HUBBLE SPACE TELESCOPE MEASUREMENTS OF VACUUM ULTRAVIOLET LINES OF INTERSTELLAR CH

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ABSTRACT

Three interstellar absorption lines near 1370 Å seen toward ζ Oph have been assigned by Watson to Rydberg transitions in the G−X (or 3d−X) band of CH. Our survey of a dozen diffuse interstellar lines of sight shows that the three absorption lines are consistent with the known column densities of CH, by deriving the following oscillator strengths: \( f(1368.74) = 0.019 \pm 0.003 \), \( f(1369.13) = 0.030 \pm 0.005 \), and \( f(1370.87) = 0.009 \pm 0.001 \). We also determined intrinsic line widths that correspond to decay rates of \((1.5 \pm 0.6) \times 10^{11} \text{ s}^{-1}, (3.8 \pm 0.7) \times 10^{11} \text{ s}^{-1}\), and \((1.1 \pm 0.6) \times 10^{10} \text{ s}^{-1}\) for \( \lambda 1368, 1369, \) and 1370, respectively. These rates are significantly higher than those associated with radiative decays, and thus are readily attributable to predissociation of the Rydberg state. A fourth interstellar line near 1271 Å has been conjectured by Watson to be the strongest transition in the 4d−X Rydberg band of CH. We detected this line along four sight lines and our spectrum syntheses show that with \( f(1271.02) = 0.007 \pm 0.002 \), it is also consistent with the known column densities of CH. In addition, we conducted a search for the F−X band of CH near 1549 Å, and successfully discovered two of its absorption features along four sight lines. The astronomical oscillator strengths derived for these features are \( f(1549.05) = 0.021 \pm 0.006 \) and \( f(1549.62) = 0.013 \pm 0.003 \). Finally, the X Per sight line provided us with an astronomical detection of another CH band, via two D−X features near 1694 Å. Comparisons with results of available theoretical calculations for the four CH bands are presented.

Subject headings: ISM: lines and bands — ISM: molecules — molecular data — ultraviolet: ISM

1. INTRODUCTION

The first listing of three unidentified (UID) features around 1369 Å and along the ‘classic’ diffuse interstellar sight line toward ζ Oph was provided by Cardelli, Savage, & Ebbets [1991]. Their listing included two lines at 1368.74 and 1370.87 Å, as well as the feature λ1369.13, which according to their remark, resembled a diffuse interstellar band (DIB) by virtue of its uncommon larger and asymmetric width. This proposition was studied further by Tripp, Cardelli, & Savage [1994], who introduced the UID1 through UID3 nomenclature for these features and suggested that UID2 at 1369.13 Å is probably the first ultraviolet (UV) analog of CH, by deriving the following oscillator strengths: \( f(1369.13) = 0.030 \pm 0.005 \), and \( f(1370.87) = 0.009 \pm 0.001 \). We also determined intrinsic line widths that correspond to decay rates of \((1.5 \pm 0.6) \times 10^{11} \text{ s}^{-1}, (3.8 \pm 0.7) \times 10^{11} \text{ s}^{-1}\), and \((1.1 \pm 0.6) \times 10^{10} \text{ s}^{-1}\) for \( \lambda 1368, 1369, \) and 1370, respectively. These rates are significantly higher than those associated with radiative decays, and thus are readily attributable to predissociation of the Rydberg state. A fourth interstellar line near 1271 Å has been conjectured by Watson to be the strongest transition in the 4d−X Rydberg band of CH. We detected this line along four sight lines and our spectrum syntheses show that with \( f(1271.02) = 0.007 \pm 0.002 \), it is also consistent with the known column densities of CH. In addition, we conducted a search for the F−X band of CH near 1549 Å, and successfully discovered two of its absorption features along four sight lines. The astronomical oscillator strengths derived for these features are \( f(1549.05) = 0.021 \pm 0.006 \) and \( f(1549.62) = 0.013 \pm 0.003 \). Finally, the X Per sight line provided us with an astronomical detection of another CH band, via two D−X features near 1694 Å. Comparisons with results of available theoretical calculations for the four CH bands are presented.

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1557 Å, and $F-X$ at 1549 Å may be detected in the interstellar medium via their vacuum UV (VUV) transitions from a Λ component of the $J'' = 1/2$ level of the $X^2\Pi$ ground state. Our search resulted in positive detections of the $F-X$ and the $D-X$ bands, but none of the $E-X$ band.

A note concerning spectroscopic notation and molecular predissociation is in order. The diatomic molecule’s rotation is designated by $J$, with $N$ being its component that is perpendicular to the internuclear axis of symmetry. Radiative dipole transitions between lower ($J',N''$) and upper ($J',N'$) levels obey $\Delta J = J' - J'' = 0, \pm 1$. Such transitions are designated by a primary letter $R$, $Q$, or $P$ for $\Delta J = +1, 0, -1$, respectively. In addition, a superscripted $S$, $R$, $Q$, or $O$ stand for $\Delta N = N' - N'' = +2, +1, 0, -1, -2$, respectively. For $\Delta N = \Delta J$ transitions the superscripted letter will repeat the primary letter, and is thus customarily omitted. Electronic states with angular momentum greater than 0, i.e., non-Σ states, interact with the nuclear spin to produce Λ-doubling of their rotational levels. Thus the $X^2\Pi$ ground state has two Λ levels 0.11 cm$^{-1}$ (1.4 km s$^{-1}$) apart, which are selectively connected by allowed transitions to upper states. Figure 1 indicates the transitions analyzed here. Owing to space limitations, Λ levels and individual $J' = N' \pm 1/2$ levels are not shown, while $N'$ level separations are shown in a highly magnified and schematic way. Since we show those levels involved with transitions discussed here, only the lowest $N'$ level for each state is properly positioned with respect to the excitation energy axis. Once a transition to an upper electronic state has occurred, the strength of overlap between state wavefunctions determines the probability of radiative predissociation. If the predissociation occurs via a state of similar electronic character, it is called homogeneous, and the rate will not vary strongly with $J'$ of the predissociated state. Otherwise, heterogeneous predissociation occurs between states of differing characters, and a strong dependence on $J'$ is observed.

