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Room temperature absorption spectroscopy of GeH₂ near 585 nm

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Abstract

The absorption spectrum of the germylene radical produced in a continuous flow discharge of germane diluted in argon has been recorded in the $17090-17135 \text{ cm}^{-1}$ region. This range corresponds to the central part of the $\tilde{A}^1B_1(0, 1, 0) - \tilde{X}^1A_1(0, 0, 0)$ rovibronic transition, which has been analysed for the first time. The spectrum was measured by Intracavity Laser Absorption Spectroscopy with an equivalent pathlength of 15 km. The experimental resolution and wavenumber accuracy are of the order of 0.06 and 0.015 cm⁻¹, respectively. Each rovibronic absorption is made up of five lines corresponding to the five germanium isotopomers appearing in a natural abundance sample. We have assigned around 25 transitions for each species, from which the rotational constants of the excited state and the band origin of the transition have been calculated. The equilibrium structure of the excited electronic state has been estimated with the help of ab initio data for some vib-rotational parameters. Good agreement is found with previous ab initio determinations of this structure. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Similarly to silylene (SiH₂), germylene (GeH₂) is believed to be an important intermediate species in the production of hydrogenated amorphous films, by plasma-induced deposition or laser assisted chemical vapour deposition (CVD) [1]. Germylene has been detected both in deposited thin layers and as an absorption product on the germanium surface [2,3]. The infrared detection, by matrix-isolation technique, of germylene produced in deposition plasmas has been reported by Lloret et al. [4]. However, in situ detection of gas phase germylene would be the most

desirable method to understand the gas phase and surface chemistries in these CVD plasmas of industrial interest. In the case of silvlene, we have recently shown [5.6] that Intracavity Laser Absorption Spectroscopy (ICLAS) and CW-Cavity Ring Down Spectroscopy (CW-CRDS) can be applied to detect SiH₂ in the gas phase and measure its concentration. These measurements performed in an argon-5% silane DC discharge used some Doppler-limited absorption lines of the $\tilde{A}^1 B_1 \leftarrow \tilde{X}^1 A_1$ electronic transition in the visible range. However, the extraction of the absorber concentration from the measurement of a single rovibronic absorption line requires both a preliminary rotational analysis of the band under consideration and a knowledge of the electronic transition moment [6]. Very similar experiments were carried by Kawasaki et al. [7] who monitored the

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spatial distribution of the absolute GeH₂ density in a RF plasma by ICLAS of the ${}^{P}P_{1}(1)$ transition of the $\tilde{A}^{1}B_{1}(0,0,0) - \tilde{X}^{1}A_{1}(0,0,0)$ band at 16312 cm⁻¹. However, no details were given in this report about the procedure followed to obtain the absolute concentration of GeH₂ [7].

As far as we know, a very limited number of studies has been devoted to the spectroscopy of germylene in the gas phase [8-12]. All these previous reports focused on the $\tilde{A}^1 B_1(0, \nu'_2, 0)$ – $\tilde{X}^{1}A_{1}(0,0,0)$ system (noted $2_{0}^{\nu'_{2}}$ hereafter), consisting of a progression of bands between 615 and 485 nm corresponding to the excitation of the bending vibration ($\nu'_2 = 0-6$). Saito, Obi and Fukushima [8,10,11] reported the laser-induced fluorescence (LIF) spectrum of jet cooled germylene produced by photolysis of phenylgermane and measured the fluorescence lifetimes from the ${}^{p}P_{1}(1)$ transition. Karolczak et al. [12] generated germylene by applying an electric discharge at the exit of a supersonic expansion of a mixture of GeH₄ in argon. They observed a sufficient number of rovibronic transitions of the 0_0^0 band to derive the rotational constants and then the r_0 structures of the ground and excited states. They also determined the upper state fundamentals, ν_1 and ν_2 , and studied the isotope effect from the ${}^{p}P_{1}(1)$ lines of the $2_0^{\nu'_2}$ progression. Another important result of this work [12] is that, as a consequence of J-dependent predissociation process, only fluorescence from low J value rotational states could be detected. Indeed, only the ${}^{p}P_{1}(1)$ line reaching the 0_{00} excited rotational level could be recorded for the $2_0^{\nu'_2}$ bands with $\nu_2' > 0$, while only fluorescence from low angular momentum states could be detected for the 0_0^0 band. Similar conclusions were previously derived by Obi, Fukushima and Saito [11] who proposed a second order predissociation mechanism $(A^{1}B_{1} \rightarrow X^{1}A_{1} \rightarrow$ $a^{3}B_{1}$) leading to Ge(³P) + H₂, to account for their observations.

