THE ASTROPHYSICAL JOURNAL, 296:L35–L38, 1985 September 15

LABORATORY AND ASTRONOMICAL DETECTION OF THE DEUTERATED ETHYNYL RADICAL CCD

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Received 1985 May 8; accepted 1985 June 25

ABSTRACT

Two rotational transitions of CCD, $N = 1 \rightarrow 2$ at 144 GHz and $2 \rightarrow 3$ at 216 GHz, were detected in a laboratory glow discharge through deuterated acetylene and helium, after which one, $N = 2 \rightarrow 1$, was detected toward the rich molecular cloud behind the Orion Nebula. The 144 GHz transition is a well-resolved spin doublet split by 55 MHz, the components of which contain hyperfine structure of the order of 1 MHz, so far only partially resolved. From observations toward two positions in Orion, at and near the Kleinmann-Low nebula, the column density of CCD is determined to be $\sim 1.8 \times 10^{13}$ cm^{-2} and the isotopic ratio CCD/CCH ≈ 0.05. CCD was not detected at two positions in TMC-1.

Subject headings: deuterium — interstellar: molecules

The ethynyl radical CCH, the simplest carbon chain with a radio-frequency spectrum, is one of the most abundant polyatomics in molecular clouds, and its deuterated species is an excellent candidate for detection. With abundances that depend strongly on the reaction pathways involved in formation and on fractional ionization and temperature, deuterated molecules are sensitive indicators of the physical and chemical state of molecular clouds; measurements of deuterium fractionation have been used to study the formation of a number of carbon-chain molecules, including HC_3N (Langer *et al.* 1980) and HC_5N (Schloerb *et al.* 1981). Both CCD and CCH, with resolvable hyperfine structure permitting line optical depth corrections and therefore good determinations of column density, are particularly interesting because recent interstellar cloud models (Prasad and Huntress 1980; Graedel, Langer, and Frerking 1982) suggest that their abundances may depend strongly on cloud age.

The rotational spectrum of CCD in its $^2\Sigma$ electronic ground state consists of well-resolved spin doublets, the three lowest falling in readily observed bands of the millimeter wave spectrum at frequencies of 72, 144, and 216 GHz. This *Letter* reports laboratory identification of the $N = 1 \rightarrow 2$ and $2 \rightarrow 3$ rotational transitions at 144 GHz and 216 GHz, respectively, and the subsequent astronomical detection of CCD through its $N = 2 \rightarrow 1$ transition. While finishing our laboratory measurements we received a preprint from Bogey, Demuynck, and Destombes (1985) describing their laboratory detection of CCD; our line frequencies and spectroscopic constants and theirs are in excellent agreement, and it is now possible to predict the entire radio spectrum of CCD to an accuracy adequate for radio astronomy (i.e., corresponding to an uncertainty in radial velocity of less than 1 km s^{-1} for $\nu \leq 650$ GHz).

Our laboratory search for CCD was based on the value of B_e obtained from an ab initio CI calculation by W. P. Kraemer (1983, private communication) corrected for CCD by the ratio B_0/B_e for CCH, following DeFrees, Binkley, and McLean (1984; see their method 3), a procedure that yields B_0 to ~ 10 MHz for several linear triatomic molecules. We used the free-space millimeter-wave spectrometer previously used to detect CCH as well as the same method of radical production (Gottlieb, Gottlieb, and Thaddeus 1983): a liquid nitrogen–cooled DC glow discharge through a 1:20 molar mixture of helium and 99% deuterium-enriched acetylene (Icon Services). Lines were best observed at a total pressure of approximately 25 millitorr, at which the full line width at half-intensity was 1.0 MHz and the flow rate of C_2D_2 was about 1 liter hr^{-1} at STP. To conserve C_2D_2, integrations were limited to approximately 25 minutes. An example of our laboratory spectra is shown in Figure 1.