2. DATA AND ITS MODELING

Our sample of 13 sight lines is obtained from spectra acquired with the Space Telescope Imaging Spectrograph (STIS) and the Goddard High-Resolution Spectrograph (GHRS). We analyzed the data, which are available from the HST archive, in order to derive $3d-X$ f-values for $\lambda\lambda1368, 1369,$ and 1370 along 12 lines of sight. We obtained smaller samples of sight lines to be analyzed in the search for additional CH absorption features from its $4d-X$, $F-X$, and $D-X$ bands. Whenever multiple exposures were available, we combined them in wavelength space for an improved signal to noise ($S/N$) ratio. In addition, when a feature (band) appeared in two adjacent orders, we combined them after correcting for any small wavelength inconsistencies. All our reductions were in IRAF and STSDAS.

Although it is known that the STIS line spread function (LSF) possesses weak wings, we could not see any obvious signatures for such wings in the highest-$R$ data. (The fact that $3d-X \lambda1369$ looks wider than other lines shows that this characteristic cannot be attributed to a global effect caused by prominent instrumental wings.) Therefore, we used a single Gaussian to describe the instrumental profile of STIS, in agreement with the findings of [Jenkins & Tripp (2001)]. Nevertheless, the STIS handbook does show that the LSF wings have a larger role in the profile for wider slits. As a result, we did allow for $R$ to be a fitted parameter during modeling of CO absorption lines (bands) taken from the same spectra used here.

We found that $R$ is lower for data taken through wider slits, and vice versa. There is a good match between the range of resolving powers for a given slit and the range found by [Bowers (1998)]. We will discuss these findings in a forthcoming publication about the CO molecule.

Table 1 provides a list of sight lines in terms of the star observed, its spectral type and Galactic direction, as well as the literature values for total $W_{4300}$ (CH), total $N$(CH), and cloud structure fractions along each line of sight. For the first three sight lines, as well as the ninth, we use our latest $N$(CH) results based on modeling with Ismod.f (see below) of high-$R$ ($\approx 170,000$) optical spectra from McDonald Observatory. For the two stars in common, $\alpha$ and $\zeta$ Per, our results agree within 5% with those of [Crane, Lambert, & Sheffer (1997)]. A more detailed description of the new optical syntheses will be provided in a future publication. All $N$(CH) determinations to date have utilized the $A^2\Delta-X^2\Pi$ 4300.313 Å “line”, which is a Λ-doublet of two $R(1/2)$ transitions only 1.4 km s$^{-1}$ apart [Black & van Dishoeck (1988)]. Table 2 lists the instrumental source for the VUV data, dataset names, exposure times, $S/N$ ratios, fitted values for the spectral resolving power, $R$ (from fits of CO absorption present in the same spectra), and CH bands detected in the HST data.

All line profiles analyzed in this paper were modeled by spectrum synthesis using Y. S.’s code, Ismod.f. The basic radiative transfer equations in this code are taken from [Black & van Dishoeck (1988)]. Fit parameters include radial velocity, $N$(CH), $f$-value, line width, and cloud component structure, which involves relative velocities, fractional abundances, and Doppler b-values. Both $N$(CH) and the cloud component structure were known a priori for each sight line and were kept fixed during the CH fits. Ismod.f employs the Voigt profile to describe the line shape as a combination of a Gaussian Doppler core and Lorentzian wings. The resulting profile is then convolved with the appropriate instrumental Gaussian profile before a comparison with the data is performed via root-mean-square computation. Ismod.f employs the simplex method to converge onto the final fit, which is found by an automated trial and error inspection of the parameter space in decreasing steps, until a certain tolerance level (usually $10^{-4}$ of the parameter’s value) has been reached. Figure 2 shows the data and Ismod.f profile syntheses of the three $3d-X$ lines toward the star $X$ Per.

3. INDIVIDUAL SIGHT LINES

We first compare a pertinent selection of our results with previously published values. Most of the work done previously concerned the well-known sight line toward $\zeta$ Oph. Our results from profile syntheses of $\lambda\lambda1368, 1369,$ and 1370 show that fitted $W_A$ values for the three lines are $5.6 \pm 0.2, 7.5 \pm 0.2,$ and $2.2 \pm 0.3$ mA, respectively, where our uncertainties reflect noise contribution over the extent of the profile from the expression $\text{FWHM}/(S/N)$. When compared to the two previous publications, our $W_{1368}$ and $W_{1370}$ agree more with
Cardelli et al. (1991) measured $W_{1369}$ toward six stars, of which three sight lines are in common with this study. Therefore, we may compare our synthesized $W_\lambda$ values (in mÅ) with those of Gnaciński et al. X Per, 8.0 ± 0.3 vs. 8.4; ζ Oph, 7.5 ± 0.2 vs. 6.3; and λ Cep, 7.5 ± 0.5 vs. 6.9. There are no major disagreements between the two sets of values. Note that for the ζ Oph sight line, the value from Gnaciński et al. is also higher than those from Cardelli et al. (1991) and Tripp et al. (1994).