In the case of non- or weakly-fluorescent transitions, high sensitive absorption spectroscopy is the ideal alternative to LIF. Very recently, Becerra et al. [9] and Alexander et al. [13] studied the germylene kinetics at room temperature by monitoring the time dependence of the concentration of GeH₂ produced by a flash photolysis of phenylgermane. They observed by direct multipass absorption, two rovibronic transitions of the $2\frac{1}{0}$ band, which were attributed (but not rotationally assigned) to GeH_2 from the characteristic intensity variation of their components, due to the five germanium isotopomers. These transitions will be rotationally assigned in the forthcoming analysis.

For quantitative in situ and real time optical diagnostics of CVD plasmas, absorption techniques are much more suitable than LIF. For this purpose, the rovibrational assignment of the absorption spectrum recorded at room temperature (i.e. close to real CVD conditions) is a necessary prerequisite to monitor the GeH₂ concentration from a single line. In this context, we present below the first rotational analysis of a vibronic band of GeH₂ recorded at room temperature, namely the 2_0^1 band near 17 100 cm⁻¹.

2. Experimental

The experimental set up is essentially the same as the one used for our SiH_2 studies [5,6]. The germylene radical was generated by a continuous discharge (about 640 V) in a slowly flowing mixture (35 sccm) of germane (5%) in argon. The total pressure was about 1 torr. The flow of argon entered the plasma tube close to the two Brewster angle windows to prevent deposition of germanium. The discharge cell was inserted into the dye (Rhodamine 590) laser cavity of our ICLAS spectrometer (see Ref. [14] for more details on the principle and experimental arrangements of ICLAS). The distance between the two cylindrical electrodes was 60 cm leading to an occupation ratio of the laser cavity by the absorber of about 50%. A generation time of 80 µs, corresponding to an absorption equivalent pathlength of 15 km was adopted for the recording. The wavenumber calibration was performed by simultaneous recording of the iodine absorption spectrum [15]. The wavenumber accuracy in the GeH₂ line positions is estimated to be 0.015 cm^{-1} as checked for some NH₂ rovibronic transitions [16] which appear superimposed on the GeH₂ spectrum (see Fig. 1). The NH_2 radical is produced from N_2 probably present in the discharge as a result of a small leak in the discharge cell. The spectrum, recorded between 17000 and 17250 cm^{-1} , appeared to be congested and highly dependent of the discharge conditions, with many lines which could not be attributed to N_2^* ,



Fig. 1. Upper: Observed ICLAS spectrum in the 17105–17123 cm⁻¹ region, of natural abundance GeH₂. The rotational assignment is indicated for the more intense lines, corresponding to the ⁷⁴Ge isotopomer. Lower: predicted spectra, with the weight of the spectrum of each isotopomer scaled by its corresponding abundance ratio. A Gaussian line profile (0.06 cm⁻¹ FWHM) was attached to each transition of the simulated spectrum. The lines marked by + are due to NH₂ rovibronic transitions [16].

NH₂, GeH₂ or Ar^{*}. As a consequence, we were obliged to restrict our analysis to the 17 090–17 135 cm⁻¹ spectral region, as described below, which corresponds to the central region of the 2_0^1 band.

