



# The electronic emission spectrum of aluminum carbide

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## ABSTRACT

The gas phase spectrum of the aluminum carbide radical has been observed at low temperature in emission from a corona excited supersonic expansion source. The original rotational assignment of the  $B^4\Sigma^- - X^4\Sigma^-$  system is confirmed. Numerous bands of the previously unknown  $A^4\Pi - X^4\Sigma^-$  system with  $v' = 0-3$  and  $v'' = 1-13$  have been observed allowing for characterization of a significant part of the ground state potential energy surface.

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## 1. Introduction

The  $B^4\Sigma^- - X^4\Sigma^-$  system of aluminum carbide was first observed in emission from a hollow cathode source [1]. The high temperature and low signal to noise ratio in that spectrum meant that the first lines could not be observed in either the *P* or the *R* branches. The rotational assignment was made indirectly by comparing measured and calculated centrifugal distortion constants. While the probability of misassignment was low, it is always better to have a direct observation of the first lines. In this work we report the observation of the  $B^4\Sigma^- - X^4\Sigma^-$  system of aluminum carbide from a corona excited supersonic expansion (CESE) source. With a rotational temperature of  $\sim 60$  K the first lines of the *P* and *R* branches of the  $B^4\Sigma^- - X^4\Sigma^-$  system were strong and the original assignment was confirmed. In a recent study [2] of the isoelectronic silicon boride molecule, strong emission in the  $A^4\Pi - X^4\Sigma^-$  system was observed. A search for the  $A^4\Pi - X^4\Sigma^-$  system of aluminum carbide was successful, and a large number of vibrational bands were observed.

The search for this and other new electronic transitions were guided and helped greatly by the theoretical predictions of Bauschlicher et al. [3] who also provided a guide as to the relative intensities of the different transitions, and Tzeli and Mavridis [4,5] who provided the most accurate potential curves and molecular constants. The only other experimental observations of aluminum carbide all used matrix isolation techniques. These include the first detection of AlC using ESR by Knight et al. [6], absorption and laser induced fluorescence spectra of the  $B^4\Sigma^- - X^4\Sigma^-$  system by Thoma et al. [7], and ground state vibrational spectra by Chertihin et al. [8].

## 2. Experimental

Aluminum carbide was produced in a corona excited supersonic expansion (CESE) source [9], the experimental apparatus was the same as that used to observe silicon boride [2]. Approximately, 200 ppm of the precursor gas, trimethyl aluminum, were seeded in helium at a pressure of 4 atm, expanded through a pinhole glass nozzle of about 0.4 mm diameter, and subjected to the corona electric discharge which is sufficient to atomize the trimethyl aluminum. The main products, CH, AlH, C<sub>2</sub>, Al<sub>2</sub>, and AlC, are formed by recombination in the high pressure portion of the discharge. Spectra of all these diatomic molecules were identified; additionally there are many weak unassigned features that may arise from larger species. Since all of the diatomic products are formed simultaneously it is difficult to distinguish features due to AlC other than the known vibrational bands of the  $B^4\Sigma^- - X^4\Sigma^-$  system, all of which were readily observed.

The observation of the  $A^4\Pi - X^4\Sigma^-$  system was aided by theoretical predictions of the transition energy and spectroscopic constants [3–5] as well as our previous work on the  $A^4\Pi - X^4\Sigma^-$  system of SiB [2] which helped predict the appearance of the spectrum in the CESE source. 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 [10]. Absolute calibration is limited by whether the light from the calibration lamp and the CESE source are exactly coincident. To correct for misalignment a spectrum was recorded with a small amount of xenon gas added to the CESE source each time the nozzle was moved or a new spectral region studied. The xenon line positions were compared to those in the NIST Atomic Spectra Database to obtain the appropriate frequency correction which was then applied to all spectra recorded under the same

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conditions. All adjustments and measurements of line positions were made using GRAMS<sup>®</sup> spectroscopy software. The instrument limited linewidths varied from 0.2 to 0.5 cm<sup>-1</sup> depending on the region of observation. The uncertainties in the line positions varied from 0.02 to 0.1 cm<sup>-1</sup> depending on the linewidth and signal-to-noise ratio of the lines.

