

## CONSTRAINING THE ENVIRONMENT OF CH<sup>+</sup> FORMATION WITH CH<sup>+</sup><sub>3</sub> OBSERVATIONS

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## CONSTRAINING THE ENVIRONMENT OF CH<sup>+</sup> FORMATION WITH CH<sub>3</sub><sup>+</sup> OBSERVATIONS

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### ABSTRACT

The formation of CH<sup>+</sup> in the interstellar medium (ISM) has long been an outstanding problem in chemical models. In order to probe the physical conditions of the ISM in which CH<sup>+</sup> forms, we propose the use of CH<sub>3</sub><sup>+</sup> observations. The pathway to forming CH<sub>3</sub><sup>+</sup> begins with CH<sup>+</sup>, and a steady-state analysis of CH<sub>3</sub><sup>+</sup> and the reaction intermediary CH<sub>2</sub><sup>+</sup> results in a relationship between the CH<sup>+</sup> and CH<sub>3</sub><sup>+</sup> abundances. This relationship depends on the molecular hydrogen fraction,  $f_{\text{H}_2}$ , and gas temperature,  $T$ , so observations of CH<sup>+</sup> and CH<sub>3</sub><sup>+</sup> can be used to infer the properties of the gas in which both species reside. We present observations of both molecules along the diffuse cloud sight line toward Cyg OB2 No. 12. Using our computed column densities and upper limits, we put constraints on the  $f_{\text{H}_2}$  versus  $T$  parameter space in which CH<sup>+</sup> and CH<sub>3</sub><sup>+</sup> form. We find that average, static, diffuse molecular cloud conditions (i.e.,  $f_{\text{H}_2} \gtrsim 0.2$ ,  $T \sim 60$  K) are excluded by our analysis. However, current theory suggests that non-equilibrium effects drive the reaction  $\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H}$ , endothermic by 4640 K. If we consider a higher effective temperature due to collisions between neutrals and accelerated ions, the CH<sub>3</sub><sup>+</sup> partition function predicts that the overall population will be spread out into several excited rotational levels. As a result, observations of more CH<sub>3</sub><sup>+</sup> transitions with higher signal-to-noise ratios are necessary to place any constraints on models where magnetic acceleration of ions drives the formation of CH<sup>+</sup>.

*Key words:* astrochemistry

## 1. INTRODUCTION

### 1.1. Background

Although CH<sup>+</sup> was first discovered in interstellar space nearly 70 years ago (Dunham 1937; Douglas & Herzberg 1941), the mechanism by which this simple molecule forms has remained elusive. This is because many theoretical chemical models have been unable to reproduce the large observed abundance of CH<sup>+</sup> in diffuse cloud sight lines. At present, it is thought that CH<sup>+</sup> is primarily formed by the reaction

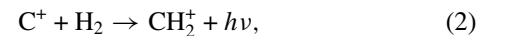


However, this reaction is highly endothermic ( $k_1 = 1.0 \times 10^{-10} \exp(-4640/T) \text{ cm}^3 \text{ s}^{-1}$ ; Federman et al. 1996), such that non-equilibrium chemistry must be invoked in order for it to proceed rapidly enough to produce the observed amounts of CH<sup>+</sup>, without vastly overproducing observed abundances of OH.

Over the past several decades, various theories have been proposed to account for an increased rate of reaction (1), including, but not limited to, neutral shocks (e.g. Elitzur & Watson 1978, 1980), magnetohydrodynamic (MHD) shocks (e.g. Draine & Katz 1986), Alfvén waves (Federman et al. 1996), and turbulent dissipation (e.g. Duley et al. 1992; Godard et al. 2009; Pan & Padoan 2009). While both neutral and MHD shocks seem to have been ruled out by observations (Gredel et al. 1993; Crawford 1995), turbulent dissipation and Alfvén waves in diffuse clouds remain viable mechanisms by which the rate of reaction (1) may be increased, and there is no clear reason to favor one theory over the other at present.

