

LABORATORY MEASUREMENT OF THE 6-CENTIMETER FORMALDEHYDE TRANSITIONS

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ABSTRACT

The $1_{10}-1_{11}$ rotational transition of $\text{H}_2^{12}\text{C}^{16}\text{O}$ in its ground and first two excited vibrational states, and that of $\text{H}_2^{13}\text{C}^{16}\text{O}$, $\text{H}_2^{12}\text{C}^{18}\text{O}$, and $\text{HD}^{12}\text{C}^{16}\text{O}$ in their vibrational ground states, all of which lie at a wavelength of about 6 cm, have been studied with a beam-maser spectrometer. Line widths in the range 1-3 kHz have been attained, allowing the hyperfine structure of the transitions to be rather thoroughly resolved, and transition frequencies to be measured to an accuracy of the order of 100 Hz. All significant features of the observed spectra have been successfully interpreted in terms of the current theory of molecular hyperfine structure, and the appropriate hyperfine coupling constants have been determined.

I. INTRODUCTION

The 6-cm wavelength, $1_{10}-1_{11}$ rotational transition of formaldehyde is likely to become an important tool for the investigation of galactic structure, isotopic ratios, and physical and chemical conditions in interstellar clouds. This transition of the normal isotopic species, H_2CO (we will indicate the atomic weight only for the rare isotopes), has been found in the majority of H II regions surveyed (Zuckerman *et al.* 1970; Whiteoak and Gardner 1970), and in "anomalous" absorption in dark nebulae (Palmer *et al.* 1969); that of H_2^{13}CO has already been detected in the galactic center and in Sgr B2 (Zuckerman *et al.* 1969); and that of $\text{H}_2\text{C}^{18}\text{O}$ is likely to be found in the near future. In this paper we will present very precise laboratory measurements of this transition and its hyperfine structure (hfs) in all the formaldehyde vibrational states and isotopic species which we think likely to prove of interest to radio astronomy, namely, in the ground and first two excited vibrational states of the normal species, and in the ground vibrational state of H_2^{13}CO , $\text{H}_2\text{C}^{18}\text{O}$, and HDCO . Linewidths as narrow as 1.3 kHz (0.08 km s^{-1}) have been attained, making it possible to resolve most of the hfs of each transition and to measure transition frequencies to an absolute precision exceeding one part in 10^7 .

In this article the observed hfs will be analyzed in terms of hyperfine coupling constants; but the interpretation of these in terms of more basic molecular properties will be discussed only briefly. More detailed discussions of the results and of experimental techniques will appear in other articles and in a dissertation (Tucker 1971).

II. APPARATUS

Formaldehyde hyperfine spectra have been obtained with a molecular-beam maser, shown schematically in Figure 1, which is a direct descendant of the original maser, constructed in this laboratory in 1954 (Gordon, Zeiger, and Townes 1955; the parent of the present instrument has been described by Thaddeus and Krisher 1961). The resonant cavity, operating in the TM_{010} mode, is a silver-plated brass cylinder, slotted lengthwise so that tuning over several tens of megacycles is simply accomplished by mechanical squeezing; it is surrounded by a mu-metal shield to cancel out the terrestrial magnetic field, which even for diamagnetic molecules such as formaldehyde can produce Zeeman

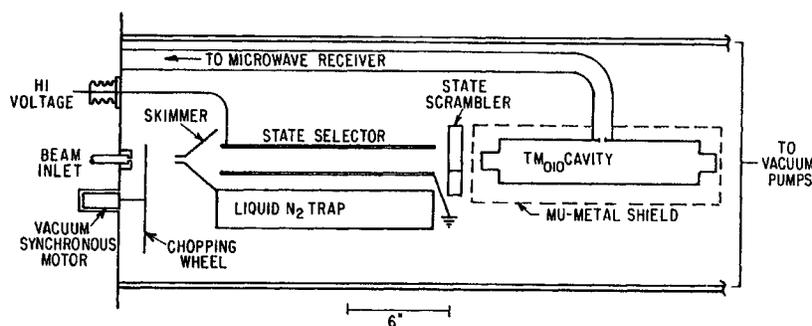


FIG. 1.—Schematic diagram of the beam maser

shifts that amount to an appreciable fraction of 1 kHz. The beam source is either a hydrodynamic nozzle or a crinkly-foil effuser: the nozzle, a single $\frac{1}{8}$ -inch-diameter hole driven at a comparatively high back pressure (10 torr or higher), produces the more intense molecular beam and the stronger lines; the effuser, a stack of many fine channels, similar to the one described by Gordon *et al.* (1955), yields the narrower linewidths.