### 3. Results

The 0–0 band of the  $B^4\Sigma^- - X^4\Sigma^-$  system of AlC was readily observed when about 200 ppm of trimethyl aluminum was added to the CESE source. The spectrum obtained, which has a rotational temperature of  $\sim 60$  K, is shown in Fig. 1. The first *R* and *P* branch lines are readily apparent and the original rotational assignment was confirmed. The 1–1, 0–1, 1–2, and 2–3 bands which had been observed with rotational resolution in the hollow cathode spectrum were also recorded. Table 1 lists additional lines near the origins of these bands that were not observed in the previous work. Line positions are also given for the 3–4, 4–5, and 5–6 bands for which only bandheads were observable in the hollow cathode experiment due to the poor signal-to-noise ratio. The spin splittings of each rotational line are not observable due to the slightly lower resolution in this experiment so each transition is the average of the 4 spin components,  $P_1$  through  $P_4$  or  $R_1$  through  $R_4$ , that occur in a case b–case b  $^4\Sigma^- - ^4\Sigma^-$  transition.

With trimethyl aluminum as the reagent gas the aluminum and carbon concentrations in the discharge cannot be varied independently, hence it is difficult to find new transitions due to AlC among the strong bands of the known species. There are a large number of predicted excited states for AlC [3,5], however, it is rare to find emission from electronic states that lie above the lowest dissociation limit using the CESE source. Among the quartet states only the  $A^4\Pi$  and  $B^4\Sigma^-$  states have minima below the lowest dissociation limit. The calculated fluorescent lifetime for the  $v' = 0$  level of the  $B^4\Sigma^-$  state is fairly short at 99 ns [3], consequently this transition was best observed fairly close to the tip of the nozzle, and that close to the Corona discharge there is only time for moderate cooling to a rotational temperature of  $\sim 60$  K to occur. In contrast, the  $A^4\Pi - X^4\Sigma^-$  transition is predicted to be quite weak with a transition dipole moment of 0.0257 a.u. at  $3.8 a_0$  [3], corresponding to a fluorescent lifetime of 125  $\mu$ s.

The terminal velocity for an ideal free expansion of room temperature helium into a vacuum is 1800 m/s or 1.8 mm/ $\mu$ s. Emission from excited states with short fluorescent lifetimes ( $< \sim 1 \mu$ s) usually drops very rapidly with distance from the nozzle. There is also

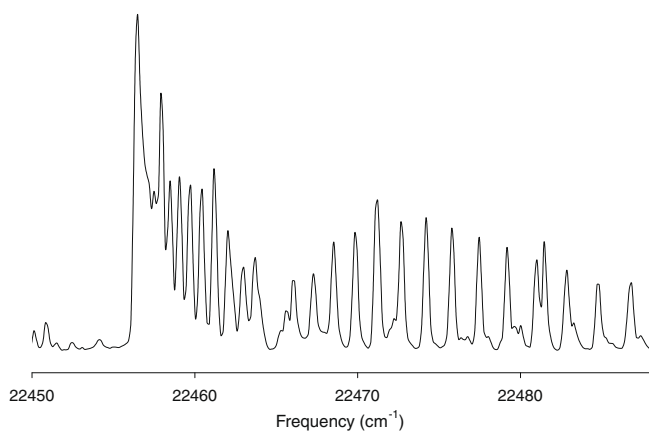


Fig. 1. The 0–0 band of the  $B^4\Sigma^- - X^4\Sigma^-$  system of AlC. The first lines in the *P* and *R* branches are clearly visible in the jet-cooled spectrum confirming the rotational assignment.

Table 1  
Observed Lines in the  $B^4\Sigma^- - X^4\Sigma^-$  system of AlC (in cm<sup>-1</sup>).<sup>a</sup>

