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The first spectroscopic observation of germanium carbide

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ABSTRACT

The gas phase spectrum of the germanium carbide radical has been observed at low temperature in emission from a corona excited supersonic expansion source. Many vibrational bands involving the $\Omega = 0$, 1, and 2 components of the $(2)^3\Pi$–$X^3\Pi$ system were recorded and analyzed. The equilibrium transition energy is found at 21120.3 cm^{-1}, in good agreement with theoretical predictions. The fundamental vibrational frequency for the lowest energy ground state $\Omega = 2$ component is 795.3 cm^{-1}.

1. Introduction

The electronic spectrum of the C_2 molecule has been extensively studied [1] and there are numerous well known band systems, most notably the $^3\Pi$–$X^3\Pi$ Swan system with an origin at 517 nm. In contrast until more recently there were no known spectra of the other group IVA carbides. An infra-red electronic emission spectrum of the lightest member of the series, SiC, was first observed by Bernath et al. in 1988 [2]. The ground state of SiC was observed in the form of the $A^3\Sigma^-$–$X^3\Pi$ transition in the same spectrum [3], and later at higher signal to noise by Deo and Kawaguchi [4]. Subsequently several other electronic transitions of SiC were observed, including the $C^3\Pi$–$X^3\Pi$ transition in the visible region near 440 nm [5–7]. In this work we report the first spectroscopic observation of GeC, the next member of the series. The comparable $^3\Pi$–$^3\Pi$ electronic transition, in this case labeled $(2)^3\Pi$–$X^3\Pi$, was observed near 480 nm.

The GeC molecule was first detected in 1959 by mass spectrometry by Drowart and De Maria [8]; they obtained thermodynamic properties including the dissociation energy. A more recent mass spectrometric study by Shim et al. [9] confirmed the earlier results. Shim et al. [9] also performed ab initio calculations on GeC, but their calculated dissociation energy was in significant disagreement with their experimental result. This disagreement prompted Sari et al. [10] to perform very high level ab initio calculations on the low lying electronic states of GeC. They examined every possible source of inaccuracy in the theoretical dissociation energy and concluded that the experimental results were in error. Their dissociation energy, $D_0 = 91.4$ kcal/mol, is clearly the best available value for GeC. Recently, Ueno et al. [11] performed ab initio calculations for a much larger number of electronic states of GeC. They also calculated transition probabilities between many of the GeC electronic states. Their predictions proved invaluable in our search for the electronic emission spectrum of GeC.

2. Experimental

Germanium carbide was produced in a corona excited supersonic expansion (CESE) source [12], the experimental apparatus was the same as that used to observe silicon boride [13]. Approximately 200 ppm each of the precursor gases, germane and methane, were seeded in helium at a pressure of 3 atm, expanded through a pinhole glass nozzle of about 0.5 mm diameter, and subjected to the corona electric discharge with a current of 7 mA. The reagent gases are atomized in the high pressure region of the discharge although it is likely some CH and GeH remain. The main products, CH, GeH, C_2, Ge_2, and GeC, are formed by recombination in the high pressure portion of the discharge. Spectra of all these diatomic molecules were identified as well as CH^+ and GeH^+. The discharge conditions tend to favor diatomic products; however, strong spectra of C_3 were observed. In addition some weak features likely due to polyatomic species that depended on the presence of both germane and methane were observed. To aid in the identification of which molecule was responsible for each feature, spectra were always recorded with the addition of only methane, or only germane, as well as with both gases present.

Emission from electronically excited product molecules in the region from 0 to 10 mm from the tip of the nozzle was collimated and focused on the entrance slit of a 1.3 m spectrometer (Acton

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AM-511) and the spectrum recorded with a cooled CCD camera (Princeton Instruments Pixis). The best GeC spectra were obtained by collecting light about 6 mm from the tip of the nozzle. Each spectral region was calibrated by recording the emission of a thorium/neon hollow cathode lamp and comparing the line positions to those in the atlas of Palmer and Engleman [14]. All measurements of line positions were made using GRAMS® spectroscopy software. The instrument limited linewidth varied from 0.2 to 0.8 cm^{-1} depending on the region of observation. The uncertainties in the line positions varied from 0.02 to 0.2 cm^{-1} depending on the linewidth, degree of overlap, and signal-to-noise ratio of the lines.

3. Results and analysis

An initial search for the spectrum of GeC was carried out in the 20 000 to 25 000 cm^{-1} region as the theoretical calculation of Ueno et al. [11] suggested that several band systems of GeC were likely to occur in this region. Several bands with rotationally resolved, but closely spaced lines were observed; an example is shown in Fig. 1. The structure of the bands was difficult to interpret as there were no obvious branches. The spectrum of GeC is complicated by the presence of five naturally occurring germanium isotopes with Ge-74 (36.5%), Ge-72 (27.4%), and Ge-70 (20.5%) being the most abundant. The overlapping branches from the different isotopic forms are the cause of the strange appearance of the spectra.

While most bands exhibited complex structure, the region around 21 250 cm^{-1} showed easily recognizable structure; see Fig. 2. The two strongest bands have R branch bandheads, clear P branches, and fairly weak Q branches characteristic of the $^3\Pi_2$–$^3\Pi_2$ and $^3\Pi_1$–$^3\Pi_1$ components of a $^3\Pi$–$^3\Pi$ electronic transition. The low rotational temperature (~8 K) makes the Q branches, whose intensities fall rapidly with J, appear quite strong. Ueno et al. [11] calculated T_e for the $(2)^3\Pi$–$X^3\Pi$ electronic transition of GeC to be 20 970 cm^{-1} so it was likely that this was the transition we had observed. Based on the absence of germanium isotope structure the observed bands were initially assumed to be the 0–0 vibrational band. The calculated ground state vibrational frequency is 830 cm^{-1} and another group of bands was soon found near 20 470 cm^{-1}, however the bands shown in Fig. 1 lie about 800 cm^{-1} higher suggesting that they are also separated by one quantum of ground state vibration. However no additional bands were observed about 800 cm^{-1} higher still, indicating that the bands in Fig. 1 terminate in $v'' = 0$.

