DETECTION OF THE $N = 3–2$ TRANSITION OF CCH IN ORION AND DETERMINATION OF THE MOLECULAR ROTATIONAL CONSTANTS

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Received 1981 July 27; accepted 1981 September 3

ABSTRACT

We report the detection of five hyperfine components of the $N = 3–2$ transition of CCH in Orion A. From an analysis of this data combined with $N = 1–0$ data from previous observations, the rotational constants ($B_0$ and $D_0$) were determined, and the values of the fine structure ($\gamma$) and hyperfine constants ($b$, $c$) were improved. We predict the frequencies of additional rotational transitions of CCH up to $N = 5–4$. A rotational temperature and column density are estimated on the basis of the 3–2 data.

Subject headings: interstellar: molecules — molecular processes — transition probabilities

I. INTRODUCTION

The ethynyl radical, CCH, was first detected in interstellar space by Tucker, Kutner, and Thaddeus (1974), who observed several hyperfine components of the $N = 1–0$ rotational transition. At the time, CCH had been studied in the laboratory only while frozen in an argon matrix (Cochran, Adrian, and Bowers 1964; Mulligan, Jacox, and Abouaf-Marguin 1967; Graham, Dismuke, and Weltner 1974) and had never been detected as a free molecule. These matrix studies yielded estimates of the hyperfine constants, which Tucker et al. used to identify the unknown lines. More recent observations (Tucker and Kutner 1978; Wootten et al. 1980) have shown that CCH is relatively abundant ($nL \approx 10^{14}–10^{15} \text{ cm}^{-2}$) in a wide variety of interstellar sources. Because CCH has a rather small dipole moment of 0.8 debyes (Hillier, Kendrick, and Guest 1975), it is excited in regions of moderate density (Tucker, Kutner, and Thaddeus 1974). Except when low elemental oxygen abundance is assumed, chemical steady-state models (Mitchell, Ginsburg, and Kuntz 1978, and references therein) predict a lower CCH concentration than is actually observed in the interstellar medium. Prasad and Huntress (1980) have proposed time-dependent models in order to resolve this apparent discrepancy.

The CCH fine structure and hyperfine constants were precisely calculated by Tucker and Kutner (1978) from the astrophysical data. Because only one rotational transition ($N = 1–0$) of CCH had been detected, the rotational constants $B_0$ and $D_0$ could not be separately determined, however. The $N = 6–7$ transition of free CCH has been recently detected in the laboratory using laser magnetic resonance spectroscopy (Saykally and Evenson 1978), but the complex nonlinear Zeeman mixing of the energy levels made the extraction of exact values for $B_0$ and $D_0$ impossible.

Here we report observations of the $N = 3–2$ transition of CCH toward Orion A. From an analysis of these spectra and the $N = 1–0$ lines, we have accurately determined the constants $B_0$ and $D_0$ for CCH. In addition, we derive a rotational temperature and column density based on the two rotational transitions.

II. OBSERVATIONS

The measurements were made in 1981 February with the 4.9 m telescope of the Millimeter Wave Observatory (MWO). At 262 GHz, the $N = 3–2$ CCH frequency, the FWHM beamwidth of the telescope was $\sim 12$. The receiver used for these observations was similar to that described by Erickson (1981), except that the diode mixer and intermediate frequency amplifier were cooled to 17 K by a closed cycle refrigerator. Three 128-channel filter banks with filter widths of 1000, 250, and 62.5 kHz, corresponding to velocity resolutions of 1.15, 0.29, and 0.07 km s$^{-1}$, were used for the measurements; two of the three filter banks could be used simultaneously. The observations were done in position switching mode. The pointing accuracy is estimated to be one-third of the beamwidth. The temperature scale was established using the synchronous chopper wheel method of Davis and Vanden Bout (1973), and is expressed as $T_\text{a}$, antenna temperature corrected for atmospheric opacity. This temperature is related to the radiation temperature by:

