LIMITS TO INTERSTELLAR $C_4$ AND $C_5$ TOWARD $\zeta$ OPHIUCHI

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Received 2001 September 8; accepted 2001 October 9

ABSTRACT

We have made a sensitive search for the origin bands in the known electronic transitions of the linear carbon chains $C_4$ and $C_5$ at 3789 and 5109 Å toward $\zeta$ Oph ($A_v \leq 1$). The incentive was a recent detection of $C_3$ in this interstellar cloud with a column density of $1.6 \times 10^{12}$ cm$^{-2}$, plus the availability of laboratory gas phase spectra of $C_4$ and $C_5$. Further, some models of diffuse interstellar clouds predict that the abundance of these latter species should be within an order of magnitude of $C_3$. Despite achieving a signal-to-noise ratio (S/N) of 2300 to 2600 per pixel at a resolution of $\sim 110,000$, the searches were negative, leading to 3σ upper limits to the column density of $N(C_4) = 2 \times 10^{11}$ cm$^{-2}$ and $N(C_5) = 4 \times 10^{12}$ to $10^{13}$ cm$^{-2}$ where these values rely on theoretically calculated oscillator strengths. The implication of these limits is discussed along with the identification of molecules for study in future attempts to identify the carriers of the stronger diffuse interstellar bands.

Subject headings: ISM: clouds — ISM: molecules — stars: individual ($\zeta$ Ophiuchi)

1. INTRODUCTION

Carbon chain molecules are often at the forefront in discussions of diffuse interstellar bands (DIBs, see Douglas 1977; Smith, Snow, & York 1977), which are found mainly in the optical part of the spectrum (Herbig 1995). They became more appealing candidates with the discovery at mm wavelengths (McCarthy & Thaddeus 2001) of numerous polar carbon chains in dense interstellar clouds. However, only in the past few years have the gas phase electronic spectra of a number of such species (e.g., $C_4$, $C_5$, $C_{2n+1}H \ n = 3-6$), as well of related cations (e.g., $HC_{2n+1}H^+$ $n = 2-4$, $HC_{2n+1}^+$ $n = 2-4$) and anions (e.g., $C_n^- \ n = 3-11$) been detected in the laboratory, enabling direct comparison with astronomical data (e.g., Motylewski et al. 1999). The results were negative in all cases where comparisons could be made, leading to the conclusion that the column densities of these species are $\leq 10^{12}$ cm$^{-2}$ in diffuse clouds.

However, with the detection of the rotational lines in the electronic transition of $C_3$ near 4052 Å (Maier et al. 2001), corresponding to total column densities of $1-2 \times 10^{12}$ cm$^{-2}$, and the prediction of certain models of such diffuse clouds (e.g. Terzieva & Herbst 1998) that the abundances of $C_4$ and $C_5$ are less than a factor of 10 smaller than that of $C_3$, it became appealing to search for these molecules. A disadvantage compared to the electronic spectrum of $C_3$ is that, according to theoretical predictions, the oscillator strengths of the transitions appear to be smaller. Unfortunately, experimentally determined oscillator strengths are unavailable. These smaller oscillator strengths result in higher abundance limits than was the case for $C_3$. Apart from the abundances predicted for $C_4$ and $C_5$, the detection of both $C_3$ and $C_5$ in the infrared by Bernath, Hinkle, & Keady (1989) in a circumstellar shell provides a guideline. In the latter work, the concentration of $C_3$ proved to be some ten times less than that of $C_5$.

Here we report an attempt to detect the origin bands of the electronic transitions of $C_4$ ($3\Sigma_u^- - 3\Sigma_u^+$) at 3789 Å and of $C_5$ ($\Pi_u^- - \Sigma_u^+$) at 5109 Å in absorption toward the reddened star $\zeta$ Oph (HD 149757) with the Gecko spectrograph of the Canada-France-Hawaii (CFHT) 3.6 m telescope. There is already one report in the literature of a nondetection of $C_5$ (Galazutdinov, Musaev, & Kreloski 2001). The present study is an order of magnitude more sensitive. There is no prior attempt reported to detect $C_4$ in interstellar clouds, but the electronic spectrum in the gas phase was only obtained a year ago (Linnartz et al. 2000).