Federman et al. (1995) have been the only authors to report the presence of the $\lambda_{1271}$ feature, in the direction of ζ Oph. Their reported value was $W_\lambda = 0.75 \pm 0.19$ mÅ, while our fitted result is $1.1 \pm 0.1$ mÅ. The latter agrees within 2σ of the earlier value.

4. THE 3D$^-$X 2Π BAND OF CH
4.1. Oscillator Strengths

An absorption line is produced by the combined action of $N$ absorbers per cm$^2$ along the line of sight, each removing photons from the beam at the transition wavelength ($\lambda$ in Å) at a rate that corresponds to an oscillator strength, or $f$-value. The mutual product $fN$ appears in the equation that determines the optical depth in the transition, which then generates the $W_\lambda$ of the line profile through exponential absorption along the line of sight. It is customary to have at hand transitions with known $f$-values that consequently allow the determination of $N$ of the absorbers. Here, on the other hand, we use the known values of $N$(CH) from 12 sight lines to determine the $f$-values for $\lambda\lambda$1368, 1369, and 1370.

Table 3 provides the results of our spectrum syntheses for the three 3d$^-$X lines toward our target stars: fitted $W_\lambda$, $f$-values, and inferred intrinsic Lorentzian line widths (see more about the width in the next section). Normally, $N$(CH) is determined from the A$^1$X doublet of $J'' = 1/2$ transitions at 4300.313 Å, where the two blended A levels have their populations combined. Indeed, ultra-high-$R$ spectra at 4300 Å (e.g., Lambert, Sheffer, & Crand 1990) sometimes resolve the 1.4 km s$^{-1}$ doublet, revealing equal populations for the two components. Here, we emphasize that each of our profile syntheses employs only half the value of $N$(CH) (taken from Table 1) because in all resonance transitions to higher (than $A$) electronic states of CH, the individual A components are well separated (see Lien 1984). Therefore, the $f$-values derived here are twice as large as they would have been, had the full value of $N$(CH) been used. Within the uncertainties listed, there is good agreement among all sight lines for each $f$-value. Non-weighted means for the three lines are $f(1368) = 0.019 \pm 0.003$, $f(1369) = 0.030 \pm 0.005$, and $f(1370) = 0.009 \pm 0.001$. For these averages we used fit results from the higher-$R$ STIS spectra, while avoiding 2 (in the case of $\lambda1369$) or 3 (otherwise) sight lines from lower-$R$ GHS exposures. Low-$R$ data do not provide as good a handle on intrinsic line profiles as do high-$R$ data, both in the reduction (i.e., continuum rectification) stage and in the modeling stage. Had we used the excluded results, the average $f$-values would have increased by 11%, 10%, and 3%, respectively. Thus the sum of the STIS-derived $f$-values for the three transitions is 0.058 ± 0.006, which according to Watson (2001) is providing some 76% of the total $f$-value of the 3d$^-$X band, because the three lines are the most prominent transitions in it. With the correction, this Rydberg band has a total $f$-value of 0.076 ± 0.008, as inferred by our interstellar measurements.

Watson (2001) derived a preliminary $f$-value for the 3d$^-$X band from the sum of $W_\lambda$ of the three lines in Tripp et al. (1994, 10.5 mÅ), employing $N$(CH) = 10$^{13.9}$ cm$^{-2}$ from Federman & Lambert (1998), and the expression for unsaturated line absorption, $\log(W_\lambda/\lambda) = \log(f) + \log(N)$−20.053, from Morton & Noreau (1994). From this, $f = 0.025$, which was not based on any profile spectral synthesis. Watson (2001) estimated the total band $f$-value to be 0.033. We estimate that the uncertainties associated with Watson’s $f$-values amount to 20%, based on the $W_\lambda$ uncertainties in Tripp et al.) Both values appear to be too low by a factor of 2.3 ± 0.5 when compared to our results. However, Watson’s determination was based on the full value of the $N$(CH), whereas in our modeling we use $N$(CH)/2, which is pertinent for the population of a single A-doubling level, see above. Correcting Watson’s estimate upward by a factor of 2, we get $f \approx 0.050 \pm 0.010$ for the sum of three lines, and $f \approx 0.006 \pm 0.013$ for the entire 3d$^-$X band. This happens to be in much better agreement with our rigorous spectrum synthesis results. Only two theoretical ab initio band $f$-values exist in the literature: 0.0467 from Barshain & Nebel (1978), and 0.0362 as per Watson), and 0.069 from van Dishoeck (1987). It appears that both our astronomically-derived band $f$-value, and the Watson (2001) value when corrected upward by a factor of 2, are in good agreement with the theoretical value calculated by van Dishoeck (1987), thus bolstering the case for identifying these three lines with the CH molecule. This measurement also shows 3d$^-$X to be the CH band with the largest $f$-value. Perhaps this is what Herzberg & Johns (1969) meant when they commented that G−X lines would be the strongest interstellar lines of CH.

4.2. Predissociation Widths

As mentioned in the previous section, Table 3 provides information about the Lorentzian line width derived in our modeling. The intrinsic line width is set by the lifetime of the transition’s upper level, according to the inverse quantum mechanical relationship between lifetime (limiting the interval of measurement) and line width (resulting uncertainty in measured energy). Normally, intrinsic line widths are unobservably small, owing to the relatively “long” lifetimes of radiative transitions; $\tau \geq 10^{-8}$ s yields a width of 0.01 mÅ or less, using the relationship $\Gamma$(mÅ) = $|\lambda(A)|^2/(1.884 \times 10^{16}\tau)$. Predissociation gen-
erates much shorter lifetimes for certain Rydberg states, owing to decay rates that may readily be $10^7$ times faster than radiative decay rates. Under such circumstances, the associated lifetime would be $10^{-11}$ s, leading to line widths of the order of 10 mA, which can be measured on high-$R$ ($\approx 100,000$) spectra with the help of profile synthesis. We estimate that in our highest-$R$ data it is possible to reliably extract $\Gamma$ widths of a few mA, which correspond to decay rates that are higher than a few $\times 10^{10}$ s$^{-1}$. For $f$-value syntheses that failed to converge onto a reliable $\Gamma$ solution, we fixed the line width to a value near the average from well-converged solutions. The predissociation decay rate, $k_{pr}$, is the inverse of $\tau$, and thus is directly proportional to $\Gamma$. We use both $k_{pr}$ and $\Gamma$ as descriptors of line width in terms of Lorentzian wings.