$T_\text{a} = T_\text{r} + T_\text{sys}$

The Millimeter Wave Observatory is operated by the Electrical Engineering Research Laboratory of the University of Texas at Austin, with support from the National Science Foundation and McDonald Observatory.
$T_R = T_A^*/\eta_p$, where $\eta_p$ is the forward beam efficiency for an extended source; $\eta_p = 0.85$ for MWO. The mixer response to the upper and lower sidebands (separated by 2.8 GHz) was assumed to be equal. The single-sideband system temperature referred to outside the atmosphere was $\sim 3800$ K during the observations.

III. RESULTS

Figure 1 shows the spectrum taken with the 1000 kHz filter bank towards $\alpha = 05^h32^m50^s6, ~\delta = -05^\circ21'25"0$ (1950.0) in Orion A. This position, 3N and 1E of the Kleinmann-Low (KL) Nebula, is where the strongest $N = 1$-0 CCH lines are observed (Tucker and Kutner 1978). The vertical lines underneath the profiles mark the positions of the five hyperfine components detected. The spectrum represents approximately 1 hour of integration time.

Figure 2 is the energy level diagram of the $N = 2$ and $N = 3$ rotational levels of CCH, showing the fine structure and hyperfine splittings, and the 11 allowed $N = 3-2$ transitions. CCH is a $^2 \Sigma$ molecule, and thus has electron orbital angular momentum $\Lambda = 0$ and electron spin angular momentum $S = \frac{1}{2}$. The fine structure splitting, labeled by quantum number $J$, is due to the coupling of the rotational angular momentum $\tilde{N}$ and the electron spin $\tilde{S} \left( \tilde{J} = \tilde{S} + \tilde{N} \right)$. The hyperfine splitting, labeled by quantum number $F$, results from the coupling of the angular momentum $\tilde{J}$ with $\tilde{I}$, the spin of the hydrogen nucleus ($\tilde{F} = \tilde{J} + \tilde{I}$). The Hamiltonian describing these interactions for the molecule can be written as

$$H = H_{\text{rot}} + H_{\text{fs}} + H_{\text{hfs}}.$$  

The individual contributions are

$$H_{\text{rot}} = (B_0 - N(N + 1)D_0)\tilde{N}^2,$$

$$H_{\text{fs}} = \gamma(\tilde{N} \cdot \tilde{S}),$$

$$H_{\text{hfs}} = b(\tilde{F} \cdot \tilde{S}) + c\tilde{F}\tilde{S} \cdot \tilde{I},$$

where $\gamma$ is the spin-rotation constant, and $b$ and $c$ are the Frosh and Foley (1952) hyperfine constants. For $^2 \Sigma$ CCH, $B_0 \gg \gamma > b$, so a Hund’s case $b$ basis, $|FIJSN_{MF}\rangle$, is appropriate for constructing the Hamiltonian matrices. Due to the mixing of states labeled by quantum number $J$ by the hyperfine interaction, $J$ is no longer a good quantum number. Thus, the usual selection rule $\Delta J = 0, \pm 1$ is no longer strictly maintained. The only rigorous quantum numbers are $F$ and $M_F$; electric dipole selection rules require $\Delta F = 0, \pm 1$, with $F = 0$–0 forbidden.