3. Results

3.1. Rovibronic analysis

Several features were found with the characteristic pattern for the five germanium isotopomers (⁷⁰Ge 20.5%, ⁷²Ge 27.4%, ⁷³Ge 7.8%, ⁷⁴Ge 36.5% and ⁷⁶Ge 7.8%), depicted in fig. 1 of Karolczak et al. [12], or in fig. 1 of Becerra et al. [9]. A prediction of the spectrum using the vibrational band origin of this band, and the rotational constants for the 0⁰₀ band, both from Ref. [12], enabled us to start the first assignments, based on intensity considerations and approximate wavenumber positions. The alternating spin statistical weights of the rotational levels also facilitated the assignments: $K''_a + K''_c$ odd levels have a spin weight three times larger than $K''_a + K''_c$ even levels. This band is of c type, and the central part of the spectrum should be dominated by the ${}^{p}Q_{1}(J)$ and

 $^{r}O_{0}(J)$ branches. The symmetric top formalism can safely be used here, as both of these transitions are made up of one K component only. It was soon found that the central region of this band presents a very similar structure to that of the corresponding 0_0^0 band of SiH₂ [5], whereas every feature is five-fold in the present case. This was sometimes of help in the assignment, but sometimes it greatly complicated the structure. Fig. 1 shows the observed spectrum (above) and a computer simulation (below) including all five isotopomers. Transitions labelled ${}^{p}Q_{1}(4)$ or ${}^{p}O_{1}(6)$ are very good examples of the former case; the region at the head of the ${}^{r}Q_{0}$ branch, where ${}^{p}Q_{1}(8)$ is also present, is on the other hand quite complicated indeed. The presence of NH₂ lines, labelled with a cross in the figure, adds some further complexity to the problem.

The lines near 17111.5 cm⁻¹ observed by Becerra et al. [9] and Alexander et al. [13] were in perfect wavenumber agreement with our observation, and are assigned to the ${}^{p}Q_{1}(6)$ Ge isotopomer structure. The line at 17118.67 cm⁻¹, used by Becerra et al. to monitor some experiments, coincides with one of our observations assigned by us to ${}^{r}Q_{0}(7)$ of the 74 Ge isotopomer.

Altogether we have assigned around 25 transitions for every isotopomer, as collected in Table 1. The assignment of the ${}^{p}Q_{1}(10)$ and ${}^{r}Q_{0}(9)$ lines, both fairly strong and close in frequency, was crucial to complete the whole set of assignments, extended up to J = 13. Sometimes lines of the less abundant species were overlapped by more intense absorptions, or even in the limit of the noise level for the weaker features, which made the corresponding assignments dubious, and are missing in the table. We include in this table the ${}^{p}P_{1}(1)$ observations of Karolczak et al. [12], which were used in the refinement process with the same weight as our ICLAS data, since both experiments have a similar accuracy.

In order to carry out the analysis of the spectrum, we first had to derive rotational constants for the ground state of all five isotopomers. Karolczak et al. [12] list their observations of the 0_0^0 band for ${}^{74}H_2$, and also the ground state constants they derive for this species, but they do not provide any information on the other isotopomers. They also give their estimation of the r_0 molecular structure, calculated by averaging over the three results that can be achieved