The beam is mechanically chopped at 73 Hz, and before entering the octupole state selector passes through a metal baffle or “skimmer” which helps maintain a low pressure in the state selector and cavity by deflecting unwanted molecules from the beam. The state selector electrostatically removes from the beam molecules in the lower level of the rotational transition, and retains those in the upper level, but some hyperfine levels are less efficiently retained than others. If the hyperfine intervals are small—not greater than several tens of kHz—the sudden passage of the molecules out of the high electrostatic field of the state selector is impulsive, and enough transitions occur among the hyperfine levels to overcome this effect; but if the hyperfine intervals are large, passage out of the high field region is adiabatic, and anomalous hyperfine intensity ratios are observed (cf. Gordon 1955). In the case of H_2^{13}CO this effect is so strong that certain hyperfine transitions are missing altogether. To restore a normal population of the hyperfine levels, a “state scrambler,” consisting of crossed static and resonant electric fields each of about 100 V cm^{-1} , is therefore placed just before the cavity.

The molecular resonances are detected by a conventional superheterodyne receiver with an intermediate frequency of 30 MHz, followed by a commercial phase-sensitive detector. The microwave signal source is the tenth or higher harmonic of a Hewlett-Packard model 5105A frequency synthesizer, whose frequency is known to better than one part in 10^9 by phase comparison with station WWVB.

III. RESULTS

a) H_2CO

The 1_{10} – 1_{11} rotational transition of H_2CO in its ground vibrational state, first detected in space by Snyder *et al.* (1969), is likely to remain the formaldehyde transition of greatest interest to radio astronomy. Our measurements of its hyperfine structure have already been briefly reported (Tucker, Tomasevich, and Thaddeus 1970), but will be more completely described and analyzed here. Our absolute frequencies differ significantly (by about 10 kHz) from previous beam-maser measurements made by Shigenari (1967), but they are in excellent agreement with recent beam-maser measurements obtained by Kukolich and Rubin (1971).

Monomeric H_2CO was obtained by gently heating the polymer para-formaldehyde. The upper spectrum in Figure 2 shows the observed hfs of the 4830-MHz transition ob-

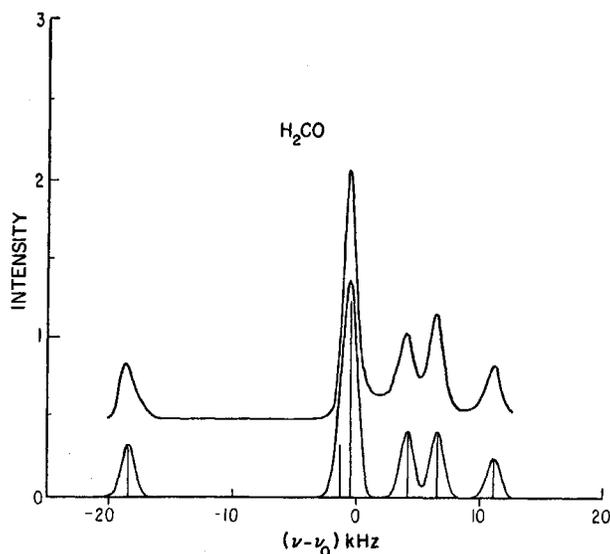


FIG. 2.—Observed (*upper spectrum*) and theoretical (*lower spectrum*) hfs of the 1_{10} - 1_{11} transition of H_2CO .

tained with the crinkly-foil beam source; the full line width at half-intensity is only 1.3 kHz (0.08 km s^{-1}), and the signal-to-noise ratio of the strongest line, obtained with a time constant of 1 s, is about 1000.

The 1_{10} and 1_{11} levels of H_2CO are ortho levels, in which the total nuclear spin of the two protons is restricted to the value $I = 1$ (cf. Townes and Schawlow 1955, chap. 4). The hyperfine interactions couple I to J , the total angular momentum of the molecule excluding nuclear spin, and thus when $J > 0$ they split each ortho rotational level into three hyperfine levels which are labeled by their total angular-momentum quantum number F , where $F = I + J$. For the 1_{10} and 1_{11} levels, $F = 0, 1, \text{ and } 2$; and thus on the basis of the electric-dipole selection rules for radiative transitions, $\Delta F = 0, \pm 1$ ($0 \leftrightarrow 0$), there exists a total of six allowed hyperfine transitions. The measured frequencies of these transitions, designated by their initial and final value of F , are given in Table 1.

