2H_x ($x = 1$–5) species.

To test the validity of this hypothesis, it is important to identify Ge_2H_x ($x = 1$–6) molecules in the atmospheres of Jupiter and Saturn. However, a potential problem for radio observations is the vanishing or relatively small dipole moments of these molecules (Carrier et al. 2006a, 2006b). Therefore, an infrared spectroscopic search of Ge_2H_x species might present a logical option. Unfortunately, the infrared spectra, with the exception of digermane, are not well documented. In this paper, we present a low-temperature spectroscopic study on strong infrared absorptions of various Ge_2H_x ($x = 2$–6) isomers. These data will help an astronomical

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TABLE 1

Average Abundances of Simple Saturated Hydrides in the Atmospheres of Jupiter and Saturn Relative to Molecular Hydrogen

Hydride	Jupiter	Saturn
CH_4	3.0×10^{-3}	4.5×10^{-3}
GeH_4	7.0×10^{-10}	4.0×10^{-10}
NH_3	2.6×10^{-3}	2.0×10^{-4}
PH_3	7.0×10^{-7}	1.4×10^{-6}
AsH_3	2.2×10^{-10}	3.0×10^{-9}
H_2O	3.0×10^{-5}[a]	2.0×10^{-7}[b]
H_2S	6.1×10^{-6}[c]	$<2.0 \times 10^{-7}$

Note.—"Less than" sign denotes upper limit.

[a] $(3.0 \pm 2.0) \times 10^{-5}$ at 6 bar level, $(4.0 \pm 1.0) \times 10^{-6}$ at 2–4 bar level.

[b] 2.0×10^{-7} at $p > 3$ bar in the troposphere.

[c] $<8.6 \times 10^{-7}$ at 3.6 bar, 6.1×10^{-6} at 8.7 bar, and 6.7×10^{-5} at $p > 16$ bar.

TABLE 2

Infrared Absorptions of the Germane Frosts at 12 K

Wavenumber (cm^{-1})	Assignment
4190	$2\nu_3$
4120	$\nu_1 + \nu_3$
3025	$\nu_2 + \nu_3 + \alpha$
3000	$\nu_2 + \nu_3$
2200	$\nu_3 + \gamma$
2140	$\nu_3 + \beta$
2114	$\nu_3 + \alpha$
1737	$\nu_2 + \nu_4 + \alpha$
1715	$\nu_2 + \nu_4$
958	$\nu_4 + \gamma$
914	ν_2
846	$\nu_4 + \beta$
826	$\nu_4 + \alpha$
790	ν_4

Note.—Here α, β, and γ denote lattice modes of the germane sample (Calvani et al. 1990, 1991).

search for hydrogenated, dinuclear germanium clusters in the atmospheres of Jupiter and Saturn.

2. EXPERIMENTAL PROCEDURE

Our experiments were carried out in a contamination-free ultrahigh vacuum (UHV) matrix isolation chamber, which can be evacuated down to 5×10^{-11} torr by a magnetically suspended turbopump backed by an oil-free scroll pump (Bennett et al. 2004; Jamieson et al. 2005). A rotatable, two-stage closed-cycle helium refrigerator is attached to the lid of the machine and holds a polished silver single crystal. The latter is cooled to 12 ± 1 K and serves as a substrate for the germane ices. The ices were prepared at 12 K by depositing germane (99.99%; Aldrich) and D4-germane (99.99%; Voltaix) at pressures of 7×10^{-8} torr for 30 minutes onto the cooled silver crystal. Figure 1 shows a typical infrared spectrum of the frost recorded at 12 K; the absorptions of phase III of the germane ice are compiled in Table 2. To determine the ice thickness quantitatively, we integrated the infrared absorption features at 2111 and 821 cm^{-1}. The ice thickness was then calculated using a modified Lambert-Beer relationship (Bennett et al. 2004). The integrated absorption coefficients of these fundamentals were approximated from the gas phase and are 5.5×10^{-17} and 4.7×10^{-17} cm $molecule^{-1}$, respectively (Carrier et al. 2006a); the density of the germane ice is 1.751 g cm^{-3} (Coats et al. 1993). This yielded an optical thickness of 54 ± 20 nm. The ices were then exposed for 60 minutes by scanning the sample over an area of 3.0 ± 0.4 cm^2 by high-energy electrons to induce a germanium-hydrogen bond rupture in the low-temperature samples. The irradiation was conducted at 12 K with 5 keV electrons at beam currents of 10, 100, and 1000 nA. Using the CASINO code (Drouin et al. 1997), we find that each 5 keV electron loses 0.20 ± 0.02 keV of its kinetic energy while penetrating the silane target. Considering the extraction coefficient of the electron beam of 78.8%, this translates into doses of 0.15 ± 0.05, 1.5 ± 0.5, and 15 ± 5 eV $molecule^{-1}$ at nominal currents of 10, 100, and 1000 nA. Background analysis was performed by collecting data with no germane in the UHV chamber. To guarantee an identification of the reaction products in the solid state, a Fourier transform infrared spectrometer was used. The Nicolet 510 DX FTIR unit (5000–500 cm^{-1}) operated in an absorption-reflection-absorption mode (reflection angle $\alpha = 75°$) at a resolution of 2 cm^{-1}. The infrared beam was coupled via a mirror flipper outside the spectrometer, passed through a differentially pumped potassium bromide (KBr) window, was attenuated in the ice sample prior to and after reflection at a polished silver waver, and exited the main chamber through a second differentially pumped KBr window before being monitored via a liquid-nitrogen-cooled detector. It should be stressed that the present studies are aimed to identify infrared absorptions of dinuclear, germanium-bearing molecules experimentally, but not to simulate the chemistry in the atmospheres of Jupiter and Saturn. This method has been used previously to assign elusive infrared absorptions of Si_2H_x (Kaiser & Osamura 2005a) and $SiCH_x$ species ($x = 1$–6; Kaiser & Osamura 2005b) and their implications to the chemistry in the circumstellar envelope of IRC+10216 in low-temperature silane and silane-methane matrices, respectively.