2. THE OBSERVATIONS

The reddened star $\zeta$ Oph (HD 149757) was observed on 2001 June 29 and 30 (UT) with the Gecko echelle spectrograph fiber-fed from the Cassegrain focus of the CFHT (Baudrand & Vitry 2000). This star is bright, having a visual extinction, $A_v$, near 1 with a rich spectrum of sharp interstellar lines. Crawford (1997) has resolved the interstellar $C_3$ at 8756 Å into two close velocity components separated by 1.1 km s$^{-1}$, which is hard to resolve at our resolution. The rapidly rotating star $\eta$ UMa (HD 120315) was observed as standard.

The detector was the rear-illuminated EEV1 CCD (13.5 μm$^2$ pixels), and the spectral regions were centered at 3789 Å in the 15th order and at 5109 Å in the 11th order. The 15th order was isolated by the Gecko ultraviolet grism, the 11th by the blue grism. Individual spectra of $\zeta$ Oph were...
spectra for \( \xi \) Oph can be seen as common residuals in the dark-subtracted and flat-fielded spectra contained a coarse structure absent from the stellar spectra, which and 5109 or 0.0109 and 0.0155 pixel (biases were taken several times each night. were recorded for each spectrograph setting, and groups of Extensive series of flat-field spectra of a quartz-iodide lamp corresponding to resolutions of stellar spectra, typically had FWHM of 3 pixels, corre-

Figure 2, we compare the stellar spectrum with one from the laboratory features, respectively. As quoted by Maier et al. (2001). These velocities were applied to each spectrum to put the interstellar features on a laboratory scale before making the comparisons discussed in the next section. The comparisons are shown in Figures 2 and 3, where the stellar spectra have been smoothed with a 3-pixel box car filter. The 3 \( \sigma \) detection limits are derived from

\[
W_{\text{max}} = 3(wd)^{1/2} (S/N)^{-1},
\]

where the 3 \( \sigma \) limiting equivalent width, \( W_{\text{max}} \), and the FWHM of the feature, \( w \), are both measured in \( \AA \), the spectrograph dispersion, \( d \), in \( \text{pixel}^{-1} \), and \( S/N \) is the signal-to-noise per pixel. We adopted \( w = 0.24 \) and 0.13 for the 3789 and 5109 \( \AA \) laboratory features, respectively.

3. RESULTS AND DISCUSSION

Our attempt to detect the \( \text{C}_4 \) 3789 \( \AA \) origin band of the known electronic systems in absorption through the diffuse cloud toward the reddened star \( \xi \) Oph was unsuccessful. In Figure 2, we compare the stellar spectrum with one from the laboratory (Linnartz et al. 2000) recorded at a temperature of around 50 K. This temperature should be representative for a nonpolar molecule in diffuse interstellar clouds; in the

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**TABLE 1**

| Wavelength (Å) | \( T^a \) | S/N\(^b\) | \( W(10^{-4} \text{ Å})\(^c\) | \( T^a \) | S/N\(^b\) | \( W(10^{-4} \text{ Å})\(^c\) | \( V_{\text{rad.} \text{ vel.}} \) (km s\(^{-1}\)) |
|----------------|-----------|----------|-----------------|-----------|----------|-----------------|---------------------|
| 3789 Å         | 11700     | 2300     | 0.67            | 10800     | 2600     | 0.50            | -14.53 ± 0.18       |
| 5109 Å         |           |          |                 |           |          |                 |                     |

\(^a\) Total exposure times in seconds.

\(^b\) Per pixel.

\(^c\) 3 \( \sigma \) equivalent width detection limit for the band head (see § 2).

\(^d\) From Maier et al. 2001.
case of $C_2$ (Lambert, Sheffer, & Federman 1995) and $C_3$ (Maier et al. 2001), comparable temperatures have been inferred. The laboratory spectrum (which differs from the published one only in that the overlapping $C_2$ lines have been removed) shows that the rotational lines are lifetime-broadened, allowing only the lines in the $P$-branch to be resolved. The intense part of the band to the blue is the $R$-head, and this feature was primarily sought in the astronomical spectrum. The $3\sigma$ upper limit for the equivalent width ($W_{\text{max}}$) detection of the $R$-head is $0.67 \times 10^{-4}$ Å. The upper limit to the column density $N_{\text{max}}$ can then be derived from

$$N_{\text{max}} = 1.13 \times 10^{20} W_{\text{max}}/\lambda^2 f \text{ cm}^{-2},$$

where $f$ is the oscillator strength of the band at wavelength $\lambda$ in Å.