Modeling the three 3$d$–$X$ lines with lsmod.f returned values for the Lorentzian width in inverse lifetimes (s$^{-1}$), which are tabulated in Table 3. We computed the means from all sight lines with high-$R$ (non-GHRS) determinations and derived the following predissociation rates: $k_{pr}(1368) = (1.5 \pm 0.3) \times 10^{11}$ s$^{-1}$, $k_{pr}(1369) = (3.8 \pm 0.7) \times 10^{11}$ s$^{-1}$, and $k_{pr}(1370) = (1.1 \pm 0.6) \times 10^{10}$ s$^{-1}$. It can be seen that all data sets returned a well-defined line width for $\lambda 1369$, thanks to its larger $\Gamma$, but that only a few syntheses were successful in converging onto a $\Gamma$ solution for $\lambda 1370$, the profile with the narrowest wings. In fact, whereas average $k_{pr}$ values for both $\lambda 1368$ and $\lambda 1369$ are better than the 2.5 $\sigma$ detection level, $k_{pr}$ for $\lambda 1370$ is a $< 2 \sigma$ result. It is thus possible that the width of $\lambda 1370$ has not been reliably determined, and that a $3 \sigma$ upper limit of $\approx 3 \times 10^{10}$ s$^{-1}$ for $k_{pr}(1370)$ should be used instead.

According to the $\Gamma$–$\tau$ relationship, the corresponding Lorentzian profile widths of the three 3$d$–$X$ lines are 11.6, 38.4, and 1.1 mA, which correspond to 0.62, 2.05, and 0.06 cm$^{-1}$. Watson (2001) used the value 2.6 cm$^{-1}$ for the width of $\lambda 1369$, which was based on the value of $10.7$ km s$^{-1}$ in Tripp et al. (1994). We also note that the original observation of $\lambda 1369$ toward $\zeta$ Oph was described as showing an asymmetric profile. Here, our impression from the entire sample of sight lines is that the observed profiles of $\lambda 1369$ are very consistent with formation by a single transition, i.e., there are no indications for asymmetries in the line profile, especially in higher-$R$ data.

Theory has no definite bearing on these $k_{pr}$ values, yet. Van Dishoeck (1987) remarked that although predissociation is present in all bands studied by Herzberg & Johns (1969), for most bands, including the 3$d$–$X$ band at 1370 Å, it is heterogeneous. Thus the predissociation rate may approach an estimated value of $10^{10}$ s$^{-1}$ for $N'=10$, but is estimated to be about $10^{9}$ s$^{-1}$ for low $N'$, i.e., of the order of the radiative decay rate of the state. These estimates are not rigorous enough to be more accurate that an order of magnitude. Indeed, our fits and Watson’s initial probe do show that in the case of both $\lambda 1368$ and $\lambda 1369$ there is a substantial contribution to CH photodissociation, since their $k_{pr}$ values are much higher than what Van Dishoeck (1987) had suggested. According to Watson (2001), all three lines are $N'=2$ transitions.

Figure 2 shows that there is good agreement between our models and observed line profiles. For $\lambda 1369$, there is no need to invoke an analogy to the DIBs in the optical, because we see that very good fits are obtained using a single transition with broad predissociation Lorentzian wings. In addition to agreeing with Watson (2001) that CH is a very good assignment for $\lambda\lambda 1368, 1369, and 1370$, one may also conclude that VUV analogs of the optical DIBs have yet to be detected.

5. The $4d$–$X$ 2$\Pi$ Band of CH

Our inspection of archival STIS data returned four candidate sight lines with $\lambda 1271$ features that appear to be astronomical detections of the strongest transition in $4d$–$X$. The sight lines are toward X Per (shown in Figure 3), $\zeta$ Oph, HD 203532, and HD 207308, as listed in Table 4. Despite varying values of S/N and $R$, all four spectrum syntheses returned rather consistent solutions, $f = 0.007 \pm 0.002$. This $f$-value is smaller than that for $\lambda 1369$, the strongest 3$d$–$X$ transition with $f = 0.030 \pm 0.005$ reported above. A theoretical prediction from Barsuhn & Nesbet (1978) gives $f$-values of 0.0198 and 0.0186 for the 2$\Delta$ and 2$\Pi$ states in the 4d complex, respectively. If we assume that the total band $f$-value is 2.5 times the value of its strongest transition, as we find for the 3$d$–$X$ band complex and A1369, then from the $f$-value for A1271 we expect $f \approx 0.0175$ for the entire 4$d$–$X$ band. This value is in close agreement with the predictions of Barsuhn & Nesbet for a single (2$\Delta$ or 2$\Pi$) state only, falling short by a factor of 2 relative to their sum. Van Dishoeck (1987) did not include the 4d state in her $f$-value calculations.