Line-center frequencies (Table 1) were obtained from a least-squares fit of theoretical line profiles to the hyperfine manifold. The Hamiltonian for CCD, previously used in the analysis of C_3N (Gottlieb *et al.* 1983), includes terms describing the rotation, spin-rotation, and hyperfine interactions. The best-fit molecular constants are given in Table 2. The evidence is overwhelming that the lines observed are produced by CCD, not some other product of the discharge: detection with Zeeman modulation in a 10 G field indicates that the carrier is a free radical with a magnetic moment of approximately 1 Bohr magneton; the disappearance of the lines when the discharge was run through normal rather than deuterium-enriched acetylene demonstrates that the lines arise from a deuterated species; the isotope shift, the spin doubling, and the hyperfine structure, as Table 2 shows, all are in good agreement with those expected for CCD.

Following laboratory identification, CCD was detected astronomically in 1985 January and March using the Bell 7 m

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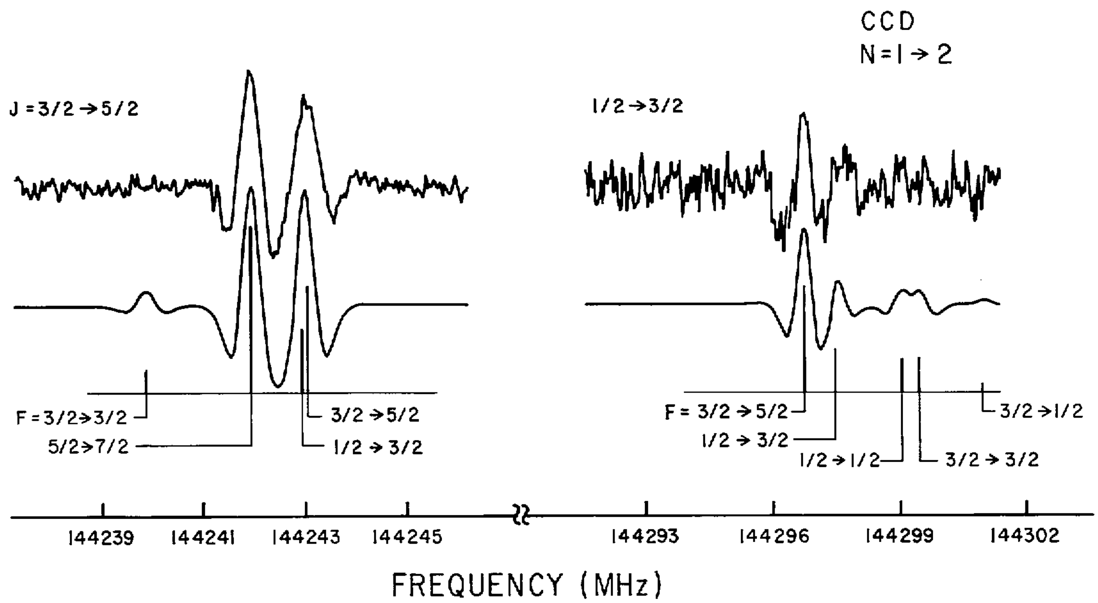

FIG. 1.—Spectrum of the $N = 1 \rightarrow 2$ transition of CCD showing laboratory lines and superposition of theoretical line profiles (second derivative Lorentzians). Total integration time for each spectrum was approximately 25 minutes.

TABLE 1

LABORATORY CCD FREQUENCIES

$N \rightarrow N'$	$J \rightarrow J'$	$F \rightarrow F'$	Measured Frequencies[a] (MHz)	Measured-Calculated (MHz)
1 → 2 ...	3/2 → 5/2	5/2 → 7/2	144,241.96 ± 0.03	−0.01
		1/2 → 3/2, 3/2 → 5/2	144,243.05 ± 0.03	0.02
	1/2 → 3/2	3/2 → 5/2	144,296.72 ± 0.08	−0.05
2 → 3 ...	5/2 → 7/2	7/2 → 7/2	216,368.56 ± 0.05	−0.01
		5/2 → 5/2	216,369.99 ± 0.07	−0.02
		7/2 → 9/2	216,372.83 ± 0.02	−0.01
		3/2 → 5/2, 5/2 → 7/2	216,373.32 ± 0.02	0.01
	3/2 → 5/2	5/2 → 7/2, 3/2 → 5/2	216,428.32 ± 0.02	0.02
		1/2 → 3/2	216,428.76 ± 0.04	−0.07
		3/2 → 3/2	216,430.34 ± 0.06	−0.02
		5/2 → 5/2	216,431.26 ± 0.05	−0.01

[a]Uncertainties are an estimated 1 σ.