TABLE 1
MEASURED HYPERFINE FREQUENCIES OF THE
 $1_{10} \rightarrow 1_{11}$ H_2CO TRANSITION, WITH RESPECT
TO $\nu_0 = 4829659.96 \pm 0.05 \text{ kHz}$

Transition* $F \rightarrow F'$	Relative Intensity (Theoretical)	$\nu - \nu_0 \dagger$ (kHz)
$1 \rightarrow 0$	4	-18.53 ± 0.06
$0 \rightarrow 1$	4	$-1.34 \pm 0.12 \ddagger$
$2 \rightarrow 2$	15	-0.35 ± 0.05
$2 \rightarrow 1$	5	$+4.05 \pm 0.05$
$1 \rightarrow 2$	5	$+6.48 \pm 0.05$
$1 \rightarrow 1$	3	$+11.08 \pm 0.05$

* F refers to the upper level of the transition and F' to the lower level.

† Quoted uncertainties represent the standard deviations of eight measurements.

‡ Unresolved, therefore calculated from the hyperfine constants.

The lower trace in Figure 2 is the best-fit theoretical spectrum, calculated from the hyperfine Hamiltonian and intensities given by Thaddeus, Krisher, and Loubser (1964, hereafter referred to as TKL). Since the shape of isolated lines is found to be very nearly Gaussian, we have assumed such a line shape when computing theoretical spectra in this article; it is also assumed that the populations of the hyperfine levels are normal, i.e., proportional to statistical weights. The theoretical spectrum in Figure 2 reproduces to within 50 Hz all the observed hfs. The slight discrepancies between theoretical and observed intensity ratios that are discernible in Figure 2 result from the state selection process, since the "state scrambler" was not used in obtaining the H₂CO data.

Hyperfine structure of the 4830-MHz transition of H₂CO is entirely magnetic in origin, being produced by the spin-spin interaction of the protons and by their spin-rotation interaction with the weak magnetic field caused by the rotation of the molecule (the carbon and oxygen nuclei, having no spin, do not contribute to the hfs). The hfs is completely determined (cf. TKL) by three parameters: $C_H(1_{10})$ and $C_H(1_{11})$, the spin-rotation constants for, respectively, the upper and lower states; and $\langle r_{HH}^{-3} \rangle$, the inverse cube of the distance between the protons averaged over the ground vibrational state. The best-fit values of these hyperfine constants are listed in Table 2.

Often the quantity of immediate interest to radio astronomy is neither the frequency of the most intense hyperfine component nor the line center ν_0 , but is instead the frequency ν_p of the peak intensity of the envelope of hyperfine lines. The difference between this frequency and ν_0 is given in Figure 3 for the 4830-MHz transition as a function of line width. In the calculation of the curve of Figure 3, the line shape has again been taken to be Gaussian; and the hyperfine intensities have been taken to be the normal ones listed in Table 1. Note that for large line widths, ν_p converges to ν_0 as it should.

b) Excited Vibrational States of H₂CO

The 1₁₀-1₁₁ transition has been observed with such a large signal-to-noise ratio at 4830 MHz that its detection in excited vibrational states is feasible. By employing a

TABLE 2
LINE CENTERS AND HYPERFINE COUPLING CONSTANTS

Molecule	Line Center (kHz)	Hyperfine Constant (kHz)
H ₂ CO.....	4829659.96 ± 0.05	$C_H(1_{10}) = -0.82 \pm 0.04$ $C_H(1_{11}) = -3.05 \pm 0.04$ $g_H^2 \mu_N^2 \langle r_{HH}^{-3} \rangle = 17.68 \pm 0.10$
H ₂ ¹³ CO.....	4593088.54 ± 0.06	$C_C(1_{10}) = 73.87 \pm 0.14$ $C_C(1_{11}) = 67.79 \pm 0.14$ $C_H(1_{10}) = -0.77 \pm 0.06$ $C_H(1_{11}) = -3.03 \pm 0.06$ $g_H^2 \mu_N^2 \langle r_{HH}^{-3} \rangle = 17.52 \pm 0.17$ $g_H g_C \mu_N^2 \langle r_{HC}^{-3} \rangle = 21.65 \pm 0.18$
H ₂ C ¹⁸ O.....	4388796.98 ± 0.10	$C_H(1_{10}) = -0.98 \pm 0.10$ $C_H(1_{11}) = -2.98 \pm 0.10$ $g_H^2 \mu_N^2 \langle r_{HH}^{-3} \rangle = 17.90 \pm 0.25$
HDCO.....	5346141.59 ± 0.09	$C_D(1_{10}) = 0.11 \pm 0.04$ $C_D(1_{11}) = -0.12 \pm 0.04$ $C_H(1_{10}) = -1.43 \pm 0.08$ $C_H(1_{11}) = -3.70 \pm 0.12$ $g_H g_D \mu_N^2 \langle r_{HD}^{-3} \rangle = 2.75 \pm 0.10$ $(eV_{aa}Q)_D = 8.15 \pm 0.45$ $(eV_{bb}Q)_D = -76.60 \pm 0.45$