$\overline{J' K'_{a}}$		$K'_{\rm c}$	J''	$K_{\rm a}''$	$K_{\rm c}''$	⁷⁶ Ge ⁷⁴ Ge		⁷⁴ Ge	re ⁷³ Ge			⁷² Ge		⁷⁰ Ge	
						obs.	10^{3} (o–c)	obs	10^{3} (o–c)	obs	$10^{3} (o-c)$	obs	$10^{3} (o-c)$	obs	$10^{3} (o-c)$
0	0	0	1	1	0	17 094.693 ^a	-0.7	17094.978 ^a	-1.4	17095.122 ^a	2.2	17095.280	8.0	17095.589 ^a	3.1
2	0	2	2	1	2	17105.306	26.2	17105.573	12.9	17105.707	9.4	17105.864	8.9	17106.160	-6.1
3	0	3	3	1	3	17105.573	[-16.6]	17 105.864 ^b	2.5	17106.071	[75.5]	17 106.165 ^b	11.7	17106.381	[-78.3]
1	0	1	1	1	1	17105.864	[-26.6]	17 106.165 ^b	- 8.9	17106.381	[67.6]	17106.458	-10.0	17106.792	10.9
4	0	4	4	1	4	17 106.792	-12.8	17107.055	-10.9	17107.198	1.7	17107.332	-18.6	17107.630 ^b	-20.8
5	0	5	5	1	5	17108.695	-16.2	17 108.949	-11.6	17109.079	-9.0	17109.215	-19.0	17109.510	[-18.5]
6	0	6	6	1	6	17111.065	-14.9	17111.312	-6.4	17111.435	-8.4	17111.578	0.3	17111.852	-14.5
7	0	7	7	1	7	17113.724	0.4	17113.965	11.6	17114.082	5.6	17114.211	12.3	17114.485	3.2
8	0	8	8	1	8	17116.550	28.6	17116.782	36.5	17116.888 ^b	20.7	17117.030	50.0	17117.286	28.2
4	1	4	4	0	4	17116.712	[68.4]	17116.895	[33.9]	17117.023	[-9.2]	17117.183	[33.4]	17117.534	[70.7]
5	1	5	5	0	5	17116.712	-1.0	17116.895	-41.8	17117.023	[-72.3]	17117.183	-40.3	17117.534	11.3
3	1	3	3	0	3	17117.130	[-54.0]	17117.398	2.1	17117.534 ^b	-44.7	17117.703	17.3	17118.025	12.4
6	1	6	6	0	6	17117.285	[-45.0]	17117.534	-26.2	17117.706	-0.1	17117.839	-4.9	17118.117	-12.1
7	1	7	7	0	7	17118.422	-11.9	17118.671	0.8	17118.803	-1.4	17118.941	-10.0	17119.251	[28.2]
2	1	2	2	0	2	17118.422	[11.6]	17118.671	[53.8]	17118.803	[-8.1]	17118.941	[31.9]	17119.251	[3.3]
9	0	9	9	1	9	17119.434	16.1	17119.643	4.1	17119.748	-12.8	17119.893	[24.7]	17120.162	19.9
8	1	8	8	0	8	17 119.958 ^b	-10.1	17120.221	11.4		[17120.334]	17120.488	-0.3	17 120.752 ^b	2.8
1	1	1	1	0	1	17 120.488 ^b	-28.7	17 120.752	28.7		[17120.924]	17121.031	14.8	17121.349	-16.2
9	1	9	9	0	9	17121.917	33.7	17122.142	13.6	17 122.296	48.4	17 122.394	-13.0	17122.619	[-41.6]
10	0	10	10	1	10	17122.394	-9.8	17122.619	- 3.9	17 122.727 ^b	-20.7	17 122.850	-4.5	17 123.087	-40.4
10	1	10	10	0	10	17124.146	7.4	17124.424	39.4	17124.522	[19.5]	17124.703	36.1	17125.030	[111.6]
11	0	11	11	1	11		[17 125.495]	17 125.673	-37.9		[17 125.844]	17125.906	-46.9	17126.302	[71.5]
11	1	11	11	0	11		[17 126.702]	17 126.905	-40.0	17127.076	7.2	17127.284	[47.8]	17 127.502	9.3
12	0	12	12	1	12	17128.671	-44.4	17128.916	-8.8		[17 129.073]	17129.135	[-50.9]	17 129.390	[-86.5]
12	1	12	12	0	12	17129.568	18.8	17129.808	23.8	17129.902	-20.7	17130.105	14.0		[17130.36
13	0	13	13	1	13	17132.000	[-64.3]	17132.294	7.3		[17132461]	17132489	[-86.8]	17132.779	[-111.8]

Table 1 Observed wavenumbers, in cm⁻¹, for the $\tilde{A}^1B_1(0,1,0)-\tilde{X}^1A_1(0,0,0)$ transition of GeH $_2$

The rotational assignment is indicated, with the observed minus calculated deviation, in 10^{-3} cm⁻¹ units. Heavily blended lines, or absorptions coincident with NH₂ lines, were not included in the fit, and their deviation is listed within brackets. Predicted wavenumbers for very weak transitions, not found in the observations, are also given in brackets. ^aRef. [12].

^bBlended lines assigned to more than one transition are given half weight in the fit.