TABLE 2

THE MICROWAVE CONSTANTS OF CCD

Molecular Constant	Measured[a] (MHz)	Calculated (MHz)
B_0	36068.035 ± 0.014	36053.[b]
D_0	0.0687 ± 0.0007	0.073[c]
γ	−55.84 ± 0.03	−51.7[d]
b	6.35 ± 0.07	6.20[e]
c	1.59 ± 0.26	1.88[e]
eQq	0.21 ± 0.09	0.22[f]

[a]Uncertainties are 1 σ from a least-squares fit.
[b]From an adjusted ab initio calculation (see text).
[c]D_{CCH} $(B_{CCD}/B_{CCH})^2$.
[d]γ_{CCH} (B_{CCD}/B_{CCH}) (Brown and Watson 1977).
[e]Obtained by scaling the corresponding *hf* constants for CCH by $(\mu_I/I)_D/(\mu_I/I)_H$.
[f]From a near Hartree-Fock SCF wave function at the calculated equilibrium geometry (S. Green 1985, private communication).

antenna in Holmdel, New Jersey, with a half-power beamwidth of 1′.3 at 144 GHz. Measurements were obtained with a cryogenic SIS tunnel junction receiver through a single-sideband filter which terminates the image sideband in a 20 K absorber; the noise temperature was 420 K at 144 GHz. The receiver was calibrated by chopping between room temperature and liquid nitrogen temperature absorbers; the sky temperature, needed to correct for atmospheric attenuation, was measured by reference to a liquid nitrogen load. Observations were made with filter-bank spectrometers directly at spectral resolutions of 1 MHz and 250 kHz, and at 100 kHz with a spectrum expander.

In Orion, CCD was detected toward the Kleinmann-Low (KL) infrared nebula and at a position 0′.5 E and 2′.5 N near the peak of CCH emission (Tucker and Kutner 1978). The spectra at the NE position are shown in Figure 2 and the line parameters, from fitting Gaussian profiles, are given in Table 3. At the offset position CCD, like CCH, is about twice as strong as at KL. Both components of the 144 GHz spin doublet, each a blend of several hyperfine components, are seen clearly in the spectrum at 1 MHz resolution (Fig. 2*a*); at 250 kHz resolution (Fig. 2*b*), the lower frequency spin component is seen to be flanked by an unidentified line of comparable intensity, which cannot be CCD because no CCH emission