However, van Dishoeck suggested that $k_{pr}(4d)$ would be smaller than that of the 3$d$ state owing to a smaller overlap of the 4$d$ state with the nuclear wavefunctions. Three sight lines with either the highest $R$ or the highest S/N values yielded solutions for $\Gamma$, while for HD 207308 the fit did not converge onto a reliable Lorentzian line width. With an average of $k_{pr} = (2.5 \pm 1.5) \times 10^{11}$ s$^{-1}$, this transition has a predissociation rate between those of $\lambda 1368$ and A1369. Owing to small number ($n = 3$) statistics, this $< 2 \sigma$ result seems to suffer from either noise and/or continuum biases. Furthermore, because only a single $J'' = 1/2$ transition has been found so far, the detection of 4$d$–$X$ is not as secure as those of the other CH bands described here.

6. The $F$ 2$\Sigma^+–X$ 2$\Pi$ Band of CH

Herzberg & Johns (1969) observed this band at 1549 Å, i.e., it is located between the two components of the C IV doublet $\lambda\lambda 1548, 1550$ seen in stellar and interstellar spectra. They noticed an increasing diffuseness with higher $J$, signaling heterogeneous predissociation. We detected two $J'' = 1/2$ absorption features from the $F$–$X$ band along the sight lines toward X Per (see Figure 4), HD 147683, $\zeta$ Oph, HD 207308, and $\lambda$ Cep, as listed in Table 4. The redder, weaker line at 1549.62 Å belongs to a single transition, $P^1Q_{12}$, while the stronger line at 1549.05 Å is an unresolved blend of the two transitions $Q_2$ and $Q^1R_{12}$. According to Lién (1984), who analyzed the C 2$\Sigma^+–X$ 2$\Pi$ band of CH, both $Q_2$ and $P^1Q_{12}$ have a Hön-London factor (HLF) of 4/3, while $Q^1R_{12}$ has HLF = 2/3. (Since the $F$ state is also of a 2$\Sigma^+$ character, the same HLFs should apply in $F$–$X$ and $C$–$X$ transitions.) The line of sight toward HD 23478 shows only
the strongest feature from the $F - X$ band, i.e., the blend $\lambda 1549.05$.

The averages of our fitted $f$-values, based on the known values of $N(\text{CH})/2$, are $f(1549.05) = 0.021 \pm 0.006$ and $f(1549.62) = 0.013 \pm 0.003$. The $f$-value ratio is $1.6 \pm 0.6$ for $\lambda 1549.05$ vs. $\lambda 1549.62$. Based on the actual transitions that constitute these lines and their individual HLF values, the predicted $f$-value ratio is $1.5$, showing good agreement with our measurements. The total $f$-value of $\lambda 1549.05$ equals the total band $f$-value, according to the sum of HLFS, or $4/3 + 2/3 = 6/3$. Here we derive a sum of $f = 0.021 \pm 0.006$, whereas Barsuhn & Nesbet (1978) and van Dishoeck (1987) theoretically computed values of 0.031 and 0.0095, respectively. Our value lies between the predicted $f$-values, about a factor of 2 from either one.

There is another potentially detectable $J'' = 1/2$ absorption line belonging to the $F - X$ band, $R_2$ at 1547.87 A (Herzberg & Johns 1969). We were not able to detect it owing to blending with the blue wing of the much stronger line of C IV at 1548.204 A. According to its HLF of 2/3, the $R_2$ transition would constitute the weakest $J'' = 1/2$ absorption line. Since we measure two lines composed of the three strongest transitions with verified $f$-value ratios, these first astronomical detections of the $F - X$ band of CH seem secure.

We also extracted Lorentzian widths for the absorption lines of the $F - X$ band, as listed in Table 4. As is the case for the lines of the $3d - X$ band, under conditions of high-$R$ the lines readily show that different predissociation widths are involved, confirming Herzberg & Johns's observation of heterogeneous predissociation for $F - X$. Also in a similar fashion to $3d - X$, the strongest line in the band appears to be the widest. Thus, for the blend $Q_2 + Q R_{12}$ at 1549.05 A, we find $k_{pr} = (2.7 \pm 1.3) \times 10^{11}$ s$^{-1}$, whereas $k_{pr}$ for $Q' R_{12}$ at 1549.62 A is $(1.6 \pm 0.9) \times 10^{10}$ s$^{-1}$. A Golden Rule approximation by van Dishoeck (1987) yielded a computed $k_{pr}$ of $7.6 \times 10^9$ s$^{-1}$ for the $N' = 1$ levels of the $F$ state, with a stated uncertainty of “an order of magnitude”. The two transitions with $N' = 1$ ($Q_2$ and $Q R_{12}$) are those that make up the blend at $\lambda 1549.05$, for which we find $k_{pr}$ that is larger by 1.5 orders of magnitude than the approximate prediction.

We attempted a more detailed spectrum synthesis of $\lambda 1549.05$ toward X Per that explicitly included the two transitions $Q_2$ and $Q R_{12}$, subject to the constraint of a 2:1 ratio in their HLF values. Although the fit returned a separation of $-6.2$ km s$^{-1}$ for the weaker $Q R_{12}$ relative to $Q_2$, we take this to be an upper limit because the fit yielded a solution with residuals that are somewhat smaller that the ambient noise level away from the feature. The actual energy level splitting in the $F 2 \Sigma^+$ state that controls the velocity separation between the two $\lambda 1549.05$ transitions is unknown, but we note that the $C - X$ band has its $Q R_{12}$ line located 2.2 km s$^{-1}$ to the blue of $Q_2$ (Lien 1984).