Though the $3\Sigma_u^+ - 3\Sigma_g^-$ electronic transition of $C_4$ has been observed in the gas phase, the oscillator strength $f$ is not known experimentally. Two values from ab initio calculations are available which, however, differ by an order of magnitude. The first study yielded $f = 0.003$ (Pacchioni & Koutecký 1988), whereas the second gave $f = 0.0005$ (Mühlhäuser et al. 2000). The values are for the whole band system, and thus the $f_{0\to0}$ for the $3789$ Å band, will be reduced by the Franck-Condon factor for this transition. Based on the intensity distribution of the vibrational bands observed in the absorption spectrum measured in a neon matrix (Freivogel et al. 1996), this may be a factor of 5. Thus, taking $f_{0\to0}$ in the 0.0001 to 0.001 range leads to $N(C_4) \leq 4 \times 10^{12}$ to $10^{13}$ cm$^{-2}$.

Two more recent models of diffuse interstellar clouds (for which the data have been made available to the authors) with characteristics comparable to the one toward ζ Oph (van Dishoeck & Black 1986) yield $N(C_3)/N(C_4)$ ratios of about 2 (Terzieva & Herbst 1998) and 13 (Turner 2000). The detected total column density of $C_3$ is $1.6 \times 10^{12}$ cm$^{-2}$ (Maier et al. 2001). Thus, in view of the uncertainty in the oscillator strength, it is not possible to assess the predictive value of the models.

The situation is similar for $C_5$. The band system with the 5109 Å origin band shown in Figure 3 was observed first in absorption in a 5 K neon matrix (Forney et al. 1996) and then in the gas phase (Motylewski et al. 1999). It was assigned as the $1\Pi_u - 1\Sigma_g^+$ electronic transition by analogy to the comet band system of $C_3$. The rotational structure is only partially resolved due to line widths of 0.7 cm$^{-1}$ (homogeneous broadening due to intramolecular processes). The oscillator strength $f_{0\to0} = 0.02$ was estimated by taking the experimentally known value for $C_3$ ($f_{0\to0} = 0.016$) and scaling this up by the length of the molecule, as simple quantum models such as particle-in-a-box predict.

However, on the basis of recent theoretical calculations, it is proposed that the 5109 Å band system is, in fact, a forbidden transition to $1\Delta_u$ and/or $1\Sigma_u^-$ states (Hanrath & Peyerimhoff 2001). The oscillator strength could not be calculated because the vibronic effects which lead to its intensity would have to be correctly accounted for.

There is another band system in the neon absorption spectrum, with the origin band at 4454 Å (unpublished data from the laboratory at Basel), which would then be the $1\Pi_u - 1\Sigma_g^+$ electronic transition, with calculated oscillator strength of 0.03 (Hanrath & Peyerimhoff 2001); an earlier $f$ value for this transition was 0.037 (Kolbuszewski 1995). A pragmatic approach to the estimation of the oscillator strength for the 5109 Å band is to use the relative intensities of the absorption systems in the 5 K neon matrix. The 4454 Å absorption band system appears about a factor of 5 more intense than the 5109 Å one, implying an $f$ value for the system of around 0.006. The $f_{0\to0}$ value for the 5109 Å band will then be reduced further by its Franck-Condon factor to yield $f_{0\to0}$ around 0.001. The lower spectrum in Figure 3 is that recorded toward ζ Oph. The signal-to-noise ratio (2600) is high, leading to a 3σ detection limit of $5 \times 10^{-5}$ Å. As the laboratory spectrum corresponds to a temperature of around 50 K, about 10 rotational lines comprise the $Q$-band head. This means that our astronomical measurements had a detection limit for an individual rotational line of $\sim 5 \times 10^{-6}$ Å. For a lower temperature of 10 K, for example, there would still be some five lines unresolved within the band to give a 3σ limit per line of $\sim 10^{-5}$ Å.