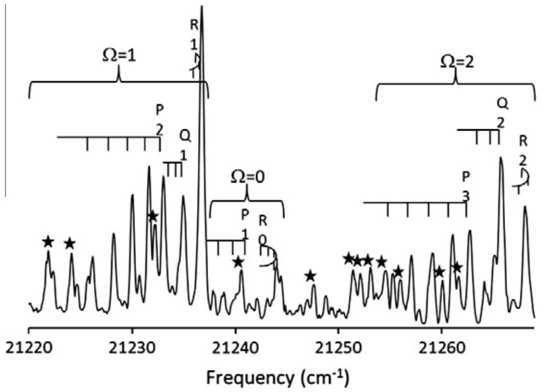

Fig. 2. The 2–1 band of the $(2)^3\Pi$–$X^3\Pi$ system of GeC. Lines marked ★ are not from GeC. The $\Omega = 1$ and 2 components are readily recognized from the Q branch intensity and first lines. The $\Omega = 0$ component was only recognized later when other stronger $\Omega = 0$ components were found.

The calculated vibrational frequency for the $(2)^3\Pi$ state is 520 cm^{-1} which suggests that the 2–1 vibrational band should have a near zero vibrational isotope effect. With this assignment for the group of bands near 21 250 cm^{-1} the other observed bands could all be assigned and additional bands searched for. At least one of the spin–orbit components of the following bands were observed with sufficient intensity to be analyzed: 0–0, 0–1, 0–2, 0–3, 1–0, 1–1, 1–2, 1–3, 2–0, 2–1, 2–2, 3–0, 3–1, 4–0, 4–1, 5–0, 6–0, and 6–2. Weaker emission from the 7–0 and 8–0 bands was also observed, but not analyzed.

The 0–0 band is extremely weak due to the large difference in r_e for the $(2)^3\Pi$ and $X^3\Pi$ states and was only observed directly by integrating the signal for 25 min, the other bands could typically be recorded with good signal-to-noise in only 1 min. The $\Omega = 2$ component, the only one clearly discernable, is shown in Fig. 3. The lines are broadened due to partially resolved isotope structure.

The intensities of the branches in the observed bands, and an apparent strong $\Delta\Omega = 0$ selection rule, are consistent with a large spin–orbit splitting of the same sign in both the $X^3\Pi$ and $(2)^3\Pi$ electronic states. The predominant configuration of the $X^3\Pi$ state in terms of the valence molecular orbitals is $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^3$ based on the theoretical calculations [11]. Following the method of Lefebvre-Brion and Field [15], and assuming equal C and Ge atomic contributions to the 1 Π molecular orbital, the spin–orbit splitting in the $X^3\Pi$ state is estimated to be $A = -1/4(\zeta(\mathrm{Ge\ 4p}) + \zeta(\mathrm{C\ 2p})) = -1/4(940 + 29)\ \mathrm{cm}^{-1} \approx -240\ \mathrm{cm}^{-1}$. The excited state configuration is more mixed, but the leading configuration in terms of the valence molecular orbitals is $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2 2\pi^1$ [16]. While the greater degree of configuration mixing makes calculation of the spin–orbit splitting more difficult for this state, it is also expected to have a large negative value of A. The close spacing of

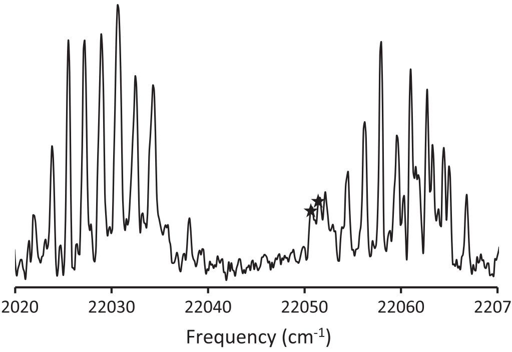

Fig. 1. A typical band of GeC. Each group of lines has overlapping branches from the different isotopomers making assignment difficult. The lower frequency group is the overlapped $\Omega = 0$ and 1 components and the higher frequency group the $\Omega = 2$ component of the $(2)^3\Pi$–$X^3\Pi$ system. Lines marked ★ are not from GeC.

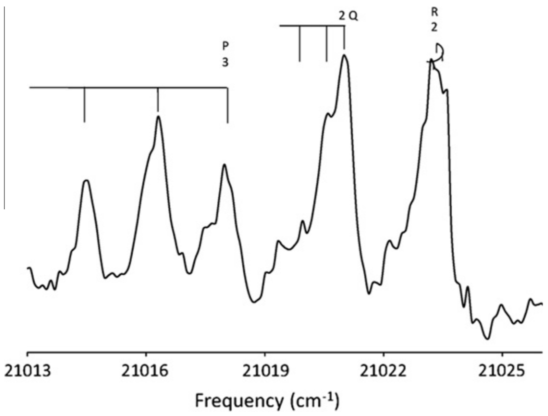

Fig. 3. The $\Omega = 2$ component of the 0–0 band of the $(2)^3\Pi$–$X^3\Pi$ system of GeC. The lines appear broadened and irregular due to partially resolved isotope structure. The large difference in geometry between the states makes the 0–0 band very weak.