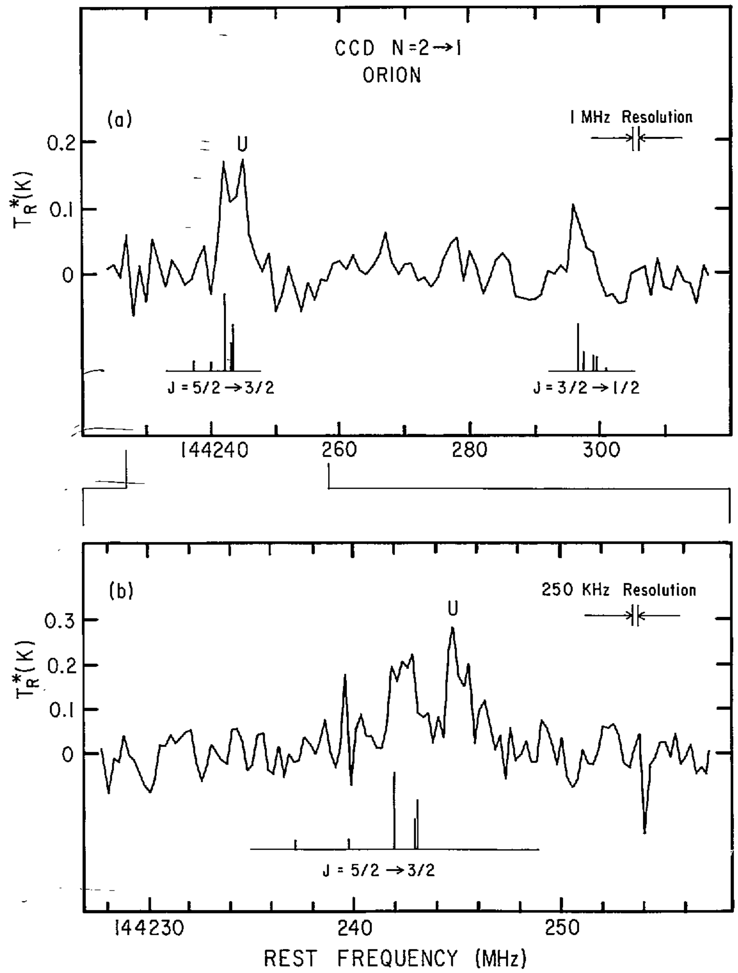

FIG. 2.—Astronomical $N = 2 \rightarrow 1$ CCD spectrum observed 2'.5 north and 0'.5 east of the KL position with (*a*) 1 MHz and (*b*) 250 kHz resolution. The frequency scale assumes $v_{LSR} = 9.5$ km s^{-1}. The indicated unidentified (U) line cannot be a velocity component of CCD, since there is no corresponding component in CCH at 87 GHz or 262 GHz.

TABLE 3

CCD $N = 2 \rightarrow 1$ LINES IN ORION

Position ($\Delta\alpha, \Delta\delta$)[a]	Transition $J \rightarrow J'$	T_R^*[b] (K)	V_{LSR} (km s^{-1})	Δv[c] (km s^{-1})	$\int T_R^* \, dv$ (K km s^{-1})
(0',0')	5/2 → 3/2[d]	0.13 ± 0.03	9.1 ± 0.3	2.3 ± 0.8	0.31 ± 0.09
	3/2 → 1/2[e]	0.09 ± 0.03	...	5.0 ± 2.2	0.39 ± 0.14
(0'.5, 2'.5)	5/2 → 3/2[d]	0.21 ± 0.03	9.5 ± 0.2	3.1 ± 0.6	0.66 ± 0.09
	3/2 → 1/2[e]	0.10 ± 0.03	...	4.5 ± 1.5	0.50 ± 0.13

[a] Relative to the Kleinmann-Low nebula: $\alpha(1950) = 5^h32^m47^s$, $\delta(1950) = -5°24'30''$.

[b] T_R^* is the antenna temperature corrected for atmospheric and ohmic losses, spillover, and scattering, but not for the coupling between the antenna diffraction pattern and the source (Kutner and Ulich 1981).

[c] Full line width at half-intensity. The intrinsic velocity dispersion of the source is smaller because the hf components are not resolved. The 100 kHz data which partially resolve the $F = 7/2 \rightarrow 5/2$ component indicate that $\Delta v \approx 0.9 \pm 0.3$ km s^{-1}. The 100 kHz data are not presented because the 250 kHz data have a higher signal-to-noise ratio.

[d] Data taken with 250 kHz resolution.

[e] Observed only with 1 MHz resolution.

is detected at a corresponding velocity in the $N = 1 \rightarrow 0$ (Gottlieb, Gottlieb, and Thaddeus 1983) or $3 \rightarrow 2$ (Ziurys *et al.* 1982) transitions.