Figure 3 shows the line profiles of the four strongest hyperfine transitions, observed with the 62.5 kHz filter bank. The vertical lines underneath the profiles indicate the calculated frequencies and relative intensities of these transitions. The bandwidth of this filter bank allowed simultaneous observation of only two of the four hyperfine components. Results from fitting the line profiles with a Gaussian line shape function are listed in Table 1, which gives the corrected antenna temperature ($T_R^*$), FWHM line width ($\Delta V_{1/2}$) and frequency ($\nu$), assuming a
$V_{\text{LSR}} = 9.7$ km s$^{-1}$. Parameters were estimated for the fifth hyperfine component ($F = 2–2$), which was observed only in the 1000 kHz filter bank. Uncertainties quoted are $1 \sigma$ formal errors determined by the Gaussian fitting program. The value of $V_{\text{LSR}}$ was chosen primarily on the basis of NH$_3$ spectra (Ziurys et al. 1981), which uniformly exhibit a $V_{\text{LSR}}$ of 9.5–9.9 km s$^{-1}$ for positions in Orion north of KL, and also show a local maximum in line temperature at about 3N, 1E. CN and N$_2$H$^+$ (Turner and Gammon 1975; Turner and Thaddeus 1977) also peak in intensity at 3N, 1E and exhibit velocities of 9.5 and 10.2 km s$^{-1}$, respectively. The value of the $V_{\text{LSR}}$ is thus accurate to only about 0.4 km s$^{-1}$, which corresponds to an uncertainty in frequency of approximately 0.35 MHz at 262 GHz.

The relative intensities of the observed $N = 3–2$ hyperfine components differ slightly from the predicted values, suggesting that the transition is not optically thin. We derive an optical depth for the $(J, F) = \left(\frac{3}{2}, 2\right)–\left(\frac{3}{2}, 2\right)$ hyperfine component of $\tau = 1.1\pm0.3,-1.1$, comparing the intensity ratio of the two strongest $J = \frac{3}{2}\frac{3}{2}$ hyperfine lines; an optical depth of $\tau = 1.5\pm1.1,-1.4$ is obtained for the $(J, F) = \left(\frac{3}{2}, 2\right)–\left(\frac{1}{2}, 1\right)$ component from the ratio of intensities of the strongest $J = \frac{1}{2}\frac{1}{2}$ lines. Observations of the $N = 1–0$ lines indicate that those transitions are optically thin (Tucker and Kutner 1978). The difference in optical depth may imply that the gas is clumped.

The $(J, F) = \left(\frac{3}{2}, 4\right)–\left(\frac{3}{2}, 3\right)$ transition seems to have a noticeably larger line width than the other hyperfine components. This apparent broadening might be due to self-absorption in the $F = 4–3$ line, or to a blend of this line and another from a different molecule. Self-absorption would decrease the antenna temperature of the hyperfine component and cause the optical depth of the $F = 3–2$ line to be overestimated. If the self-reversal is real, it indicates the presence of cold foreground gas which is optically thick in the $F = 4–3$ hyperfine line. This component should have the greatest optical depth because it is statistically favored over the other hyperfine transitions.

### IV. SPECTROSCOPIC ANALYSIS

The uncertainties in the $N = 1–0$ and $N = 3–2$ CCH frequencies used in our analysis are due mainly to uncertainties in the radial velocities of the sources observed. Wooten et al. (1980) have made the most accurate measurement of the $N = 1–0$, $(J, F) = \left(\frac{3}{2}, 2\right)–\left(\frac{1}{2}, 1\right)$ line; their value, accurate to 0.04 MHz, is based on observations of dark clouds, where the CCH lines are narrow and source radial velocities are well determined from observations of other molecules. The frequencies of three other $N = 1–0$ hyperfine components can be calculated from the $(\frac{3}{2}, 2)–(\frac{1}{2}, 1)$ frequency using the hyperfine splittings of Tucker and Kutner (1978), which are also known to 0.04 MHz accuracy. The frequencies obtained via this method are within the quoted error limits of Tucker, Kutner, and Thaddeus (1974).