Table 2 Rotational constants of all five GeH₂ isotopomers, in cm⁻¹, for the $\tilde{A}^1B_1(0,1,0) - \tilde{X}^1A_1(0,0,0)$ transition

	⁷⁶ Ge	⁷⁴ Ge	⁷³ Ge	⁷² Ge	⁷⁰ Ge
<i>A</i> ″	6.99262	6.99764 (212) ^a	7.00018	7.00262	7.00826
B''	6.53331	6.53330 (136) ^a	6.53331	6.53331	6.53331
C''	3.33080	3.33195 (50) ^a	3.33254	3.33310	3.33439
ν	17108.2196 (140)	17108.5104 (160)	17108.6533 (122)	17108.8079 (141)	17109.1274 (93)
A'	18.74150 (1667)	18.65388 (2206)	18.71439 (1558)	18.64895 (2142)	18.68115 (1156)
B'	4.58821 (407)	4.58555 (493)	4.58604 (382)	4.59095 (495)	4.59124 (382)
C'	3.40518 (179)	3.40762 (221)	3.40678 (173)	3.40489 (237)	3.40482 (176)
$\Delta_I' \times 10^{-6}$	0	10.22 (325)	0	11.14 (440)	0
$\Delta'_{IK} \times 10^{-3}$	-7.250 (694)	-8.354 (782)	-7.728 (656)	-10.406 (830)	-9.580 (701)
$rms \times 10^{-3}$	20	21	20	22	17

Constants for the initial state have been derived from the observations of Karolczak et al. [12] for the ⁷⁴Ge isotopomer, and scaled for the other species according to their moments of inertia. Constants of the excited state have been fitted from the vib-rotational transitions of Table 1. Uncertainties in parentheses are one standard error in units of the least significant digit. The root mean square (rms) deviation of each fit is also given.

^aRotational constant derived from the fit of the ground state energy levels deduced from the observations of Karolczak et al. [12] by constraining the distorsion constants to zero.

by deriving two molecular parameters, r_0 and θ_0 , from three data, the A_0 , B_0 and C_0 constants. To calculate the rotational constants of the other four species, we scaled the values of the ⁷⁴Ge isotopomer. using as scaling factors the corresponding ratios of the moments of inertia, obtained with the r_0 and θ_0 parameters of Ref. [12]. These scaling factors are of course only approximate, since the inertial defect is ignored in such calculation, but we believe that this approximation results in smaller errors than using the same ground state constants for all five species. Besides, it is interesting to remark that the r_0 structure of Karolczak et al. [12] is very similar to the equilibrium structure predicted in the theoretical works of Bunker. Phillips and Buenker [17] (1.591 Å and 91.4°), Balasubramanian [18] (1.587 Å and 91.5°) and Mineva et al. [19] (1.598 Å and 91.8°, from their local spin density calculation). It should be noted that a substitution of one germanium isotope by another does not induce a change in the B rotational constant within this approximation, and thus all five B_0'' values are equal. The rotational constants derived in this way are given in Table 2.

The analysis then proceeded in the standard way. We chose Watson's A-reduction, in the I^r representation. We tried to release only a limited number of parameters, namely the rotational constants and the vibrational band origin, but we found it necessary to also release at least one centrifugal distortion constant, Δ_{IK} , and in some cases Δ_{I} as well, in order to reproduce the data with a satisfactory mean square

deviation, of the order of the wavenumber accuracy of the experimental measurements. The resulting parameters for all five species are listed in Table 2. The shift in the vibrational origin is regular and of the order of 0.30 cm^{-1} for a change of two units in the isotopic mass. This is the only clear trend that is detected in the refined parameters of the different isotopomers. The band origins are estimated with good accuracy (~ 0.014 cm⁻¹), whereas Δ_{t} is the least well determined parameter. As expected, there is a very large variation in the A rotational constant with respect to the ground electronic state value. corresponding to the large increase in the equilibrium angle that takes place upon excitation of the ${}^{1}B_{1}$ state. This change in the geometrical structure also induces a reduction of the B constant, whereas the moment of inertia with respect to the axis perpendicular to the plane, and consequently the Cconstant, is little affected. The A constant is also increased, by ~ 2.25 cm⁻¹, with respect to the value estimated by Karolczak et al. [12] for the ground vibrational state of this excited electronic state ${}^{1}B_{1}$. The variation of B' with the vibrational excitation of the bending coordinate is also positive, but small, ~ 0.06 cm⁻¹, which is similar but of opposite sign to that of C'.