### 1.2. CH<sub>3</sub><sup>+</sup> Chemistry

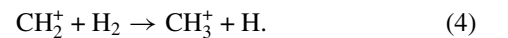
To place constraints on the physical conditions of the interstellar medium (ISM) where CH<sup>+</sup> forms—and potentially discriminate between the various proposed formation mechanisms—we have investigated the reaction network linking CH<sup>+</sup> and CH<sub>3</sub><sup>+</sup>, and made/obtained observations searching for both species. In diffuse molecular clouds, the carbon chemistry is either initiated by reaction (1), or by the radiative association reaction



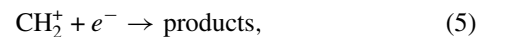
which “bypasses” CH<sup>+</sup> production. The branching fraction between these reactions is temperature dependent, and reaction (1) will dominate when collision temperatures are greater than about 400 K. Assuming CH<sup>+</sup> is formed, it will react with molecular hydrogen,



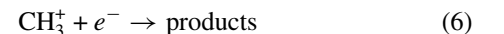
and eventually form CH<sub>3</sub><sup>+</sup> via



In addition to reaction (4) though, the CH<sub>2</sub><sup>+</sup> intermediary is also destroyed by dissociative recombination with electrons,



thus decreasing the CH<sub>3</sub><sup>+</sup> production rate. Dissociative recombination with electrons also happens to be the primary process by which CH<sub>3</sub><sup>+</sup> is destroyed:



(there are multiple product channels for reactions (5) and (6), but our analysis only depends on the overall dissociative

recombination rates). While CH<sub>3</sub><sup>+</sup> will be formed starting from both reactions (2) and (3), the latter process will dominate in clouds containing CH<sup>+</sup> ( $k_3x(\text{CH}^+)/k_2x(\text{C}^+) \gtrsim 100$ , where  $k_3 = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , McEwan et al. 1999;  $k_2 = 4 \times 10^{-16}(T/300)^{-0.2} \text{ cm}^3 \text{ s}^{-1}$ , Herbst 1982, 1985;  $x(\text{CH}^+) \sim 10^{-8}$ , Sheffer et al. 2008; and  $x(\text{C}^+) \sim 1.4 \times 10^{-4}$ , Cardelli et al. 1996). Because we are studying cloud components with CH<sup>+</sup>, we omit reaction (2) from our analysis. Note, though, that if CH<sub>3</sub><sup>+</sup> were observed in a cloud component lacking CH<sup>+</sup>, the following analysis would not be applicable.

Assuming steady state for both CH<sub>2</sub><sup>+</sup> and CH<sub>3</sub><sup>+</sup>, we can derive a relation between the concentrations of CH<sub>3</sub><sup>+</sup> and CH<sup>+</sup>, given by

$$\frac{n(\text{CH}_3^+)}{n(\text{CH}^+)} = \frac{f_{\text{H}_2}^2 k_3}{2k_6 x_e (f_{\text{H}_2} + 2x_e k_5/k_4)}. \quad (7)$$

Here, the  $k_i$ 's are the rate coefficients for reaction  $i$ ,  $f_{\text{H}_2} \equiv 2n(\text{H}_2)/n_{\text{H}}$  is the molecular hydrogen fraction (where  $n_{\text{H}} \equiv n(\text{H}) + 2n(\text{H}_2)$ ), and  $x_e$  is the electron fraction ( $x_e \equiv n_e/n_{\text{H}}$ ). The rate coefficients used in this study are  $k_4 = 1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (Smith & Adams 1977),  $k_5 = 6.4 \times 10^{-7}(T/300)^{-0.6} \text{ cm}^3 \text{ s}^{-1}$  (Larson et al. 1998), and  $k_6 = 3.5 \times 10^{-7}(T/300)^{-0.5} \text{ cm}^3 \text{ s}^{-1}$  (Mitchell 1990). However, Sheehan & St.-Maurice (2004) note that  $k_6$  was determined using vibrationally excited CH<sub>3</sub><sup>+</sup>. The rate coefficient for dissociative recombination from the ground vibrational state—the only state likely to be populated in diffuse cloud conditions—may differ from the above experimental value by about a factor of 3. Because of this possibility, during our analysis we also consider using  $3k_6$  and  $k_6/3$  in Equation (7).