### TABLE 1

**LINE PARAMETERS FOR $N = 3–2$ CCH TOWARD ORION A: 3N, 1E**

<table>
<thead>
<tr>
<th>Transition</th>
<th>$T_a$ (K$^*$)</th>
<th>$\Delta V_{1/2}$ (km s$^{-1}$)</th>
<th>$\nu$ MHz$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left(\frac{3}{2}, 4\right)–\left(\frac{3}{2}, 3\right)$</td>
<td>$3.5\pm0.3$</td>
<td>$1.90\pm0.10$</td>
<td>$262,004.52\pm0.06$</td>
</tr>
<tr>
<td>$\left(\frac{3}{2}, 3\right)–\left(\frac{3}{2}, 2\right)$</td>
<td>$3.0\pm0.4$</td>
<td>$1.07\pm0.09$</td>
<td>$262,006.76\pm0.05$</td>
</tr>
<tr>
<td>$\left(\frac{3}{2}, 3\right)–\left(\frac{3}{2}, 2\right)$</td>
<td>$2.8\pm0.2$</td>
<td>$1.30\pm0.07$</td>
<td>$262,065.12\pm0.04$</td>
</tr>
<tr>
<td>$\left(\frac{3}{2}, 1\right)–\left(\frac{3}{2}, 2\right)$</td>
<td>$2.4\pm0.2$</td>
<td>$1.35\pm0.09$</td>
<td>$262,067.65\pm0.05$</td>
</tr>
<tr>
<td>$\left(\frac{3}{2}, 2\right)–\left(\frac{3}{2}, 2\right)$</td>
<td>$\leq0.3$</td>
<td>$\ldots$</td>
<td>$\sim262,080$</td>
</tr>
</tbody>
</table>

$^*$ All uncertainties listed are $1\sigma$, obtained from the Gaussian fits to the line profiles.

$^*$ Assuming $V_{\text{LSR}} = 9.7$ km s$^{-1}$.  

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### TABLE 2
SPECTROSCOPIC CONSTANTS FOR CCH

<table>
<thead>
<tr>
<th>Constant</th>
<th>This Work (MHz)</th>
<th>Tucker and Kutzner (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0$</td>
<td>43,674.70 ± 0.10</td>
<td>...</td>
</tr>
<tr>
<td>$D_0$</td>
<td>0.1137 ± 0.0006</td>
<td>...</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>-62.62 ± 0.02</td>
<td>-62.62 ± 0.05</td>
</tr>
<tr>
<td>$b$</td>
<td>40.39 ± 0.14</td>
<td>40.40 ± 0.19</td>
</tr>
<tr>
<td>$c$</td>
<td>12.32 ± 0.09</td>
<td>12.33 ± 0.11</td>
</tr>
<tr>
<td>$2B_0 - 4D_0$</td>
<td>87,348.95 ± 0.20</td>
<td>87,348.74 ± 0.19</td>
</tr>
</tbody>
</table>

* Uncertainties are 1 $\sigma$, based on the quality of fit of the nonlinear least-squares program. The rotational constants $B_0$ and $D_0$ are subject to additional error of ±0.05 and ±0.0005 MHz, respectively, due to uncertainty in radial velocity local standard of rest ($V_{LSR}$) of the observed source.

### CORRELATION MATRIX

<table>
<thead>
<tr>
<th></th>
<th>$B_0$</th>
<th>$D_0$</th>
<th>$\gamma$</th>
<th>$b$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0$</td>
<td>1.00</td>
<td>0.95</td>
<td>0.12</td>
<td>-0.05</td>
<td>0.24</td>
</tr>
<tr>
<td>$D_0$</td>
<td>1.00</td>
<td>0.08</td>
<td>0.04</td>
<td>-0.04</td>
<td>0.24</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.00</td>
<td>1.00</td>
<td>0.43</td>
<td>-0.43</td>
<td>-0.28</td>
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<tr>
<td>$b$</td>
<td>1.00</td>
<td>1.00</td>
<td>0.12</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$c$</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