The Δ_{JK} parameter takes a fairly large value, of the order of 10^{-2} cm⁻¹. This may be due to the presence of some hidden perturbation among the data, even for the low K_a levels involved in the observed transitions. We found a similar behaviour

Table 3

Vibrational dependence of the rotational constants (α_i^B parameters), equilibrium values of the rotational constants derived from them (all in cm⁻¹), and equilibrium geometrical structure of the ${}^{1}B_1$ electronic state of ${}^{74}H_2$

B	B	B	Eq. volues			0
α_1	α_2	α_3	Eq. values		r _e	<i>o</i> e
0.3061	-2.2389	0.4775	15.6874	$(A_{\rm e}, B_{\rm e})$	1.5441	122.73
0.0773	-0.0674	0.0610	4.5537	$(B_{\rm e}, C_{\rm e})$	1.5412	123.13
0.0618	0.0525	0.0503	3.5424	$(C_{\rm e}, A_{\rm e})$	1.5413	122.61
				Average	1.5422 (13)	122.82 (20)
				ab initio ^a , SCF	1.544	123.4
				ab initio ^a , CI	1.566	123.2
				ab initio ^b	1.553	122.1
	α _I ^b 0.3061 0.0773 0.0618	$\begin{array}{ccc} \alpha_1^p & \alpha_2^p \\ \hline 0.3061 & -2.2389 \\ 0.0773 & -0.0674 \\ 0.0618 & 0.0525 \end{array}$	α_1^{P} α_2^{P} α_3^{R} 0.3061 -2.2389 0.4775 0.0773 -0.0674 0.0610 0.0618 0.0525 0.0503	α_1^{P} α_2^{P} α_3^{P} Eq. values 0.3061 -2.2389 0.4775 15.6874 0.0773 -0.0674 0.0610 4.5537 0.0618 0.0525 0.0503 3.5424	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

The α_2^B parameters are experimental values (from this work and Ref. [12]), and the α_1^B and α_3^B parameters are taken from the calculation of Allen and Schaeffer [20] (table 20) for SiH₂. The r_e (Ge–H) and θ_e (H–Ge–H) values have been derived from the three pairs of rotational constants and are given in Å and degrees, respectively. Comparison with previous ab initio works is also shown. ^aRef. [21].

^bRef. [18].

in the spectrum of SiH₂ [5], where the $3_{1,3}$, $4_{1,4}$ and $5_{1,5}$ levels of the excited state were shifted by a local perturbation by as much as 0.15 cm⁻¹. The perturbation, if present, is smaller in the germylene radical. The centrifugal distortion parameter becomes in this case an *effective* constant, taking an abnormally large value in order to accommodate the perturbation. The predictive character of the refined parameters for higher values of the rotational quantum numbers, especially K_a , may be limited.

The lower part of Fig. 1 shows the predicted spectra in this region, with the weight of the spectrum of each isotopomer scaled by its corresponding natural abundance.

3.2. Equilibrium geometry

With the values of the rotational constants of the $\nu_2 = 1$ level of the ¹B₁ electronic state obtained in this work, and those for the $\nu_2 = 0$ level reported by Karolczak et al. [12], it is possible to calculate the vibrational dependence of the rotational constants with the bending mode, given by the α_2^B parameters (we use here B as superscript to designate either of the rotational constants, A, B, or C). An estimation of the equilibrium structure of this electronic state requires the knowledge of the values of the α_1^B and α_3^B parameters. As far as we are aware, there has been no previous experimental or theoretical determination of these parameters. One possible approximate approach to this problem is to use the values of the SiH₂ molecule for the ν_1 and ν_3 vibrations calculated by Allen and Schaeffer [20], based on the similarity of the spectroscopic properties of these molecules. We gather in Table 3 the values of the α_i^B parameters and the equilibrium values of the rotational constants obtained therefrom. From A_{e} , $B_{\rm e}$ and $C_{\rm e}$, we have derived the equilibrium geometrical structure of the ${}^{1}B_{1}$ electronic state, taking the parameters two by two in order to determine r_{e} and θ_{e} . The results of these calculations are also listed in Table 3, with the mean average of all three values, and previous ab initio results [18,21]. It can be seen that: first, the geometrical parameters take very similar values in all three estimations, which indicates a small inertial defect error propagated in the analysis; and second, the average parameters are very close to the ab initio equilibrium structure of either Barthelat et al. [21] or Balasubramanian [18]. Interestingly, the SCF calculation of Barthelat et al. better predicts the bond distance, whereas the CI calculation gives a better result for the bond angle.