Aside from the electron fraction—estimated to be  $x_e \sim 1.4 \times 10^{-4}$  in diffuse clouds via C<sup>+</sup> observations (Cardelli et al. 1996)—Equation (7) is dependent only on the molecular hydrogen fraction and the temperature (through the rate coefficients  $k_5$  and  $k_6$ ). As a result, the ratio between the abundances of CH<sub>3</sub><sup>+</sup> and CH<sup>+</sup> is governed by the interstellar physical parameters  $f_{\text{H}_2}$  and  $T$ . Observations of CH<sup>+</sup> and CH<sub>3</sub><sup>+</sup> can thus be used to infer the physical conditions in the ISM where these molecules reside.

## 2. OBSERVATIONS AND DATA REDUCTION

### 2.1. The Cyg OB2 No. 12 Sight Line

We selected the Cyg OB2 No. 12 sight line for this study because it combines a large extinction ( $A_V \sim 10$ ; Schulte 1958) and thus gas column, with a background star that is bright enough at both optical and infrared wavelengths such that the observations described below are possible. However, there is some contention as to whether the sight line mainly probes diffuse or dense material, environments which have different electron fractions. Rotational excitation analyses have been performed using C<sub>2</sub> observations, and the resulting inferred hydrogen number densities are between  $200 \text{ cm}^{-3}$  and  $400 \text{ cm}^{-3}$  (Gredel et al. 2001; Sonnentrucker et al. 2007), typical of diffuse clouds. Also, the non-detection of H<sub>2</sub>O and CO<sub>2</sub> ices by Whittet et al. (1997) led to the conclusion that there was a lack of dense molecular gas along the sight line. On the other hand, radio observations of HCO<sup>+</sup> (Scappini et al. 2000) and <sup>13</sup>CO (Casu et al. 2005) suggest that portions of the sight line may pass through denser clumps as proposed by Cecchi-Pestellini & Dalgarno (2000). Additionally, Cecchi-Pestellini & Dalgarno (2002) show that dense clumps can still be present even with the aforementioned C<sub>2</sub> analyses. Because we are examining the chemistry related to CH<sup>+</sup>, a species thought to reside mainly

in diffuse gas with  $10 \text{ cm}^{-3} < n_{\text{H}} < 300 \text{ cm}^{-3}$  (Pan et al. 2005), we adopt the diffuse molecular cloud model for our analysis. However, in Section 4 we also consider a reduced electron fraction in order to investigate the effects of varying this parameter.

### 2.2. CH<sub>3</sub><sup>+</sup>

Observations toward Cyg OB2 No. 12 and the atmospheric standard  $\alpha$  Cyg were made on 1999 November 19 using the CGS4 spectrometer (Mountain et al. 1990) at the United Kingdom Infrared Telescope (UKIRT). The spectrometer was used with its echelle grating, 0.6 wide slit, and long camera to yield a resolving power of about 37,000, and a circular variable filter (CVF) was employed to select the correct order. Spectra were centered to cover the  $\nu R(1, 0)$ ,  $\nu R(1, 1)$ , and  $\nu R(2, 2)$  rovibrational transitions of CH<sub>3</sub><sup>+</sup> at 3.18523  $\mu\text{m}$ , 3.19578  $\mu\text{m}$ , and 3.18777  $\mu\text{m}$  (vacuum wavelengths), respectively (Crofton et al. 1985). Stars were nodded along the slit in an ABBA pattern with total integration times of 864 s for Cyg OB2 No. 12 and 672 s for  $\alpha$  Cyg.

Individual frames were processed using Starlink's ORAC-DR pipeline,<sup>5</sup> specifically designed to handle UKIRT data. Spectra were then extracted from the resultant group frame (the combination of all integrations for a given target) using NOAO's IRAF package,<sup>6</sup> and imported to IGOR Pro<sup>7</sup> where we have macros set up to complete the reduction (McCall 2001). Here, artifacts from the data acquisition methods were removed, spectra were wavelength calibrated using telluric lines, and the science target spectra were divided by the telluric standard spectra to remove atmospheric absorption features. The resulting normalized spectrum of Cyg OB2 No. 12 is shown in Figure 1.

