

Infrared diode laser spectroscopy of the GeH radical in the $2\Pi_{1/2}$ state

Yasunobu Akiyama, Keiichi Tanaka, and Takehiko Tanaka

Citation: *The Journal of Chemical Physics* **94**, 3280 (1991); doi: 10.1063/1.459800

View online: <http://dx.doi.org/10.1063/1.459800>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/94/4?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Effect of oxygen on methyl radical concentrations in a CH₄/H₂ chemical vapor deposition reactor studied by infrared diode laser spectroscopy](#)

J. Vac. Sci. Technol. A **14**, 2970 (1996); 10.1116/1.580255

[Timeresolved infrared diode laser spectroscopy of the \$\nu_5\$ band of the cyanomethyl radical \(H₂CCN\)](#)

J. Chem. Phys. **104**, 1839 (1996); 10.1063/1.471709

[Infrared diode laser spectroscopy of the PF radical](#)

J. Chem. Phys. **86**, 3804 (1987); 10.1063/1.451938

[Infrared diode laser spectroscopy of the PCI radical](#)

J. Chem. Phys. **83**, 4945 (1985); 10.1063/1.449755

[Infrared and farinfrared laser magnetic resonance spectroscopy of the GeH radical: Determination of ground state parameters](#)

J. Chem. Phys. **83**, 3275 (1985); 10.1063/1.449186



Infrared diode laser spectroscopy of the GeH radical in the $^2\Pi_{1/2}$ state

Yasunobu Akiyama, Keiichi Tanaka, and Takehiko Tanaka
 Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki,
 Higashiku, Fukuoka 812, Japan

(Received 10 September 1990; accepted 6 November 1990)

Spectroscopy of the GeH radical, which has the $^2\Pi$, ground electronic state, has been attracting interest in connection with plasma processes. Electronic spectra of GeH have been studied extensively,¹⁻⁵ but it is only recently that the rotational and rovibrational spectra of GeH have been reported. Brown *et al.*⁶ observed rotational transitions within the $^2\Pi_{1/2}$ as well as $^2\Pi_{3/2}$ manifold in the ground state by far-infrared laser magnetic resonance. They also observed transitions connecting the two spin components, $^2\Pi_{3/2} \leftarrow ^2\Pi_{1/2}$, by CO₂ laser magnetic resonance. Recently, Towle and Brown⁷ observed the fundamental and first hot bands of GeH in the $^2\Pi_{3/2}$ state by CO laser magnetic resonance. In this letter, we report detection of the fundamental band of GeH in the $^2\Pi_{1/2}$ state by infrared diode laser spectroscopy.

The diode laser spectrometer used has been reported previously.⁸ The absorption cell was a 106 cm long, 5 cm diam Pyrex tube, containing a pair of stainless-steel cylindrical electrodes for discharge near the both ends. Ac high voltage was applied between the electrodes. Discharge occurred twice in each cycle of the ac voltage, in alternating directions, and the signal was detected by a phase sensitive detector operated at twice the frequency of the ac high voltage. The cell was incorporated with a White-type multireflection optical path with an effective length of 15 m.

The GeH radical was produced directly in the absorption cell by glow discharge in the mixture of GeH₄, He, and H₂. The optimum pressure at the inlet to the cell was about 10 mTorr for GeH₄, 1 Torr for He, and 1 Torr for H₂. The GeH signal intensity was tripled by the addition of H₂, as in the case of SiH.⁹ The optimum discharge current was about 350 mA *p-p*, when the frequency of the ac voltage for discharge was 427 Hz. A high-speed mechanical booster pump backed up by a rotary pump evacuated the absorption cell.

In total 94 GeH lines were observed in the frequency range 1659–1897 cm⁻¹ (20 for ⁷⁰GeH, 22 for ⁷²GeH, 14 for ⁷³GeH, 21 for ⁷⁴GeH, and 17 for ⁷⁶GeH). These lines were assigned to the *P*(11.5)–*R*(4.5) transitions in the $^2\Pi_{1/2}$ spin state. They were all observed as doublets split by about 0.5 cm⁻¹ due to the Λ -type doubling in the $^2\Pi_{1/2}$ state. Their wave numbers were measured with an accuracy of about 0.0005 cm⁻¹. Figure 1 shows a typical recording trace, which shows three signals assigned to the *P*(5.5) lines of the ⁷⁴GeH, ⁷⁰GeH, and ⁷³GeH in the $^2\Pi_{1/2}$ spin state. Our effort to observe transitions in the $^2\Pi_{3/2}$ state has been unsuccessful.

The observed wave numbers were least-squares fitted

using the effective Hamiltonian for the $^2\Pi$ molecule described in our previous paper.⁸ Transitions of all five isotopic species were simultaneously analyzed, assuming the mass scaling relation among the constants for different isotopic species. The effective spin-orbit coupling constant A^{eff} was fixed to 892.5267 cm⁻¹, which was derived from the CO₂ laser magnetic resonance study,⁶ for both $v=0$ and $v=1$ states. The centrifugal distortion term A_D for the spin-orbit coupling constant as well as the spin-rotation interaction constant γ was simply neglected. The q constant was assumed to have the same value in the $v=0$ and $v=1$ states. The optimized constants for the ⁷⁴GeH species are listed in Table I. The standard deviation of the fit was about 0.0009 cm⁻¹, slightly exceeding the experimental error.