This detailed synthesis of the $Q_2 + Q R_{12}$ blend resulted in narrower Lorentzian wings for the two transitions and (predictably) lower $f$-values relative to the single-transition model. It returned $f(Q_2) = 0.010$ and $f(Q R_{12}) = 0.005$, i.e., a sum that is 12% smaller than the $f$-value fitted for the entire blend, and decay rates $k_{pr} = 1.3 \times 10^{11}$ and $1.1 \times 10^{11}$ s$^{-1}$, for $Q_2$ and $Q R_{12}$, respectively. These lower $k_{pr}$ values are still higher than the approximate prediction of van Dishoeck (1987). The similarity in decay rates for the two transitions is inconsistent with their $J'$ levels of 1/2 (for $Q_2$) and 3/2 (for $Q R_{12}$), because heterogeneous predissociation is normally revealed by $\Gamma$ having a dependence on $J(J+1)$, i.e., we expect $Q R_{12}$ to be 5 times wider than $Q_2$. Since detailed modeling attempts for other sight lines did not return separations and widths for the blended components that were in good agreement with the X Per result, the quality of the data must be insufficient for such detailed modeling, especially when the line separation is not available as a known input value.

7. THE D $^3 \Pi - X ^3 \Pi$ BAND OF CH

This band was observed by Herzberg & Johns (1969), who remarked on the relative weakness of its $Q$-branch and the apparent diffuse nature of its lines. A single sight line, that toward X Per, exhibits an absorption feature that is consistent with a detection of $\lambda 1695.34$, the strongest feature in $D - X$ (see Figure 5 and Table 4). Here the strongest feature is also an unresolved blend of the two transitions $Q_2$ and $Q R_{12}$ (Krishna Swamy & Tarafdar 1973). Furthermore, a shallower feature in the spectrum is consistent with the position of the $R_2 \lambda 1693.24$ transition of $D - X$, although it is partially blended with a stronger Si I $\lambda 1693.29$ line, see Figure 6. Upon modeling, the known $N(\text{CH})/2$ toward X Per returns $f$-values of 0.0038 $\pm 0.0011$ and 0.0012 $\pm 0.0006$ for $Q_2$ and $Q R_{12}$, respectively, while the ratio of their $f$-values is 3.2 $\pm$ 1.8. Krishna Swamy & Tarafdar (1973) theoretically predicted a 5:1 ratio for $\lambda 1695.34$ vs. $\lambda 1693.24$, a value that is consistent with our determinations. Theoretical computations by van Dishoeck (1987) gave $f = 0.0073$ for the 0$0 - 0$ band of the $^3 \Pi_1$ state, which she identified with the $D$ state. Barsuhn & Nesbet (1978) calculated a value of 0.0010 for $f(D - X)$. Our value of 0.0038 $\pm 0.0011$ for the strongest feature appears to be within a factor of 2 to 3 of the two quantum mechanical predictions. In light of the good agreement in wavelength and $f$-value with predicted values, we have high confidence in treating this case as the first astronomical detection of the $D - X$ band from CH.

Concerning Lorentzian line width, our synthesis of the blend at $\lambda 1695.34$ returned $k_{pr} = 7.0 \times 10^{10}$ s$^{-1}$, a rate which was kept fixed during the modeling of the partially blended $R_2$ line. However, Li & Lee (1999) measured decay rates of $(3.6 \pm 0.6) \times 10^{11}$ s$^{-1}$ in the laboratory for the $N' = 2$ levels of $D - X$, and Metropoulos & Mavridis (2000) calculated a life time of 1.6 ps for the same state, albeit they denoted it by the letter $E$. These consistent non- astronomical values show that predissociation dominates the decay of $D$ levels, as happens for the $3d$ levels. Consequently, we re-synthesized $\lambda 1695.34$ with a fixed input $\Gamma$ value from Li & Lee (1999), yielding $f = 0.0057 \pm 0.0023$, which is in good agreement with the calculated value of 0.0073 from van Dishoeck (1987). Likewise, the $f$-value of $\lambda 1693.24$ also increased by about 50%, see Table 4. According to Figure 5, it seems that owing to insufficient S/N our original fit of $\lambda 1695.34$ had converged onto a solution involving a noise glitch, leading to a $k_{pr}$ value that was too small. The revised fits with the
terrestrial value for $\Gamma$ are also consistent with the data.

8. CONCLUSIONS

We surveyed a sample of interstellar sight lines and specific spectral ranges to search for new astronomical detections of VUV transitions of the CH molecule, as well as to confirm Watson (2001)’s identification of four detections of VUV transitions of the CH molecule, as specific spectral ranges to search for new astronomicalIdenifications of CH as their source, based on known amounts of CH along the lines of sight, on predicted wavelength positions, and on theoretical $f$-values. Thus the decades-long tradition of optical observations of CH, utilizing its $A-X$, $B-X$, and $C-X$ bands, can now be extended into the VUV via observations of its $D-X$, $F-X$, $3d-X$ ($G-X$) bands, and, more readily, the $4d-X$ band.

We could not find any absorption features that might be identified with $E-X$ transitions of CH, listed by Herzberg & Johns (1969) to be near 1557 Å. This band is problematic with an unknown configuration, and could be arising either from an $E \, ^2\Pi$ state or it could be the $2-0$ band of $D-X$ (Chen, Chupka, & Colson 1985), which has a very low $f$-value of $3.0 \times 10^{-6}$ (van Dishoeck 1987) and a very high rate of predissociation, $k_{pr} = 1.4 \times 10^{13}$ s$^{-1}$ (Metropoulos & Mavridis 2000). Both characteristics of extremely weak oscillator strengths and extremely wide line profiles would easily render this band undetectable in astronomical, or low-$N$(CH), settings.

Finally, with the confirmation that wider-than-average line profiles are attributable to high predissociation rates and asymmetric Lorentzian wings in Rydberg transitions of CH, there are no candidates currently left in the VUV spectral regime that may be associated with the famous optical DIB bands.

