

INVESTIGATION OF A LABORATORY CANDIDATE FOR THE CARRIER OF THE  
4430 Å DIFFUSE INTERSTELLAR BAND

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## ABSTRACT

The 4430 Å diffuse interstellar band (DIB) is unique among DIBs in that as one of the strong bands, it is the bluest strong band with no others observed at shorter wavelengths. This position at the edge of the DIB "forrest" suggests it may be the easiest to replicate in the laboratory. In earlier experiments (Wdowiak 1980) we produced an interesting candidate using a gas discharge followed by cryogenic matrix isolation, and now report its further investigation. This absorption feature, produced when 1 part CH<sub>4</sub> in 200 parts Ar is discharged and frozen out ~10 K, is at a wavelength of 4500 Å in the argon matrix. Our recent experiments strongly indicate it is due to a carbon-based reactive species that is stable against mercury vapor UV radiation, and not likely to be from a contaminant. The effect of matrix shift can be estimated by considering the blueward shift between Ar and Ne matrices in the cases of the pyrene and C<sub>60</sub> cations. This suggests that a shift from 4500 Å for an Ar matrix to the vicinity of 4430 Å for a Ne matrix and the gas phase is not unreasonable. We are preparing a liquid He cooled Ne matrix isolation experiment to determine the wavelength of the feature in that matrix. Replacing CH<sub>4</sub> with C<sub>2</sub>H<sub>2</sub> results in an equivalent absorption due to C<sub>3</sub>, greatly diminished absorptions from C<sub>2</sub><sup>-</sup> and CH, and no observable feature at 4500 Å. To date our experiments indicate CH<sub>4</sub> is a favored precursor for production of the reactive carrier of the 4500 Å feature. Perhaps C<sub>2</sub>H<sub>2</sub> is not suitable because of its tendency to polymerize easily in the discharge.

## INTRODUCTION

The diffuse interstellar bands were first recognized by Paul Merrill in the 1930's (Merrill 1938) when it was noticed that there existed certain spectral absorption features which were common to a large variety and number of stars, thereby indicating their interstellar nature. There has been much debate ever since as to whether the bands arise from absorptions associated with solid-state transitions in dust particles or from transitions in gas-

phase molecules. However, most current researchers have focused on potential molecules. A brief survey of laboratory studies up to 1992 of complex molecules as the carriers of the DIBs has been given in a recent review (Miles & Sarre 1993). Laboratory measurements of positively ionized polycyclic aromatic hydrocarbon molecules have led to the suggestion that some of the unidentified DIBs may originate from naphthalene ( $C_{10}H_8^+$ ) and pyrene ( $C_{16}H_{10}^+$ ) cations (Salama & Allamandola 1992). The latest report on the same issue presents evidence that the highly unsaturated hydrocarbon radicals,  $C_nH_m$ , where  $n = 6-12$  and  $m < 3$ , produced in a discharge from a mixture of 10% di-acetylene ( $C_4H_2$ ) in argon in a laboratory, may be responsible for some of the interstellar bands (Fulara et al. 1993). Like the results of Salama and Allamandola, close coincidences within matrix shift limits were found, but the assignment of those bands results in a conflict that other strong features revealed in the same laboratory data do not correspond to known DIBs. An early effort on our part resulted in production of absorption bands of species frozen in isolation in an argon matrix at 13 K, that we argued correlated in wavelength with the strongest of the DIBs (Wdowiak 1980). Those experiments were inspired by the proposal of linear carbon-chain molecules suggested by Douglas (1977). We attempted to produce such free radical species in our original experiment using an electrical discharge of a gas mixture of 0.48% methane in argon. Such a discharge will produce CH,  $C_2^-$ ,  $C_3$ , and unknown species having 8 bands at wavelengths close to those of the strongest DIBs as then cataloged by Herbig (1975). Very importantly, a broad band at 4500 Å became the first to be noticed in terms of order of appearance. This wavelength is within matrix shift limits of the bluest strong DIB centered at 4428 Å. These bands satisfy the criteria to be considered for identification as described in our 1980 paper (Wdowiak 1980). Other spectral features, resulting from similar experiments, that are of astrophysical interest and are tentatively assigned to be HCO are reported in Wdowiak, Lee, & Beegle (1994). In this symposium, we report our focus on the laboratory investigation of the broadest DIB,  $\lambda 4430$ .