### 2.3. CH<sup>+</sup> and CH

The A–X(0–0) and A–X(1–0) transitions of CH<sup>+</sup> (4232.548 Å and 3957.692 Å, respectively; Carrington & Ramsay 1982) and the A–X(0–0) transition of CH (4300.308 Å; Zachwieja 1995) were observed simultaneously using the HIRES instrument at Keck (Vogt et al. 1994) by G. Blake and collaborators. Observations toward Cyg OB2 No. 12 were performed on 1999 June 17 and 18 with a slit width of 0.57", producing a resolving power of about 70,000. The total integration time on source was 8400 s.

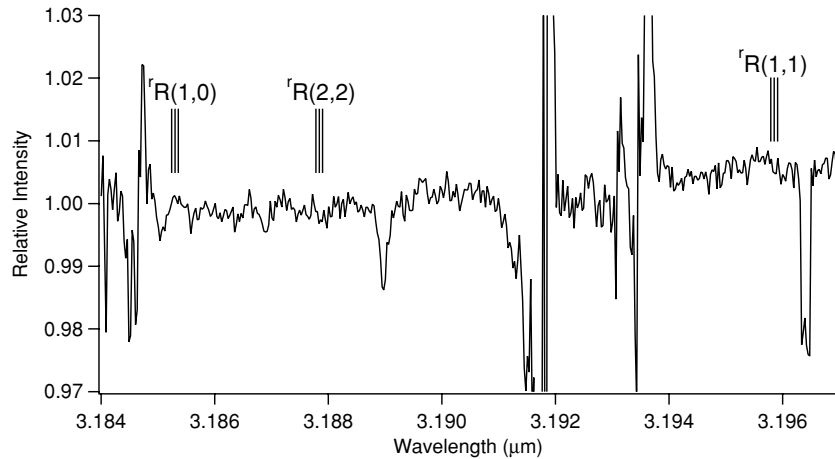
Using IRAF, the profile of the overscan region was subtracted from each image, and the frames were averaged together with the *cosmic-ray reject* option enabled. The relevant orders (10, 16, and 17) were extracted using *apall* with background subtraction enabled,<sup>8</sup> and normalized using the *continuum* routine. These astronomical spectra were then imported to IGOR PRO, along with thorium–argon arc lamp spectra used for wavelength calibration. After calibration, observed wavelengths

<sup>5</sup> See Web site at <http://www.oracdr.org/>.

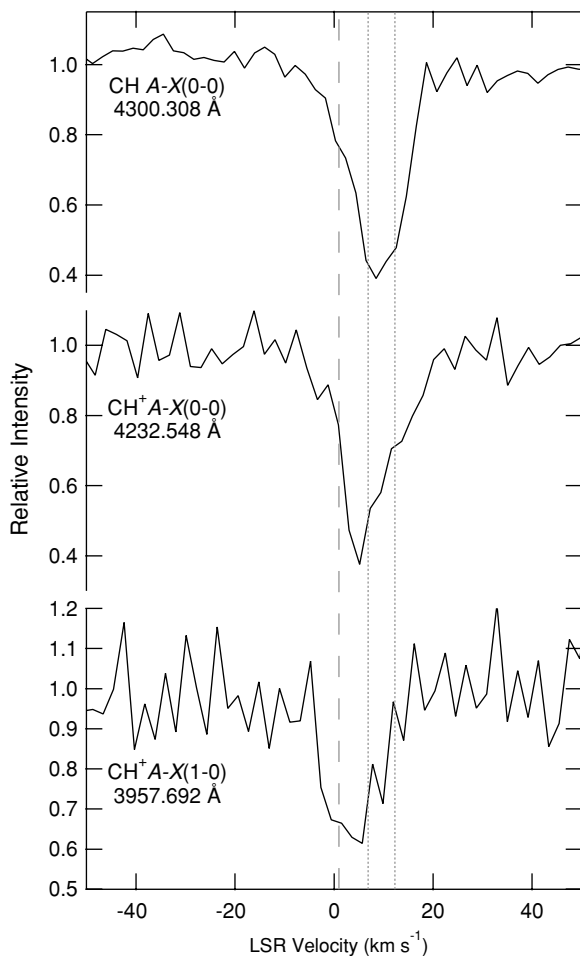
<sup>6</sup> See Web site at <http://iraf.noao.edu/>.