In the 100 kHz expander the $F = 7/2 \rightarrow 5/2$ hyperfine component is partially resolved, and a Gaussian fit yields $\Delta v_{FWHM} = 0.9 \pm 0.3$ km s^{-1}, a value somewhat smaller than those obtained for CCH. At this resolution, the unidentified line appears to separate into two components, at 144244.8 MHz and 144245.4 MHz (assuming an LSR radial velocity of 9.5 km s^{-1}), but the splitting may be an artifact of the low signal-to-noise ratio.

CCD was not detected in TMC-1 at a resolution of 100 kHz at two positions where CCH and other deuterated species are readily found (Wootten *et al.* 1980; Guélin, Langer, and Wilson 1982): at $\alpha(1950) = 4^h38^m38^s$, $\delta(1950) = 25°35'45''$ or at a position 6′ W and 8′ N. The 1 σ limit on T_R^* was set at 0.046 K, corresponding to an isotopic ratio N(CCD)/N(CCH) < 0.03 (assuming the rotational temperature, T_{rot}, is 5 K, and taking CCH observations from Wootten *et al.* 1980 without correction for optical depth effects).

In Sgr B2, the region of the spectrum containing the $N = 2 \rightarrow 1$ transition of CCD has been surveyed by Hollis *et al.* (1981). It is not clear if the line they detect at 144244.8 MHz is due to the same species as the unidentified line toward KL, to the $J = 5/2 \rightarrow 3/2$ transition of CCD, or to a combination; the weaker $J = 3/2 \rightarrow 1/2$ CCD transition was not detected.

To estimate column densities of CCD in Orion, the formula for optically thin rotational lines of a linear molecule used for CCH by Ziurys *et al.* (1982) was used, assuming, as for CCH, a dipole moment of 0.8 *D* (Hillier, Kendrick, and Guest 1975). For the $N = 2$ level, the column densities are 2.6×10^{12} cm^{-2} and 5.6×10^{12} cm^{-2} at positions (0,0) and (0.′5, 2.′5). Adopting $T_{rot} = 9$ K derived by Ziruys *et al.* (1982) from the $N = 3 \rightarrow 2$ and $1 \rightarrow 0$ transitions of CCH, and assuming a classical rotational partition function (kT_{rot}/hB_0), the column density of CCD is 8.6×10^{12} cm^{-2} at KL and 1.8×10^{13} cm^{-2} at the offset position. The isotopic ratio N(CCD)/N(CCH) = 0.046 at (0.′5, 2.′5), using unpublished $N = 1 \rightarrow 0$ CCH data obtained with the Bell antenna in 1982 February corrected for optical depth with ratios of hyperfine components from the data of Gottlieb, Gottlieb, and Thaddeus (1983). This ratio lies well above those for DCO^+/HCO^+ and DCN/HCN in Orion (Penzias 1979). Also, N(CCD)/N(CCH) in Orion is larger than the upper limit set in TMC-1, where in most species stronger deuterium fractionation is found than in Orion.

With the radio frequency spectrum of CCD firmly established from laboratory measurements, it is now possible to undertake a systematic survey of interstellar CCD. The astronomical detection reported here has already shown that CCD lines can be strong enough to be readily measurable, especially with the improved receivers expected to be available shortly; the deuterium enhancement in CCD is comparable to the strongest enhancement yet found in any molecule. We expect CCD to be a useful addition to the rather few deuterated species that have provided substantial probes of the physical and chemical state of molecular clouds.

After this *Letter* was submitted, we received a preprint from Combes *et al.* (1985) describing the astronomical detection of the 216 GHz $N = 3 \rightarrow 2$ transition of CCD; their derived column density in Orion and upper limit in TMC-1 and ours are in excellent agreement. The combined results firmly establish the detection of CCD in space.

We are indebted to W. P. Kraemer for communication of unpublished results; E. W. Gottlieb, S. Green, and M. Guélin for advice; A. Sternberg and T. Judson for assistance in the laboratory; and the AT & T BL radio physics department for assistance with the operation of the 7 m antenna. The receiver used for the astronomical detection was built by A. A. Stark, with SIS junctions provided by R. Miller.

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