## EXPERIMENTAL TECHNIQUE

Samples were prepared by introducing a mixture of 0.52%  $CH_4$  in Ar through a small capillary tube where it was exposed to a hollow electrode and then frozen out on a sapphire disk held at a constant temperature of 14 K by a cryogenic refrigerator. Spectra of frozen Ar, air, and  $CH_4/Ar$  mixture without discharge and of species produced from a mixture of 0.5%  $C_2H_2$  in Ar via electrical discharge were obtained at 14 K for comparison. Measurements of the spectral range from 3000 Å to 8000 Å were made. A thorough description of the experimental setup and technique are reported elsewhere (Wdowiak, Lee, & Beegle 1994).

## SPECTRA

Figure 1 shows the single beam spectra of four of our samples. Spectrum A presents the UV/visible measurement of the species produced in a gas discharge of  $CH_4$  (0.52%) and Ar (99.48%) and then matrix-isolated at 14 K. Bands resulting from  $C_3$ , CH, and  $C_2^-$

are indicated. Those bands due to carbon-based reactive species, which are considered to be the carriers of some of the strongest DIBs including the 4430 Å band, are stable against mercury vapor UV radiation (Wdowiak 1980; Wdowiak, Lee, & Beegle 1994) and disappear after annealing up to 40 K and back to 14 K (see Spectrum B). Spectrum C is of frozen air. The purpose of such a measurement is to determine whether that the bands appearing in the discharge tube experiments may be due to frozen O<sub>2</sub> from leakage of atmospheric gases into the vacuum system. Notice that the two strong frozen O<sub>2</sub> bands centered at 5765 and 6283 Å are not seen in spectrum A. The spectrum of species produced in a gas discharge of C<sub>2</sub>H<sub>2</sub> (0.5%) and Ar (99.5%) and then matrix-isolated at 14 K is presented in Spectrum D, which shows an equivalent absorption due to C<sub>3</sub>, greatly diminished absorptions from C<sub>2</sub><sup>-</sup> and CH, and no observable feature at 4500 Å.

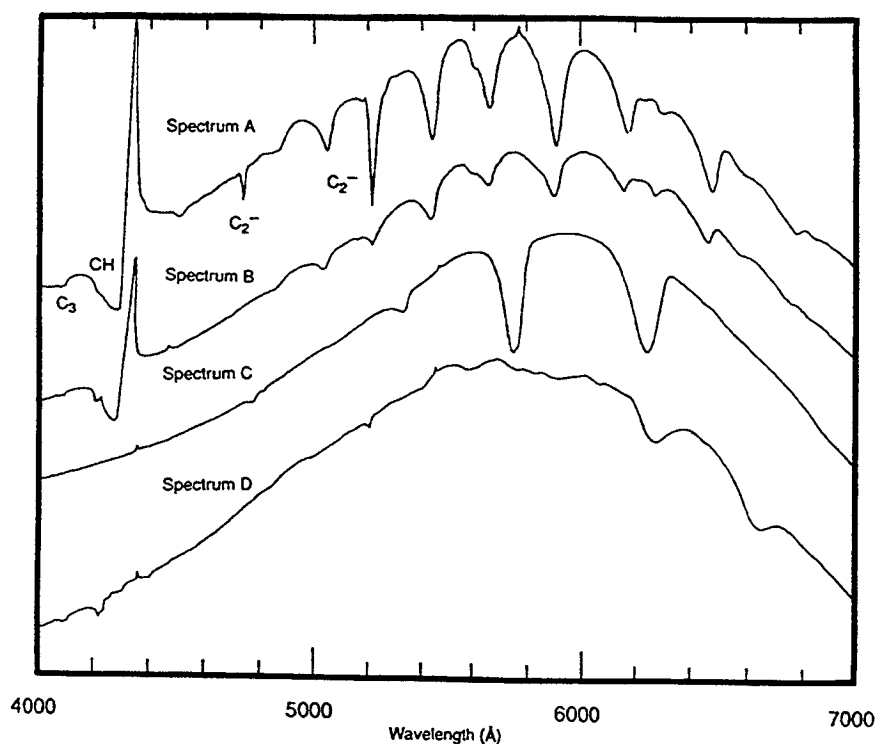


Fig. 1. Single beam absorption spectra. Spectrum A—reactive species produced in a gas discharge of CH<sub>4</sub> (0.52%) and Ar (99.48%) and then matrix isolated at 14 K. Spectrum B—after annealing up to 40 K and back to 14 K. Spectrum C—Spectrum of frozen air. Spectrum D—species produced in a gas discharge of C<sub>2</sub>H<sub>2</sub> (0.5%) and Ar (99.5%) and then matrix-isolated at 14 K.