<sup>7</sup> See Web site at <http://www.wavemetrics.com/>.

<sup>8</sup> The initial background subtraction for order 10, which contains the 3957.692 Å line of CH<sup>+</sup>, resulted in intensities below zero at the centers of Ca II lines near 3934 Å and 3968 Å. This is most likely due to the low flux and low signal-to-noise ratio of this order. A curve of growth analysis (see Section 3.2) using the equivalent width of the 3957.692 Å line from this uncorrected spectrum resulted in no value of the Doppler parameter for which the column densities determined from the A–X(0–0) and A–X(1–0) absorption lines agreed. To remedy these unphysical results, we shifted the spectrum of order 10 so that the deeper Ca II line had zero intensity at line center.



**Figure 1.** Spectrum of Cyg OB2 No. 12 covering the  ${}^rR(1,0)$ ,  ${}^rR(1,1)$ , and  ${}^rR(2,2)$  transitions of  $\text{CH}_3^+$ . The three vertical lines underneath each transition label show the expected positions for absorption due to various cloud components along this line of sight. The  $\gtrsim 2\%$  fluctuations near  $3.185\ \mu\text{m}$ ,  $3.196\ \mu\text{m}$ , and between  $3.191\ \mu\text{m}$  and  $3.194\ \mu\text{m}$  are due to strong telluric absorption features which could not be completely removed through standard star division. The feature near  $3.189\ \mu\text{m}$  is an instrumental artifact.



**Figure 2.** Spectra of Cyg OB2 No. 12 showing the  $A-X(0-0)$  transition of CH (top spectrum) and the  $A-X(0-0)$  and  $A-X(1-0)$  transitions of  $\text{CH}^+$  (middle and bottom spectra, respectively). The vertical dotted lines mark cloud components at  $6.9\ \text{km s}^{-1}$  and  $12.3\ \text{km s}^{-1}$  seen by McCall et al. (2002) in  $\text{CN}$ ,  $\text{C}_2$ ,  $^{12}\text{CO}$ ,  $\text{H}_3^+$ , and  $\text{K I}$ . The dashed line marks a  $1\ \text{km s}^{-1}$  component only seen in  $\text{H}_3^+$  and  $\text{K I}$ .

were converted to LSR velocities, and the resulting spectra are shown in Figure 2.

**Table 1**  
 $\text{CH}_3^+$  Absorption Line Parameters

Transition	$ \mu ^2$ ( $\text{D}^2$ )	$W_\lambda$ ( $\text{m}\text{\AA}$ )	$N_{\text{level}}$ ( $10^{12}\ \text{cm}^{-2}$ )
${}^rR(1,0)$	0.0313	$<1.34$	$<3.23$
${}^rR(1,1)$	0.0313	$<1.21$	$<2.91$
${}^rR(2,2)$	0.0313	$<1.10$	$<2.65$

**Notes.** Values for  $W_\lambda$  and  $N_{\text{level}}$  are  $1\sigma$  upper limits. Transition dipole moments were calculated using Hönl–London factors and the transition moment given by Pracna et al. (1993).

### 3. RESULTS

#### 3.1. $\text{CH}_3^+$

The spectrum in Figure 1 shows no indication of absorption from any of the  $\text{CH}_3^+$  transitions considered. Upper limits on the equivalent widths were computed using  $W_\lambda < \sigma \lambda_{\text{pix}} \sqrt{N_{\text{pix}}}$ , where  $\sigma$  is the standard deviation on the continuum of the spectrum,  $\lambda_{\text{pix}}$  is the wavelength per pixel, and  $N_{\text{pix}}$  is the number of pixels expected in an absorption feature given a full width at half-maximum (FWHM) of  $12.4\ \text{km s}^{-1}$  (average FWHM measured for the  $\text{CH}^+$  and  $\text{CH}$  lines). The upper limits on column densities were then calculated using the standard relation between equivalent width and column density. The results of this analysis are shown in Table 1.