The uncertainty in the average values intrinsic to the averaging process is more than five times smaller now that in the calculation of Karolczak et al. [12], based on a r_0 structure. However, the uncertainty induced by the use of SiH₂ values instead of the unavailable ⁷⁴GeH₂ results for the α_1^B and α_3^B parameters, is difficult to ascertain. In any case, we estimate a reduction of around 0.04 Å in the bond distance and an increase of around 32° in the equilibrium angle, with respect to the structure of the ¹A₁ electronic state. The corresponding increments for the SiH₂ molecule were ~ 0.03 Å and 30.5°, respectively.

4. Conclusion

We have observed and analyzed new spectral data of the germylene radical in the visible region, which augments the scarce observations previously available for this species. The analysis of the data allows the determination of the rotational constants of all five germanium isotopomers in the $\nu_2 = 1$ level of the ${}^{1}B_1$ electronic state. From these constants and those of the $\nu_2 = 0$ level determined previously, we have carried out an improved estimation of the geometrical structure of the excited electronic state. The results confirm the ab initio predictions for this structure.

Some of the lines observed here had been detected and used to monitor GeH_2 reactions before. We now provide an assignment for these transitions, and a set of new observations which can be used for the same purpose in the future.

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References

- [1] T. Motooka, J.E. Greene, J. Appl. Phys. 59 (1986) 2015.
- [2] W. Du, L.A. Keeling, C.M. Greenlief, J. Vac. Sci. Technol. A 12 (1994) 2281.
- [3] J.E. Crowell, G. Lu, J. Electron Spectrosc. Related Phenom. 54 (1990) 1045.
- [4] A. Lloret, M. Oria, B. Séoudi, L. Abouaf-Marguin, Chem. Phys. Lett. 215 (1993) 193.
- [5] R. Escribano, A. Campargue, J. Chem. Phys. 108 (1998) 6249.
- [6] A. Campargue, R. Romanini, N. Sadeghi, J. Phys. D: Appl. Phys. 31 (1998) 1168.
- [7] H. Kawasaki, J. Kida, K. Sakamoto, T. Fukuzawa, M. Shiratani, Y. Wanatabe, Japanese J. of Appl. Phys. 37 (1998) Pt. 2, no. 4B.

- [8] K. Saito, K. Obi, Chem. Phys. Lett. 215 (1993) 193.
- [9] R. Becerra, S.E. Boganov, M.P. Egorov, O.M. Nefedov, R. Walsh, Chem. Phys. Lett. 260 (1996) 433.
- [10] K. Saito, K. Obi, Chem. Phys. 187 (1994) 381.
- [11] K. Obi, M. Fukushima, K. Saito, Appl. Surf. Sci. 79/80 (1994) 465.
- [12] J. Karolczak, W.W. Harper, R.S. Grev, D.J. Clouthier, J. Chem. Phys. 103 (1995) 2839.
- [13] U.N. Alexander, N.A. Trout, K.D. King, W.D. Lawrance, Chem. Phys. Lett. 299 (1999) 291.
- [14] M. Herman, J. Liévin, J. Vander Auwera, A. Campargue, Adv. Chem. Phys. 108 (1999) 1.
- [15] S. Gerstenkorn, P. Luc, Atlas du spectre d'absorption de la molécule d'iode, Editions du CNRS, Paris, 1978.
- [16] S.C. Ross, F.W. Birss, M. Vervloet, D.A. Ramsay, J. Mol. Spectrosc. 129 (1988) 436.
- [17] P.R. Bunker, R.A. Phillips, R.J. Buenker, Chem. Phys. Lett. 110 (1984) 351.
- [18] K. Balasubramanian, J. Chem. Phys. 89 (1986) 5731.
- [19] T. Mineva, N. Russo, E. Sicilia, M. Toscano, Int. J. Quant. Chem. 56 (1995) 669.
- [20] W.D. Allen, H.F. Schaeffer III, Chem. Phys. 108 (1986) 243.
- [21] J.-C. Barthelat, B.S. Roch, G. Trinquier, J. Satgé, J. Am. Chem. Soc. 102 (1980) 4080.