### TABLE 3
OBSERVED VERSUS CALCULATED FREQUENCIES

<table>
<thead>
<tr>
<th>Transition</th>
<th>$N' \rightarrow N$</th>
<th>$(J', F') \rightarrow (J, F)$</th>
<th>Frequency (MHz)$^a$</th>
<th>Relative Intensity$^b$ ($\times 10^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 → 0</td>
<td>(1, 1) → (1, 1)</td>
<td>87,284.42 ± 0.20</td>
<td>4.25</td>
<td></td>
</tr>
<tr>
<td>1 → 1</td>
<td>(1, 2) → (1, 1)</td>
<td>87,317.23 ± 0.04</td>
<td>41.67</td>
<td></td>
</tr>
<tr>
<td>2 → 1</td>
<td>(1, 1) → (0, 0)</td>
<td>87,328.92 ± 0.06</td>
<td>20.75</td>
<td></td>
</tr>
<tr>
<td>2 → 2</td>
<td>(1, 2) → (1, 1)</td>
<td>87,407.46 ± 0.06</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>3 → 2</td>
<td>(1, 1) → (1, 0)</td>
<td>87,446.84 ± 0.20</td>
<td>8.33</td>
<td></td>
</tr>
</tbody>
</table>

* Uncertainties are based primarily on uncertainty in $V_{LSR}$ of the observed source.

* Relative intensities were calculated directly from the transition line strengths by normalizing them to total unit intensity for each rotational transition, $N' \rightarrow N$.

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The first step in the spectroscopic analysis was to solve for the rotational constants $B_0$ and $D_0$ from the pure rotational energy differences of the $N = 3\rightarrow 2$ and $N = 1\rightarrow 0$ transitions. The differences, $\Delta E = 2B_0(N + 1) - 4D_0(N + 1)^3$, were calculated by removing the hyperfine and fine structure splittings from the measured frequencies. The splittings were calculated using the values of the spin-rotation and hyperfine constants determined by Tucker and Kutzner (1978) and energy expressions derived by Carrington, Milvorton, and Sarre (1978), which are applicable to $^2\Sigma$ molecules with a single nuclear spin.

Once $B_0$ and $D_0$ were estimated, all five molecular constants were refined by means of a nonlinear least-squares computer program, which varied the constants simultaneously in order to match the calculated and the observed frequencies. The $^2\Sigma$ computer code of Dixon was used for this purpose.

### TABLE 4
CCH: PREDICTED FREQUENCIES AND INTENSITIES

<table>
<thead>
<tr>
<th>Transition</th>
<th>$N' \rightarrow N$</th>
<th>$(J', F') \rightarrow (J, F)$</th>
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* Relative intensities were calculated directly from the transition line strengths by normalizing them to total unit intensity for each rotational transition, $N' \rightarrow N$.

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and Woods (1977) was used to calculate the frequencies. The code sets up the Hamiltonian matrices in a Hund's case $b_γ$ basis, as previously described, and numerically diagonalizes the matrices to yield the energy eigenvalues. The forms of the matrices are given by Dixon and Woods (1977). The refined values of the constants obtained are listed in Table 2. The uncertainties quoted are $1σ$ and represent statistical errors based on the nonlinear fit. The rotational constants $B_0$ and $D_0$ are subject to additional uncertainties of $±0.02$ and $±0.0025$ MHz, respectively, due to the uncertainty in $V_{SR}$.

Table 3 compares the observed and calculated $N = 1–0$ and $N = 3–2$ frequencies. The observed and calculated values are in excellent agreement, indicating that the $ς^2$ computer code models the CCH rotational energy structure effectively. Table 4 lists predicted rest frequencies and LTE relative hyperfine intensities of all electric dipole-allowed CCH transitions up to $N = 5–4$.