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TABLE 1

| Star     | Name   | Sp.     | $l$  | $b$  | $W_{4300}$(CH) (mA) | $N_{tot}$(CH) $(10^{13} \text{ cm}^{-2})$ | $N_i$(CH)/$N_{tot}$(CH) | CH Ref. |
|----------|--------|---------|------|------|--------------------|----------------------------------|------------------------|---------|
| HD 23180 | o Per  | B1III   | 160.36 | 174.74 | 14.5 $\pm$ 0.5    | 1.90 $\pm$ 0.06                   | .37, .63                | 1       |
| HD 23478 | B3IV   | 160.76  | 174.42 | 14.1 $\pm$ 0.5 | 1.83 $\pm$ 0.07 | .74, .26                        | 1                     |
| HD 24398 | ζ Per  | B1lab   | 162.29 | 166.69 | 15.7 $\pm$ 0.1    | 2.14 $\pm$ 0.01                   | .56, .44                | 1       |
| HD 24534 | X Per  | O9.5pe  | 163.08 | 174.14 | 26.3 $\pm$ 0.9    | 3.69 $\pm$ 0.13                   | .14, .16, .70           | 2       |
| HD 147683| V760 Sco| B4V    | 344.86 | +10.99 | 18.4 $\pm$ 2.2    | 2.22 $\pm$ 0.26                   | .09, .68, .23           | 3       |
| HD 149757| ζ Oph  | O9V    | 6.28   | +23.59 | 19.0 $\pm$ 2.0    | 2.50 $\pm$ 0.25                   | .50, .08, .42           | 4       |
| HD 154368| V1074 Sco| O9a   | 349.97 | +3.22 | 38.7 $\pm$ 1.3    | 6.25 $\pm$ 0.21                   | .03, .01, .13, .18, .70, .04, .01 | 2       |
| HD 203374| B0IVpe | 100.51 | 8.62   | 17.3 $\pm$ 1.0 | 2.22 $\pm$ 0.11 | .05, .04, .32, .20, .28, .06, .05 | 5       |
| HD 203532| B3IV   | 309.46  | 31.74  | 18.0 $\pm$ 0.6 | 2.46 $\pm$ 0.08 | .40, .60                        | 1                     |
| HD 207308| B0.5V  | 103.11 | 6.82   | 23.7 $\pm$ 1.0 | 3.21 $\pm$ 0.16 | .07, .09, .57, .27               | 5                     |
| HD 207538| O9V    | 101.60 | 4.67   | 28.0 $\pm$ 1.2 | 3.81 $\pm$ 0.19 | .06, .18, .31, .31, .11, .03     | 5                     |
| HD 208266| B1V    | 102.71 | 4.98   | 25.5 $\pm$ 1.2 | 3.35 $\pm$ 0.17 | .01, .39, .37, .12, .11          | 5                     |
| HD 210839| λ Cep  | O6lab  | 103.83 | 2.61 | 16.5 $\pm$ 1.7    | 2.08 $\pm$ 0.21                   | .38, .62                | 4       |

a We used the SIMBAD database for spectral types and Galactic coordinates.

b (1) This paper; (2) Welty 2005, priv. comm.; (3) Andersson, Wannier, & Crawford 2002; (4) Crane et al. 1995; (5) Pan et al. 2004.
TABLE 2

| Star   | Instr. | Dataset | Grating | Slit (") | S/N | λ/Δλ | CH bands |
|--------|--------|---------|---------|----------|-----|------|----------|
| HD 23180 | STIS   | o64801–4 | E140H   | 0.2X0.05 | 100 | 120000 | 3d—X    |
| HD 23478 | STIS   | o6l01   | E140H   | 0.1X0.03 | 30  | 130000 | 3d—X, F—X |
| HD 24398 | STIS   | o64810–11 | E140H  | 0.2X0.05 | 90  | 120000 | 3d—X    |
| HD 24534 | STIS   | o64812–13 | E140H   | 0.1X0.03 | 105 | 140000 | 3d—X    |
| STIS   | o6lp01 | E140H   | 0.2X0.09 | 85  | 100000 | 4d—X, 3d—X |
| STIS   | o6lp02 | E140H   | 0.2X0.09 | 55  | 100000 | F—X     |
| STIS   | o6lp03 | E140H   | 0.2X0.09 | 110 | 100000 | D—X     |
| HD 147683 | STIS | o6l06   | E140H   | 0.2X0.09 | 35  | 120000 | 3d—X, F—X |
| HD 149757 | GHRSS | z0x201 | G160M   | 0.25  | 900  | 20000  | 4d—X, 3d—X |
| GHRSS  | z0x01  | G160M   | 2.0    | 110  | 15000 | F—X     |
| HD 154368 | GHRSS | z0wx02 | G160M   | 0.25  | 30   | 20000  | 3d—X    |
| HD 203374 | STIS | o6l090 | E140M   | 0.2X0.2 | 45  | 40000  | 3d—X    |
| HD 203532 | STIS | o5c01s | E140H   | 0.2X0.2 | 25  | 80000  | 4d—X    |
| HD 207308 | STIS | o63y02 | E140M   | 0.2X0.06 | 60  | 45000  | 4d—X, 3d—X, F—X |
| HD 207538 | STIS | o63y01 | E140M   | 0.2X0.06 | 55  | 45000  | 3d—X    |
| HD 208266 | STIS | o63y03 | E140M   | 0.2X0.06 | 60  | 45000  | 3d—X    |
| HD 210839 | GHRSS | z12j01 | G160M   | 0.25  | 230  | 20000  | 3d—X    |
| GHRSS  | z2x01–04 | G160M | 2.0    | 210  | 15000 | F—X     |