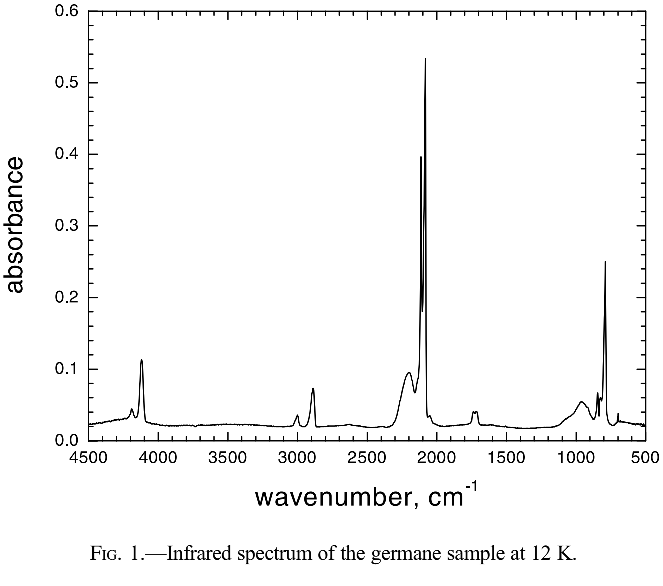

Fig. 1.—Infrared spectrum of the germane sample at 12 K.

3. EXPERIMENTAL RESULTS

The infrared spectroscopic studies indicate that the response of the matrix upon electron irradiation is governed by an initial formation of the germyl radical, $GeH_3(X\,^2A_1)$, plus atomic hydrogen via