#### 4430 Å DIB CANDIDATE

The absorption feature at 4500 Å appears in the spectrum of species produced from CH<sub>4</sub> (see Spectrum A in Figure 2). That band is the first to appear after bands of known species grow in strength. This 4500 Å DIB-like band disappears after the sample is

annealed to 40 K and back to 14 K, indicating it indeed is due to a reactive species (see Spectrum B in Figure 2). The spectrum of frozen  $\text{CH}_4$  matrix-isolated in Ar is shown in Spectrum C; notice the lack of the 4500 Å feature. Spectrum D is of species produced in a discharge of  $\text{C}_2\text{H}_2$ ; again notice the lack of features around 4500 Å. Spectra A, B, and D displayed in Figure 2 are the expanded ones of Spectra A, B, and D in Figure 1, respectively. Obviously, the 4500 Å band shown in Spectrum A is uniquely associated with the  $\text{CH}_4$  precursor and not due to the telluric contaminants.

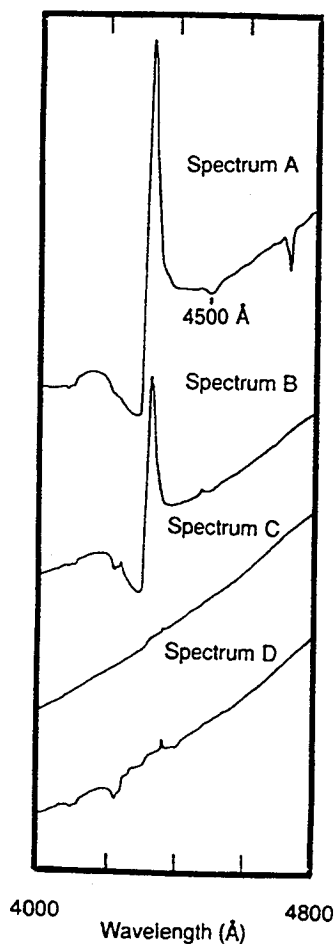


Fig. 2. Expanded spectra. Spectrum A—reactive species produced in a gas discharge of  $\text{CH}_4$  and Ar and then matrix-isolated at 14 K. Spectrum B—after annealing up to 40 K and back to 14 K. Notice the 4500 Å DIB-like band disappears after the sample is annealed. Spectrum C—frozen  $\text{CH}_4$  matrix-isolated in Ar. Spectrum D—species produced in a gas discharge of  $\text{C}_2\text{H}_2$  and Ar and then matrix-isolated at 14 K.

The problem with laboratory experiments to date is the necessity to work in inert gas matrices with the resultant shifts in wavelength away from what would occur in the gas phase. The effect of matrix shift can be estimated by considering the blueward shift between Ar and Ne matrices in the cases of the pyrene and  $\text{C}_{60}$  cations. For the fullerene

cation differences are 94 Å and 86 Å in the 9700 Å region (Gasyna et al. 1992; Joblin 1992). The shift of the pyrene ion band, which is suggested to be a candidate of the 4430 Å diffuse interstellar absorption band (Salama & Allamandola 1992), is found to be 40 Å further blueward when isolated in Ne matrix (4395 Å) as compared to when isolated in Ar (4435 Å). If the same is true for our band at 4500 Å using Ar matrix, we can expect to find our  $\lambda_{4430}$  candidate at 4460 Å in Ne with gas phase being even closer to that of the 4430 Å DIB. We demonstrated (Wdowiak 1991) that the DIB-like band produced by Kratschmer (1986) and Kurtz & Huffman (1989) initially at 4470 Å also shifts to the wavelength of our band centered at 4500 Å, upon annealing of the matrix and diffusion of reactive species while resulting in strengthening of the band. What may be going on in terms of the wavelength shift, is that the structure of the lattice of the matrix is changing. If this band, which first appears at 4470 Å when carbon is evaporated into argon, were shifted 40 Å, as pyrene does when going to neon, it would be very close to 4430 Å. Our discharge experiment by virtue of being more energetic, can be considered to incorporate the annealing process used by Kratschmer (1986) and Kurtz & Huffman (1989) while the deposition is occurring.