Our 3σ detection limit of $\sim 5 \times 10^{-5}$ Å for the band, together with $f_{0\to0} = 0.001$, leads to $N(C_5) \leq 2 \times 10^{11}$ cm$^{-2}$. Galazutdinov et al. (2001) recently reported a value of $N(C_5) \leq 10^{11}$ cm$^{-2}$; however, the authors were unaware...
of the spectroscopic problems associated with the oscillator strengths and used a value of \( f_{0-o} \) of 0.02. Taking the presently suggested \( f_{0-o} = 0.001 \) increases their value to \( N(C_3) \leq 2 \times 10^{12} \text{ cm}^{-2} \), which is an order of magnitude less sensitive than our results.

4. CONCLUSIONS

According to the results reported here, \( N(C_4) \leq 4 \times 10^{12} \) to \( 10^{13} \text{ cm}^{-2} \), and \( N(C_5) \leq 2 \times 10^{11} \text{ cm}^{-2} \) in the diffuse cloud toward \( \zeta \) Oph, while \( N(C_3) = 1.6 \times 10^{12} \text{ cm}^{-2} \) from the earlier study (Maier et al. 2001). From these column densities, we calculate abundances relative to the total column density of hydrogen \( [n(H) + 2n(H_2)] = 1.3 \times 10^{21} \text{ cm}^{-2} \) (from Table 2 of van Dishoeck & Black 1986), of \( C_3 = 2 \times 10^{-9} \), \( C_4 \leq 4 \times 10^{-9} \) to \( 10^{-10} \), and \( C_5 \leq 2 \times 10^{-10} \). The results of the two diffuse cloud models to which we have access yield abundances which are too high for \( C_3 \) by about an order of magnitude, \( 3 \times 10^{-8} \) (Terzieva & Herbst 1998) and \( 5 \times 10^{-8} \) (Turner 2000). The values from the former model correspond to quasi-steady state after \( 10^3 \) years, and the latter are for \( A_e = 1 \) and \( n = 500 \text{ cm}^{-1} \), chosen with depletions which provide a good fit for essentially all molecular species in translucent clouds and for the majority of species in diffuse clouds. Similarly, the predicted abundances are also too high for the longer chains with relative values of \( C_3:C_4:C_5 = 5:3:8 \) from Terzieva & Herbst (1998), although Turner (2000) gives \( 25:2:1 \). So it appears that photodissociation rates have been underestimated (or that other depletion mechanisms, such as electron attachment or absorption on grains, need to be included). The upper limit we have obtained of 0.1 to the \( C_5:C_3 \) ratio is consistent with the result of infrared detection of both these species in a circumstellar shell with a ratio of 0.09 (Bernath et al. 1989), suggesting that our measurements may have been close to actually detecting \( C_5 \).

The detection of polyatomic species containing carbon atoms in diffuse and translucent interstellar clouds indicates comparable column densities not larger than about \( 10^{12} \) to \( 10^{13} \text{ cm}^{-2} \). This set comprises the detection of \( C_3 \) in the optical region (Maier et al. 2001), as well as of the rotational spectra of the polar species, \( C_2H, C_3H_2 \) (Lucas & Liszt 2000), for example. So far, among polyatomic species, only \( H_4^+ \) has column densities in the diffuse medium exceeding \( 10^{14} \text{ cm}^{-2} \) (McCall et al. 1998). The implication of this for the search of appropriate molecular systems which could correspond to the stronger, narrower DIBs with typical equivalent widths of 0.1 Å, is as follows. Assuming that the species would have oscillator strengths of electronic transitions (in the visible) in the 1–10 range, as could be the case for carbon chains with 10–20 atoms, then the column density would have to be about \( 10^{11} \) to \( 10^{12} \text{ cm}^{-2} \). This column density could be easily attained by the larger carbon species, whatever their shape, because they are less efficiently photodissociated.

The suggestion by Douglas (1977) that long carbon chain molecules, \( C_n (n = 5–15) \), be considered as the carriers of DIBs, has now been tested directly for \( C_4 \) and \( C_5 \), showing that their abundance is too small. Thus, the next step in attempting to identify carriers of the DIBs would be to obtain laboratory spectra of carbon species with 10–20 atoms having electronic transitions in the visible region (e.g., as is the case for \( C_{20}, n = 8–20 \) Maier 1998), and then making a direct comparison with astronomical observations at high S/N as has been demonstrated in this work.

Support of the Swiss National Science Foundation (Project 20-63459.00) (J. P. M.), the Canadian Natural Sciences and Engineering Research Council (G. A. H. W.), and the National Research Council of Canada (D. A. B.) is gratefully acknowledged.

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