$$GeH_4(X\,^1A_1) \rightarrow GeH_3(X\,^2A_1) + H(^2S_{1/2}). \qquad (1)$$

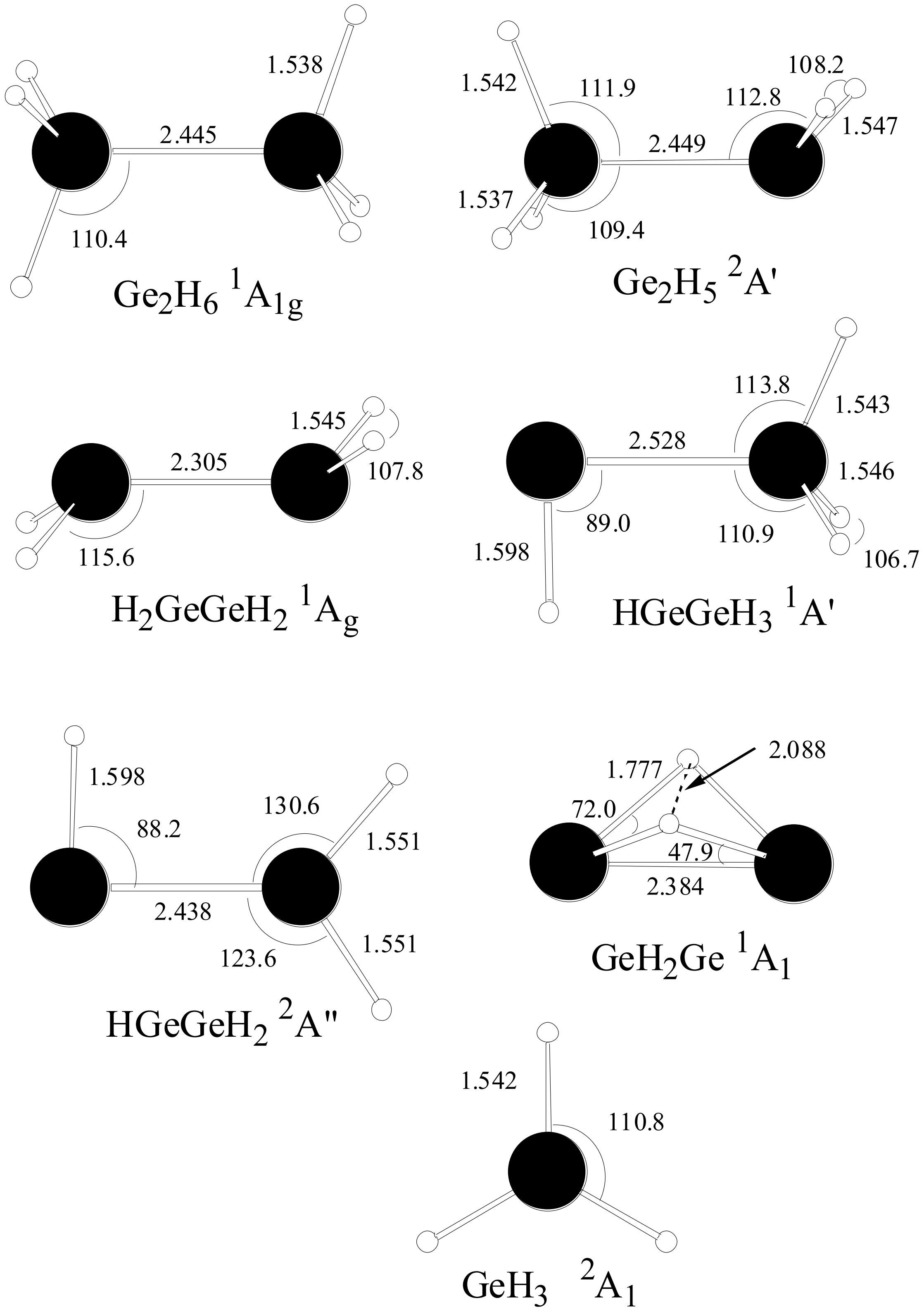

FIG. 2.—Experimentally observed hydrogenated germanium-bearing molecules. Bond lengths and bond angles are in angstroms and degrees, respectively (*black*, germanium; *white*, hydrogen atoms), and are taken from Carrier et al. (2006a). [*See the electronic edition of the Journal for a color version of this figure.*]

The absorption of the germyl radical appeared instantaneously with the onset of the irradiation of the germane samples with an electron current of 10 nA at 12 K at 665 cm^{-1} (ν_2, GeH_3; Figs. 2 and 3; Table 3). This position agrees very well with previous matrix studies (Crawford et al. 1962; Wang et al. 2002; Urban et al. 1997; Wang & Andrews 2003). Absorption features of the digermane molecule, $Ge_2H_6(X\,^1A_{1g})$, also appeared immediately after the onset of the irradiation. We monitored the umbrella mode at 752 cm^{-1} (ν_6, Ge_2H_6). These findings indicate that at low irradiation times the digermane molecule could form via