### CONCLUSIONS AND FUTURE WORK

To date our experiments indicate  $\text{CH}_4$  is a favored precursor for production of the carrier of the 4500 Å feature. Our experiment carried out using  $\text{C}_2\text{H}_2$  through electrical discharge does not produce the species having bands in the vicinity. Perhaps  $\text{C}_2\text{H}_2$  is not suitable because of its tendency to polymerize easily in the discharge. We note experiments using di-acetylene (Fulara et al. 1993) also failed to produce a 4430 Å analog. We think the reactive species produced from  $\text{CH}_4$  via electrical discharge is a good laboratory

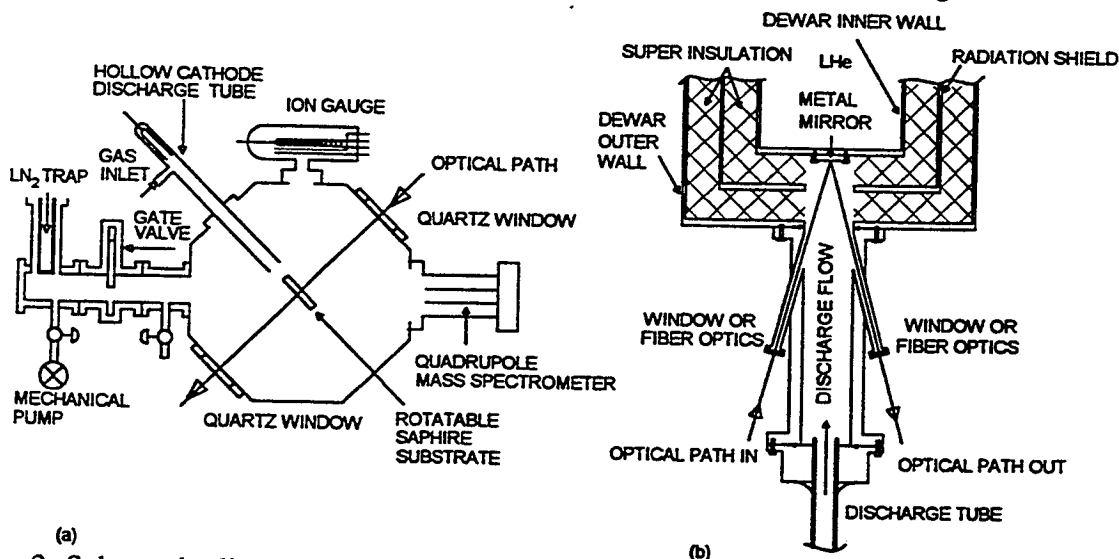


Fig. 3. Schematic diagrams of the apparatuses for future work. (a) Vacuum chamber for matrix isolation experiment with the capability for mass spectroscopy. (b) Apparatus for Ne matrix isolation at 4 K using a liquid helium dewar.

analog of the carrier of  $\lambda 4430$ . Further investigation is needed to identify the species and to determine experimentally the location of this band when the species are isolated in a Ne matrix. In the future we foresee using two different apparatuses, both schematically shown in Figure 3, for exploring the effects of matrix isolation of a hydrocarbon "soup." The first apparatus which has been built and is now being tested has the capability for mass spectroscopy using a Dycor quadrupole mass spectrometer. We anticipate being able to laser-desorb species from a discharge frozen on a sapphire disk at 11 K and to utilize the mass spectrometer to obtain mass values of those species. With this apparatus optical spectrometry is also possible. The second apparatus, which is being constructed, will allow deposition of reactive carbon-containing species in a Ne matrix at 4 K using a liquid helium dewar. We acknowledge the support of NASA grants NAGW-749 and NAGW-3902.

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