| N               | P(N)            | R(N)            |
|-----------------|-----------------|-----------------|
| <i>0–1 Band</i> |                 |                 |
| 0               |                 | 21 819.89 0.03  |
| 1               | 21 817.76 0.10  |                 |
| 2               | 21 816.74 0.02  | 21 822.37 0.03  |
| 3               | 21 815.84 0.00  | 21 823.73 0.04  |
| 4               | 21 815.05 0.03  | 21 825.15 0.02  |
| 5               | 21 814.33 0.05  | 21 826.66 0.00  |
| 6               | 21 813.64 0.02  | 21 828.24 –0.01 |
| 7               |                 |                 |
| 8               |                 | 21 831.67 –0.00 |
| <i>1–2 Band</i> |                 |                 |
| 0               |                 | 21 900.75 –0.01 |
| 1               | 21 898.56 –0.02 | 21 901.95 0.00  |
| 2               | 21 897.63 –0.02 | 21 903.18 –0.02 |
| 3               | 21 896.73 –0.04 | 21 904.51 –0.03 |
| 4               | 21 895.92 –0.03 | 21 905.95 –0.00 |
| 5               | 21 895.18 –0.04 | 21 907.42 –0.03 |
| 6               | 21 894.54 –0.01 | 21 909.00 –0.02 |
| 7               | 21 893.95 –0.03 | 21 910.62 –0.05 |
| <i>2–3 Band</i> |                 |                 |
| 0               |                 | 21 974.24 0.06  |
| 1               | 21 972.08 0.05  | 21 975.31 –0.04 |
| 2               | 21 971.11 0.01  | 21 976.60 0.01  |
| 3               | 21 970.22 –0.01 | 21 977.93 0.02  |
| 4               | 21 969.42 0.01  | 21 979.31 0.01  |
| 5               | 21 968.68 0.00  | 21 980.75 –0.01 |
| 6               | 21 968.01 0.00  |                 |
| 7               | 21 967.44 0.01  |                 |
| 8               | 21 966.91 –0.00 |                 |
| <i>3–4 Band</i> |                 |                 |
| 0               |                 | 22 038.80 –0.03 |
| 1               | 22 036.64 –0.06 | 22 040.03 0.04  |
| 2               | 22 035.72 –0.06 | 22 041.25 0.05  |
| 3               | 22 034.87 –0.04 | 22 042.51 0.03  |
| 4               | 22 034.00 –0.09 | 22 043.84 –0.01 |
| 5               | 22 033.28 –0.06 | 22 045.27 –0.00 |
| 6               | 22 032.64 –0.03 | 22 046.76 –0.02 |
| 7               | 22 032.04 –0.04 | 22 048.35 0.01  |
| 8               | 22 031.48 –0.06 | 22 049.98 0.00  |
| 9               | 22 031.05 –0.03 | 22 051.68 –0.01 |
| 10              | 22 030.64 –0.05 | 22 053.44 –0.02 |
| 11              | 22 030.31 –0.07 | 22 055.28 –0.02 |
| 12              |                 | 22 057.21 –0.01 |
| 13              |                 | 22 059.19 –0.01 |
| 14              |                 | 22 061.25 0.00  |
| 15              |                 | 22 063.37 –0.00 |
| 16              |                 | 22 065.54 –0.01 |
| 17              |                 | 22 067.80 –0.01 |
| 18              |                 | 22 070.09 –0.04 |
| <i>4–5 Band</i> |                 |                 |
| 0               |                 | 22 092.83 0.02  |
| 1               | 22 090.75 0.04  | 22 093.94 –0.00 |
| 2               | 22 089.79 –0.00 | 22 095.16 0.04  |
| 3               | 22 088.95 0.04  | 22 096.38 0.01  |
| 4               | 22 088.10 0.01  | 22 097.70 0.01  |
| 5               | 22 087.28 –0.04 | 22 099.08 0.00  |
| 6               | 22 086.63 –0.00 | 22 100.59 0.07  |
| 7               | 22 085.99 –0.02 | 22 102.07 0.05  |
| 8               | 22 085.44 0.00  | 22 103.62 0.02  |
| 9               |                 | 22 105.42 0.19  |
| 10              |                 | 22 106.97 0.04  |
| <i>5–6 Band</i> |                 |                 |
| 0               |                 |                 |
| 1               |                 |                 |
| 2               | 22 130.52 –0.06 | 22 135.75 –0.07 |
| 3               |                 |                 |
| 4               |                 |                 |
| 5               | 22 128.01 –0.06 | 22 139.55 –0.05 |
| 6               | 22 127.30 –0.04 | 22 140.97 –0.01 |
| 7               | 22 126.76 0.09  | 22 142.34 –0.06 |
| 8               |                 | 22 143.89 0.01  |

<sup>a</sup> Lines positions previously observed from a hollow cathode source are given in Ref. [1].

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