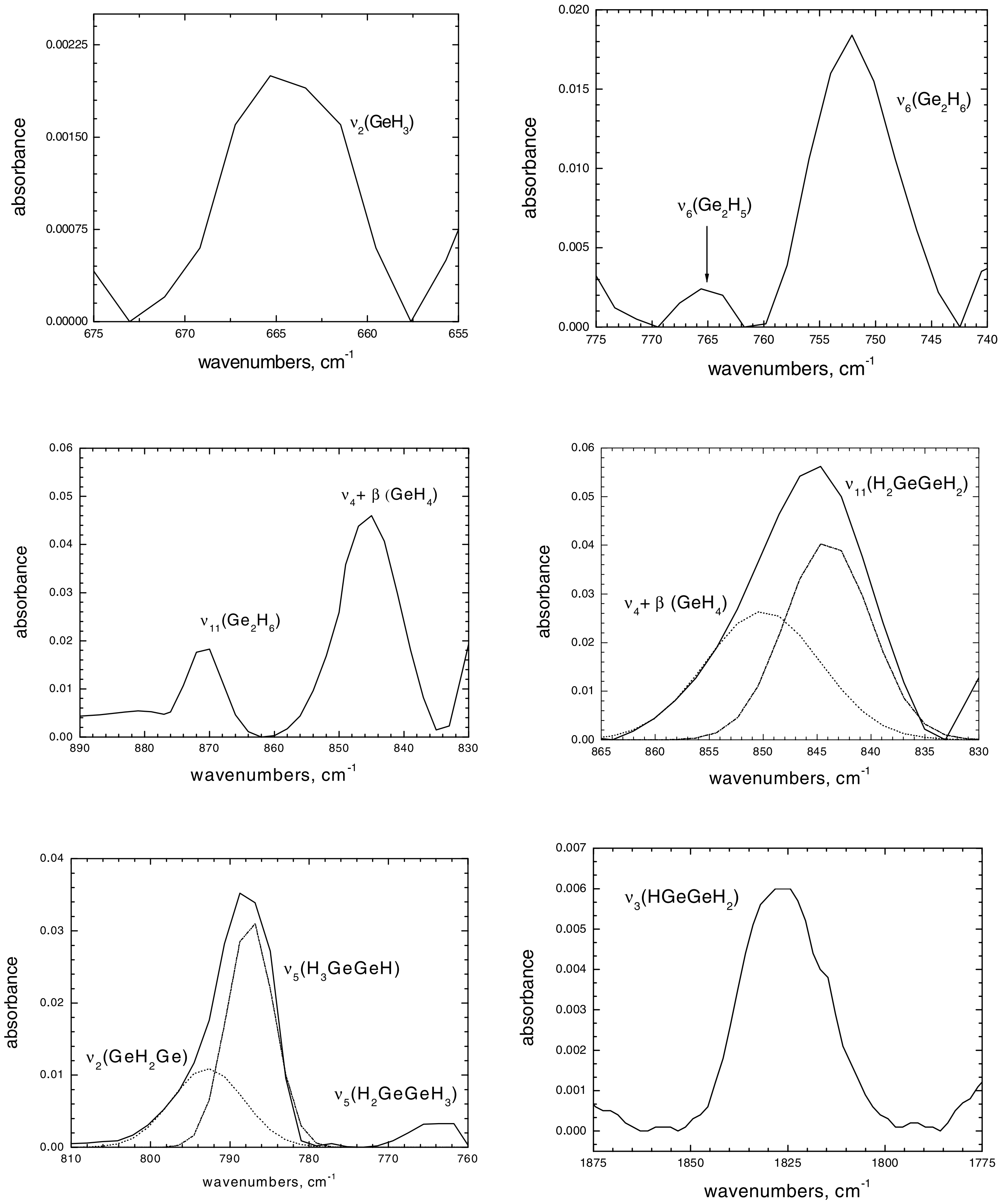

FIG. 3.—New absorption features of the germanium-bearing molecules; the positions of the absorptions are compiled in Table 3.

TABLE 3

Infrared Features Appearing after the Electron Irradiation at 12 K of the Germane and the D4-Germane Samples

Species	Wavenumber (cm^{-1})	Fundamental
GeH_3	665	ν_2
Ge_2H_6	870	ν_{11}
	752	ν_6
Ge_2H_5	765	ν_6
H_2GeGeH_2	845	ν_{11}
H_3GeGeH	787	ν_5
$HGeGeH_2$	1825	ν_3
GeH_2Ge	792	ν_2
GeD_3	608	ν_4
Ge_2D_6	626	ν_{11}
	529	ν_6
Ge_2D_5	616	ν_4/ν_{12}
	561	ν_6
D_2GeGeD_2	1476	ν_5
D_3GeGeD	558	ν_5
$DGeGeD_2$	1317	ν_3
GeD_2Ge	570	ν_2

recombination of two neighboring germyl radicals followed by a de-excitation of the internally excited digermane molecule,

$$GeH_3(X\,^2A_1) + GeH_3(X\,^2A_1) \rightarrow Ge_2H_6(X\,^1A_{1g}). \qquad (2)$$

At higher irradiation times, we also detected the digermyl radical, $Ge_2H_5(X\,^2A')$, via its absorption at 765 cm^{-1}. Both the experimentally observed ν_6 modes of digermane and of the digermyl radical agree, after scaling by 0.98 and 0.97, very well with the computed frequencies of 766 and 765 cm^{-1}, respectively; theoretical frequencies were taken from Carrier et al. (2006a, 2006b). The actual scaling factor is dependent on the degree of anharmonicity present in the given vibration due to the differing anharmonicities in the vibrations.