TABLE 3

| Star     | W_0 (mÅ) | f-value (10^-3) | k_{pr}/10^{11} (s^-1) |
|----------|-----------|-----------------|-----------------------|
| HD 23180 | 3.1 ± 0.2 | 20 ± 1          | 1.1                   |
| HD 23478 | 2.9 ± 0.7 | 20 ± 5          | 1.6                   |
| HD 24398 | 2.3 ± 0.2 | 15 ± 1          | 1.0^a                 |
| HD 24534 | 4.7 ± 0.1 | 16 ± 1          | 0.8                   |
| HD 147683 | 4.5 ± 0.8 | 25 ± 5          | 0.8                   |
| HD 149757 | 5.6 ± 0.2 | 29 ± 3          | 2.1                   |
| HD 154368 | 11.3 ± 1.2 | 24 ± 3         | 1.7                   |
| HD 203374 | 3.4 ± 1.2 | 19 ± 7          | 1.5                   |
| HD 207308 | 4.7 ± 1.0 | 19 ± 4          | 2.3                   |
| HD 207538 | 5.2 ± 0.7 | 18 ± 2          | 2.4                   |
| HD 208266 | 4.8 ± 0.7 | 18 ± 3          | 1.7                   |
| HD 210839 | 5.4 ± 0.5 | 33 ± 4          | 1.0^a                 |

TABLE 4

| Star     | W_0 (mÅ) | f-value (10^-3) | k_{pr}/10^{11} (s^-1) |
|----------|-----------|-----------------|-----------------------|
| HD 23478 | 1.6 ± 0.3 | 6 ± 1            | 3.1                   |
| HD 24534 | 1.6 ± 0.3 | 6 ± 1            | 3.1                   |
| HD 147683 | 6.6 ± 1.6 | 29 ± 7          | 2.0^a                 |
| HD 149757 | 1.1 ± 0.1 | 6 ± 1            | 3.5                   |
| HD 203322 | 1.3 ± 0.5 | 7 ± 3            | 0.8                   |
| HD 207308 | 2.2 ± 0.7 | 10 ± 3          | 3.0^a                 |
| HD 210839 | 4.2 ± 0.6 | 21 ± 3          | 4.3                   |
| Average  | 7 ± 2     | 2.5 ± 1.5        | 21 ± 6                |

| Star     | W_0 (mÅ) | f-value (10^-3) | k_{pr}/10^{11} (s^-1) |
|----------|-----------|-----------------|-----------------------|
| HD 24534 | 0.6 ± 0.3 | 1.2 ± 0.6       | 0.7^a                 |
| HD 24534c | 0.8 ± 0.4 | 1.9 ± 1.0       | 3.6^a                 |
Fig. 1.— Term diagram for electronic states of CH discussed in this paper. The levels of each state are shown according to their \( N \) values, with a schematic not-to-scale energy separation. Only the lowest \( N' \) level is positioned at the correct location along the energy axis. This diagram shows only the transitions studied here. For the 1271.02 Å transition of the 4\( d \) Rydberg complex, we assumed that it has the same \( N' = 2 \) that has been assigned by Watson (2001) to the UID transitions of the 3\( d \) Rydberg complex.

Fig. 2.— Data and fits for \( \lambda \lambda 1368, 1369, \) and 1370 from the 3\( d \)–X band of CH toward X Per, vertically separated by 0.15 continuum units. This set of data is of higher \( R \) and S/N than the spectrum used in the initial detection of these lines toward \( \zeta \) Oph. In addition, \( N(\text{CH}) \) is higher along the X Per sight line, which shows a three-cloud component structure as indicated by the fraction-scaled pointers above the spectra. The larger width of \( \lambda 1369 \) is obvious. Its slight blueshift relative to \( \lambda 1368 \) and \( \lambda 1370 \) shows that its rest wavelength should be adjusted by \( \approx -0.005 \) Å relative to the sharper lines. The line \( \lambda 1370 \) is located among lines from \( ^{13} \text{CO} \); those to the blue are from the A–X (6–0) band, while those to the red are from the d–X (12–0) intersystem band (see Figure 1 of Sheffer, Federman & Lambert 2002).
Fig. 3.— Data, fit, and residuals for \( \lambda \) 1271.02 from the 4d–X band of CH toward X Per. The cloud component structure on the line of sight is indicated above the fit. The strong absorption to the blue is from a triplet of S I lines at 1270.78 Å.

Fig. 4.— Data, fits, and residuals for \( \lambda \) 1549.05 and \( \lambda \) 1549.62 from the \( F-X \) band of CH toward X Per. The bluer 'line' is a blend of two transitions, \( Q_2 \) and \( \frac{3}{2} R_{12} \), but their separation is unknown. The redder line is the unblended \( \frac{5}{2} Q_{12} \) transition. The cloud component structure is indicated above the features.
Fig. 5.— Data, fits, and residuals for λ1695.34 from the $D-X$ band of CH toward X Per. This is a blend of the two transitions $Q_2$ and $Q_{R12}$, the separation of which is unknown. The cloud component structure is indicated above the fitted feature. Our initial fit returned a smaller line width (solid line) than the value measured in the lab (dashed line), yet both are consistent with the ambient noise in the spectrum.

Fig. 6.— Data, fits, and residuals for λ1693.24 from the $D-X$ band of CH toward X Per. This is the weaker transition $R_2$, which is partially blended with the Si I at 1693.29 Å. The cloud component structure is indicated above the fitted line. Both fits employ fixed $\Gamma$ values from the λ1695.34 fits in Figure 5. The feature at ~1693.25 Å does not appear in any tabulated interstellar line list.