V. ROTATIONAL TEMPERATURE AND COLUMN DENSITY

The observation of the $N = 3–2$ transition allows one to better estimate the populations in the CCH rotational ladder, and thus improve the determination of the total column density. One can estimate the density at which a molecular transition becomes thermalized by considering the transition to be a two-level system and applying detailed balance. Collisions, absorptions, and spontaneous and stimulated emission are considered. The collisional rate is

$n(H_2) \sigma$, where $σ$ is the molecule's collisional cross section, $v$ the mean velocity of the gas, and $n(H_2)$ the hydrogen density. If the collisional cross section for CCH is estimated to be $σ \sim 10^{−15}$ cm$^2$, densities of $n(H_2) \geq 10^8$ cm$^3$ are needed to half-thermalize the $N = 3–2$ transition. The excitation temperature $T_{ex}$ is equal to one-half the kinetic temperature, $T_k$, when the levels are half-thermalized. We assume $T_k$ to be approximately the value of the CO line temperature at $3\nu_1$, $1E$ in Orion (Scoville 1981) in our calculation. Based on H$_2$CO observations of Evans et al. (1975), the density at the $3\nu_1$, $1E$ position is on the order of $n(H_2) \geq 10^5$. Thus, it is likely that the $3–2$ transition of CCH is subthermally excited at this position.

By comparing the column densities in $N = 3$ and $N = 1$ rotational levels, we can calculate a rotational temperature. For a linear molecule, the column density in an optically thin rotational level $N + 1$ is given by:

$$nL(\text{cm}^{-2}) = \frac{3k(2N + 3)T_k\Delta V_{1/2}}{8\pi^3\mu_0^2v(N + 1)\sigma_{SR}}.$$  

where $T_k$ is the radiation temperature of a particular hyperfine component of the $N + 1 → N$ transition; $ΔV_{1/2}$ is the line width, and $\sigma_{SR}$ the relative intensity of the hyperfine transition $(F + 1 → F)$. The permanent dipole moment of the molecule is $\mu_0$. Using the $N = 1–0$ data of Tucker, Kutner, and Thaddeus (1974) and our $N = 3–2$ data, we estimate the rotational temperature between $N = 3$ and $N = 1$ levels at the $3\nu_1$, $1E$ position in Orion to be $T_{rot} ≈ 9 ± 3$ K, if the lines are optically thin. We assume the $3–2$ transition to be optically thin because of the uncertainty in the calculated values of optical depth for the $3–2$ lines, as well as uncertainties in excitation temperatures. If these lines are optically thick, the rotational temperature should increase.

The total column density can then be estimated by assuming the integral approximation for the rotational partition function: $hB_0/kT_{rot}$. If we let $T_{rot} = 9$ K, we obtain a CCH total column density of $nL(CCH) \approx 3–4 \times 10^{14}$ cm$^{-2}$, based on the $(J, F) = (3, 3)−(3, 2)$ component of the $3–2$ transition. By assuming the hyperfine line to be both optically thin and optically thick, we obtain a range of values. These column densities fall within the range of values calculated by Tucker and Kutner (1978). Such column densities yield fractional abundances several orders of magnitude larger than those predicted by most steady-state chemical models (Prasad and Huntress 1980). Thus the $N = 3–2$ data tend to confirm the discrepancy between observed and calculated CCH abundance.

VI. SUMMARY

We have detected five of the eleven hyperfine components of the $N = 3–2$ transition of CCH at the $3\nu_1$, $1E$ position in Orion. Using our results and previous observations of the $N = 1–0$ transition, we have accurately determined the CCH rotational constants $B_0$ and $D_0$ of the molecule and have refined the fine structure and hyperfine constants. The frequencies of all rotational transitions up to $N = 5–4$ are tabulated. Comparison of the $N = 3–2$ and $N = 1–0$ column densities yields a rotational temperature of 9 K at this position; the calculated total column density based on the $3–2$ transition compares with that of previous $N = 1–0$ observations.

R. J. S. and L. M. Z. thank the National Science Foundation (grant CHE 79-50005) for support. R. J. S. acknowledges a grant from the Dreyfus Foundation. Partial support was also provided by NSF grant AST 78-21037. L. M. Z. thanks P. T. P. Ho, J. Bieging, and R. M. Crutcher for useful discussions and comments.

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MOLECULAR ROTATIONAL CONSTANTS

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