#### 3.2. $\text{CH}^+$ and $\text{CH}$

The  $\text{CH}^+$  and  $\text{CH}$  spectra in Figure 2 show broad and deep absorption profiles. While it is known that there are multiple velocity components toward Cyg OB2 No. 12, the low signal-to-noise ratios of the  $\text{CH}$  and  $\text{CH}^+$  spectra make fitting multiple components to the observed absorption features highly uncertain. Because there is no unique way to fit any of the absorption features with three separate components, we simply found the equivalent widths of each feature as a whole. Using these equivalent widths, we first computed lower limits to the column densities of both species by assuming that the lines are optically thin. As this assumption is most likely incorrect, we also computed column densities using a curve of growth

**Table 2**  
CH and CH<sup>+</sup> Absorption Line Parameters

Species	Transition	$f$	$W_\lambda$ (mÅ)	FWHM (km s <sup>-1</sup> )	$N_{\text{thin}}$ (10 <sup>14</sup> cm <sup>-2</sup> )	$N$ (10 <sup>14</sup> cm <sup>-2</sup> )	$b$ (km s <sup>-1</sup> )
CH <sup>+</sup>	A-X(0-0)	0.00545 <sup>a</sup>	103 ± 6	13.7	>1.2	2.2 <sup>+1.5</sup> <sub>-0.6</sub>	3.5 <sup>-1</sup> <sub>+4</sub>
CH <sup>+</sup>	A-X(1-0)	0.00331 <sup>a</sup>	70 ± 8	11.3	>1.5	2.2 <sup>+1.5</sup> <sub>-0.6</sub>	3.5 <sup>-1</sup> <sub>+4</sub>
CH	A-X(0-0)	0.00506 <sup>b</sup>	113 ± 4	12.2	>1.4	2.8 <sup>+4</sup> <sub>-1</sub>	3.5 <sup>-1</sup> <sub>+4</sub>

**Notes.** Lower limits ( $N_{\text{thin}}$ ) were computed under the assumption that the gas is optically thin. As this is most likely not the case, we performed a curve of growth analysis for both CH<sup>+</sup> lines (which arise from the same lower state) in order to find the  $b$ -value where both lines predict the same CH<sup>+</sup> column density. This occurs at  $b = 3.5_{+4}^{-1}$  km s<sup>-1</sup>, where  $N(\text{CH}^+) = 2.2_{-0.6}^{+1.5} \times 10^{14}$  cm<sup>-2</sup>.

<sup>a</sup> Oscillator strength from Larsson & Siegbahn (1983a).

<sup>b</sup> Oscillator strength from Larsson & Siegbahn (1983b).

analysis. Both CH<sup>+</sup> lines arise from the same lower energy state, and so should result in the same column density. Plotting the column density versus the Doppler parameter,  $b$ , for both lines, we found that the curves intersect at  $b = 3.5_{+4}^{-1}$  km s<sup>-1</sup> and  $N(\text{CH}^+) = 2.2_{-0.6}^{+1.5} \times 10^{14}$  cm<sup>-2</sup> within the uncertainties of the equivalent widths (the positive uncertainty associated with  $b$  was computed from the average FWHM of the CH<sup>+</sup> lines and the relation  $b = \Delta v_{\text{FWHM}} / (2\sqrt{\ln 2})$ ). Assuming that  $b = 3.5_{+4}^{-1}$  km s<sup>-1</sup> is also applicable to CH, we computed  $N(\text{CH}) = 2.8_{-1}^{+4} \times 10^{14}$  cm<sup>-2</sup>. All of these results, as well as the various line parameters, are shown in Table 2.