As the irradiation time increased even further, additional absorptions emerged at 787 and 845 cm^{-1}. We compare these features with the computed frequencies after scaling by 0.99 and 0.96; these peaks are identified as the ν_5 and ν_{11} fundamentals of the $HGeGeH_3(X\,^1A')$ structure and of the digermene molecule $H_2GeGeH_2(X\,^1A_g)$, respectively. After 2 minutes of the irradiation, an extra band became apparent at 1825 cm^{-1}. The absorption at 1825 cm^{-1} could not be attributed to any Ge_2H_x ($x = 4$–6) isomers. Therefore, we compared our data with the fundamentals of the energetically most stable Ge_2H_3 isomer. Indeed, after scaling the computed frequency by 0.97, we assigned the $Ge_2H_3(X\,^2A'')$ isomer via its strongest absorption (ν_3) at 1825 cm^{-1}. Toward the end of the irradiation, we also observed a small peak at the high-frequency side of the 785 cm^{-1} absorption of $HGeGeH_3(X\,^1A')$. This 792 cm^{-1} absorption could be correlated with the ν_2 fundamental of the $Ge_2H_2(X\,^1A_1)$ isomer. All peak assignments were cross-checked by irradiating D4-germane ices. The peak assignments are compiled in Table 3. It should be noted that until recently, only vibrational fundamentals of Ge_2H_x ($x = 2$, 4, and 6) and their isotopomers have been reported (Wang et al. 2002); the most intense infrared absorptions of digermane, $Ge_2H_6(X\,^1A_{1g})$ (ν_6 and ν_8, 752 and 881 cm^{-1}), digermene, $Ge_2H_4(X\,^1A_g)$ (ν_{11}, 789 cm^{-1}), and the di-bridged $Ge_2H_2(X\,^1A_1)$ (ν_6, 972 cm^{-1}) have been probed experimentally in low-temperature neon matrices. Although the Ge_2H_4 absorption was suggested by the authors to be assigned to ν_{11} of the $Ge_2H_4(X\,^1A_g)$ isomer, our calculations indicated this absorption belongs to ν_5 of $HGeGeH_3(X\,^1A')$.

4. ASTROPHYSICAL IMPLICATIONS

Our matrix isolation studies make consistent infrared absorptions of astrophysically important hydrogenated, germanium-carrying molecules available. We identified seven germanium-bearing species in low-temperature ices via infrared spectroscopy. These are GeH_3 (germyl radical), Ge_2H_6 (digermane), Ge_2H_5 (digermyl radical), H_2GeGeH_2 (digermene), $HGeGeH_3$ (digermanylidene), $HGeGeH_2$ (digermenyl radical), and GeH_2Ge (di-μ-hydrodigermanium). The dinuclear germanium clusters could be formed in the atmospheres of Jupiter and Saturn. In Jupiter's and Saturn's atmospheres, the germane precursor is present with fractional abundances of 7×10^{-10} and 4×10^{-10} relative to molecular hydrogen, respectively. It should be noted that in the gas phase, the photodissociation of a germane molecule is expected to form preferentially the $GeH_2(X\,^1A_1)$ molecule (Cook et al. 2001). However, these carbene-like species can also react with germane and/or methane molecules to form digermane and/or methylgermane via insertion,

$$GeH_2(X\,^1A_1) + GeH_4(X\,^1A_1) \rightarrow Ge_2H_6(X\,^1A_{1g}), \qquad (3)$$

$$GeH_2(X\,^1A_1) + CH_4(X\,^1A_{1g}) \rightarrow CH_3GeH_3(X\,^1A_1), \qquad (4)$$

respectively. Therefore, we expect that the germane chemistry could be strongly coupled with the hydrocarbon chemistry in the atmospheres of Jupiter and Saturn. Note that the hydrocarbons ethane (C_2H_6) and acetylene (C_2H_2) have been identified in the atmospheres of the giant planets Jupiter and Saturn; ethylene (C_2H_4) was only observed in Jupiter (Fouchet et al. 2000b; Courtin et al. 1984). In summary, our laboratory studies can guide infrared searches in the Jovian and Saturnian atmospheres for the germanium-containing molecules of Table 3 using the NASA Infrared Telescope Facility or future space-based instrumentation.

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