The fundamental band origin $\nu_0 = 1831.8451 \pm 0.0012$ cm⁻¹ obtained in the present analysis of the diode laser spectrum differs from the value derived from the CO laser magnetic resonance,⁷ 1833.84577 ± 0.00026 cm⁻¹, by two wave numbers. This discrepancy resulted from the neglect of the vibrational change of the spin-orbit coupling constant in our treatment. Our ν_0 value corresponds to the energy difference between $v=0$ and $v=1$ in the $^2\Pi_{1/2}$ spin state. The rotational constant B^{eff} for the ground state in Table I disagrees with the B_0 value in Ref. 7 by about 0.0035 cm⁻¹, although the difference of the rotational constants in the $v=0$ and $v=1$ states is consistent with the α_c constant in Ref. 7. This discrepancy was caused by the neglect of the spin-rotation interaction constant γ in our treatment. Our B^{eff} value for the ground state agrees, as

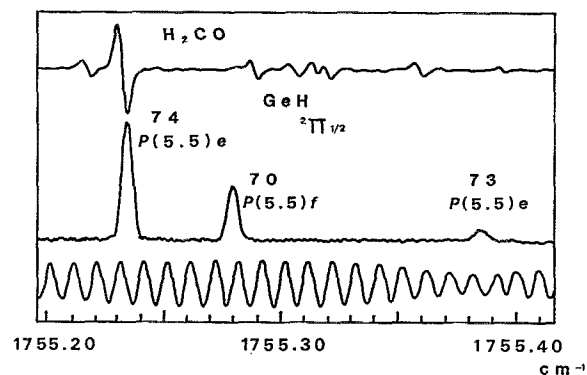


FIG. 1. Observed spectrum for *P*-branch lines of three different isotopic species. The spectrum of H₂CO (top) and etalon fringes (bottom) were used for wave number calibration.

TABLE I. Molecular constants of ^{74}GeH in the $X^2\Pi_{1/2}$ state.^a

Const.	$v=0$	$v=1$	
B^{eff}	6.627 08(20)	6.433 47(19)	cm^{-1}
D	3.348(28)	3.314(36)	10^{-4} cm^{-1}
A^{eff}	892.526 7 ^b	892.526 7 ^b	cm^{-1}
$p+2q$	0.500 92(91)	0.481 86(98)	cm^{-1}
q	0.013 70(50) ^c	0.013 70(50) ^c	cm^{-1}
ν_0	1831.845 1(12)		cm^{-1}

^aThe figures in parentheses are three standard deviations in units of the last digit.

^bFixed. Ref. 6.

^cThe q constant is assumed to have the same value in the $v=0$ and $v=1$ states.

expected, with the value of $B_0 + \gamma/(\lambda - 2)$ in Ref. 7, where $\lambda = A/B$. Other molecular constants in Table I are consistent with the results of Refs. 6 and 7, except that the present q constant is about twice as large as the q value of Ref. 7. The harmonic frequency, $\omega_e = 1897.3 \pm 1.6 \text{ cm}^{-1}$, and the anharmonic constant, $\omega_e x_e = 32.73 \pm 0.78 \text{ cm}^{-1}$, derived for ^{74}GeH through the isotope dependence of the vibrational frequency are consistent with $\omega_e = 1908 \pm 35$

cm^{-1} and $\omega_e x_e = 37 \pm 19 \text{ cm}^{-1}$ from electronic spectroscopy⁴ as well as with the LMR result,⁷ $\omega_e x_e = 32.862 62(17) \text{ cm}^{-1}$.

Dr. K. Kawaguchi kindly measured the FTIR spectrum of D_2CO , which was used as the wave number standard in the present study. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas from Ministry of Education, Science, and Culture. Calculations for the present study were carried out at the Computer Center of Kyushu University.

¹B. Klemm and E. Werhagen, Ark. Fys. 6, 359 (1953).

²B. Klemm and E. Werhagen, Ark. Fys. 6, 399 (1953).

³R. F. Barrow, G. Drummond, and W. R. S. Garton, Proc. Phys. Soc. London, Sect. A 66, 191 (1953).

⁴L. Klynning and B. Lindgren, Ark. Fys. 32, 575 (1966).

⁵L. Veseth, J. Mol. Spectrosc. 48, 283 (1973).

⁶J. M. Brown, K. M. Evenson, and T. J. Sears, J. Chem. Phys. 83, 3275 (1985).

⁷J. P. Towle and J. M. Brown, Mol. Phys. 70, 161 (1990).

⁸K. Tanaka, Y. Akiyama, and T. Tanaka, J. Mol. Spectrosc. 137, 55 (1989).

⁹W. Seebas, J. Werner, W. Urban, E. R. Comben, and J. M. Brown, Mol. Phys. 62, 161 (1987).