### 3.3. Interstellar Conditions

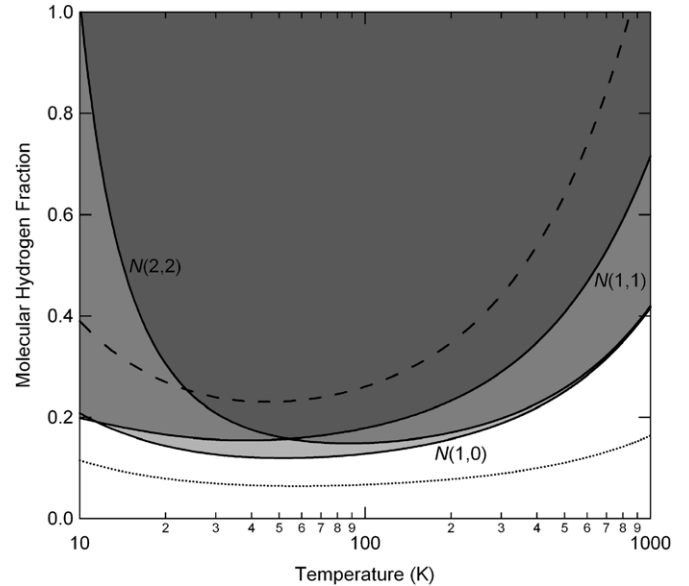
Using both CH<sup>+</sup> and CH<sub>3</sub><sup>+</sup> observations, and assuming that the two species have the same distribution along the line of sight (i.e.,  $N(\text{CH}_3^+)/N(\text{CH}^+) = n(\text{CH}_3^+)/n(\text{CH}^+)$ ), Equation (7) can be used to constrain the temperature and molecular fraction of the gas where these species reside. However, Equation (7) requires the *total* abundance of CH<sub>3</sub><sup>+</sup>, whereas we only have upper limits for the column densities of three particular states. As a result, the equation must be recast such that the left-hand side is the ratio between the column density of an individual state of CH<sub>3</sub><sup>+</sup> with the total column of CH<sup>+</sup>. This is achieved by using the partition function for CH<sub>3</sub><sup>+</sup> (computed using molecular constants from Crofton et al. 1988 and Jagod et al. 1994) to calculate the fractional population,  $P_{J,K}(T)$ , in each individual state as a function of temperature. The definition  $N(\text{CH}_3^+)P_{J,K}(T) = N(J, K)$  is then substituted into Equation (7), giving

$$\frac{N(J, K)}{N(\text{CH}^+)} = P_{J,K}(T) \frac{f_{\text{H}_2}^2 k_3}{2k_6 x_e (f_{\text{H}_2} + 2x_e k_5 / k_4)}. \quad (8)$$

Using the observed CH<sup>+</sup> column and the individual 3 $\sigma$  upper limits for CH<sub>3</sub><sup>+</sup>, we can put three separate upper limits on the left-hand side of the equation. The  $(f_{\text{H}_2}, T)$  parameter space can then be explored to determine which molecular-fraction–temperature combinations are excluded by our observations. This analysis is shown in Figure 3.

## 4. DISCUSSION

It is quite clear from Figure 3 that our analysis using CH<sup>+</sup> and CH<sub>3</sub><sup>+</sup> observations excludes a large portion of the  $(f_{\text{H}_2}, T)$  parameter space. Indeed, typical diffuse molecular cloud conditions ( $f_{\text{H}_2} \gtrsim 0.2$ ,  $T \sim 60$  K) are excluded by our upper limits to the column densities of all three observed CH<sub>3</sub><sup>+</sup> transitions. While this may not be especially surprising—equilibrium chemistry in diffuse clouds is unable to account



**Figure 3.** Plot of the  $(f_{\text{H}_2}, T)$  parameter space. The three solid curves represent contours corresponding to the values of  $f_{\text{H}_2}$  and  $T$  which reproduce the ratios  $N(1, 0)/N(\text{CH}^+)$ ,  $N(1, 1)/N(\text{CH}^+)$ , and  $N(2, 2)/N(\text{CH}^+)$  (where the  $N(J, K)$  values are 3 $\sigma$  upper limits) using Equation (8), and are labeled accordingly. Shaded regions are excluded by our analysis, and progressively darker shading indicates regions excluded by more than one observation. The dashed and dotted curves show the parameter space excluded by the  $N(1, 0)$  upper limit using  $3k_6$  and  $k_6/3$ , respectively.

for the large abundances of CH<sup>+</sup>—our observations add a new, independent method for determining that CH<sup>+</sup> cannot form under such conditions.

However, as mentioned in Section 1.2, the dissociative recombination rate coefficient for CH<sub>3</sub><sup>+</sup> with electrons,  $k_6$ , is most likely uncertain by a factor of about 3. If we allow variations between  $3k_6$  and  $k_6/3$  during our analysis using  $N(1, 0)$  with Equation (8), the dashed and dotted contours in Figure 3 result, respectively. With  $k_6/3$  essentially every temperature is excluded when the molecular fraction is greater than 0.1. For  $3k_6$ , high molecular fractions are allowed as the temperature increases beyond a few hundred Kelvin. Even with this higher rate coefficient though, most typical diffuse molecular cloud conditions are still excluded by this analysis.

While we have assumed diffuse cloud conditions throughout our analysis and given reasons for doing so, we feel it is prudent to revisit the dense clump scenario described in Section 2.1. For the sake of completeness, we examine the effects that a lower electron fraction (due to denser material) would have on our

analysis. If we decrease the electron fraction by a factor of 10 to  $x_e = 1.4 \times 10^{-5}$  (still much higher than  $x_e \sim 4 \times 10^{-8}$  assumed in dense clouds; Woodall et al. 2007), then interstellar clouds with  $f_{\text{H}_2} > 0.04$  and  $10 \text{ K} < T < 1000 \text{ K}$  are excluded. This demonstrates that as  $x_e$  decreases, regions with even smaller molecular hydrogen fractions are ruled out by our analysis.

A potentially larger uncertainty in our analysis is that we only consider a single kinetic temperature of the gas and do not account for any non-equilibrium effects. If ions are magnetically accelerated relative to neutrals, our analysis changes drastically. Assuming an effective temperature for collisions can be described as (Flower et al. 1985; Federman et al. 1996)

$$T_{\text{eff}} = T_{\text{kin}} + \frac{\mu}{3k_B}(\Delta v)^2, \quad (9)$$

where  $\mu$  is the reduced mass of collision partners,  $k_B$  is Boltzmann's constant, and  $\Delta v$  is the turbulent velocity (about  $3.3 \text{ km s}^{-1}$  according to Sheffer et al. 2008), the effective temperatures for collisions of  $\text{CH}_3^+$  with  $\text{H}_2$  and  $\text{H}$  are about 800 K and 400 K higher, respectively, than the kinetic temperature of the gas. These higher temperatures are important because it is generally assumed that the fractional populations of  $\text{CH}_3^+$  states are "thermalized" by collisions with  $\text{H}$  and  $\text{H}_2$ . If collision temperatures are hundreds of Kelvin instead of  $\sim 60 \text{ K}$ , then the expected populations of the (1,0), (1,1), and (2,2) states we observed are significantly decreased. In this case, our analysis is unable to exclude any significant portion of the ( $f_{\text{H}_2}$ ,  $T$ ) parameter space.

To use our method of analysis assuming high effective temperatures due to accelerated ions, new observations must be made. Such observations should cover the three transitions we have already examined, search for absorption due to higher energy states of  $\text{CH}_3^+$ , and obtain a higher signal-to-noise ratio in all cases. If absorption from  $\text{CH}_3^+$  can be detected, instead of only excluding portions of ( $f_{\text{H}_2}$ ,  $T$ ) space, we will be able to constrain the conditions where  $\text{CH}^+$  does form.

## 5. CONCLUSIONS

We have used observations of  $\text{CH}_3^+$  and  $\text{CH}^+$  toward the diffuse molecular cloud sight line Cyg OB2 No. 12 in an attempt to constrain the physical conditions of the ISM where these species reside. If we assume equilibrium chemistry, our analysis excludes the portion of ( $f_{\text{H}_2}$ ,  $T$ ) parameter space corresponding to average diffuse molecular clouds. This acts as an important independent check on previous studies which also concluded that the slow rate of  $\text{CH}^+$  formation ruled out equilibrium chemistry in such environments. However, our analysis cannot exclude non-equilibrium effects in diffuse clouds, and neither supports nor refutes any of the current proposed theories for  $\text{CH}^+$  formation. To do so, new observations of  $\text{CH}_3^+$  with signal-to-noise ratios much higher than those obtained in this study ( $\sim 600$ ) would be required. Also, it would be highly advantageous if the dissociative recombination rate coefficient for  $\text{CH}_3^+$  were measured at low vibrational temperatures, i.e., for the ground vibrational state.

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