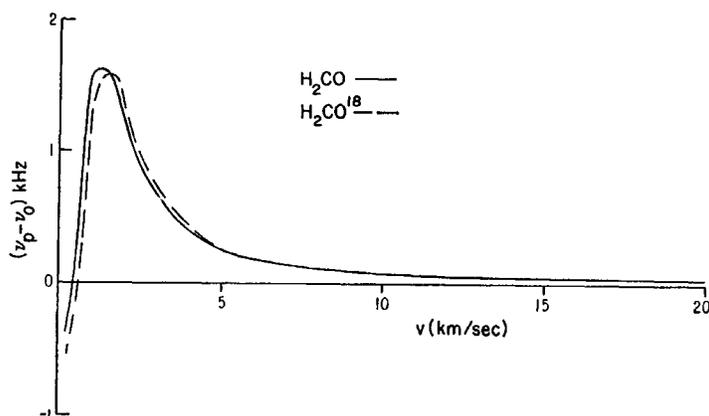


FIG. 3.—Peak frequency of the hyperfine envelope for the 6-cm transitions of H_2CO and $\text{H}_2\text{C}^{18}\text{O}$, as a function of line width at half-intensity (given in velocity units $v = c\Delta\nu/\nu$).

nozzle-beam source heated to 200–250° C, we succeeded in detecting it in the first excited states of both the ν_6 and ν_5 bending modes, which lie respectively 1167 and 1280 cm^{-1} above the ground state (Herzberg 1945, p. 300; see also Nakagawa *et al.* 1969). Although the transitions we observed had not been previously measured, it was possible to calculate their frequencies to within about 200 kHz from the work of Oka, Takagi, and Morino (1964) and thus a lengthy line search was avoided. Line widths of about 3 kHz and signal-to-noise ratios of about 15 were obtained with a 3-s time constant.

Both the $\nu_5 = 1$ and $\nu_6 = 1$ vibrational states are antisymmetric on exchange of the protons (cf. Herzberg 1945, chap. 2), and thus the 1_{10} and 1_{11} rotational wave functions require an $I = 0$ para spin state. The observed transitions therefore have no hfs. The measured frequencies are

$$\nu(\nu_6 = 1) = 4235952.38 \pm 0.11 \text{ kHz}$$

and

$$\nu(\nu_5 = 1) = 4968862.47 \pm 0.16 \text{ kHz} .$$

c) H_2^{13}CO

The 1_{10} – 1_{11} transition of H_2^{13}CO has been previously observed with a Stark-modulated absorption spectrometer by Flygare and Weiss (1966), who succeeded in resolving the hfs caused by the large spin-rotation interaction of the ^{13}C nucleus but were unable to resolve the further structure produced by the magnetic interactions of the protons. Determination of the hfs was the aim of their work, and absolute frequencies were given to a precision of only several parts in 10^6 .

Our source of molecules was the 1.1 percent naturally occurring H_2^{13}CO in para-formaldehyde. The observed spectrum, obtained by using the nozzle-beam source and the state scrambler, is shown in Figure 4. Line widths are about 2 kHz; the signal-to-noise ratio of the strongest line, obtained with a 3-s time constant, is about 40.

The measured hyperfine frequencies are listed in Table 3. The transitions are designated by the upper and lower values of the quantum numbers F_1 and F , which are defined by the coupling scheme

$$J + I = F_{1C} , \quad F_1 + I_C = F ,$$

where I_C is the spin of the ^{13}C nucleus, and I and J are as previously defined. The selection rules for electric dipole transitions are

$$\Delta F_1 = 0, \pm 1 \quad (0 \leftrightarrow 0) ; \quad \Delta F = 0, \pm 1 \quad (0 \leftrightarrow 0) .$$

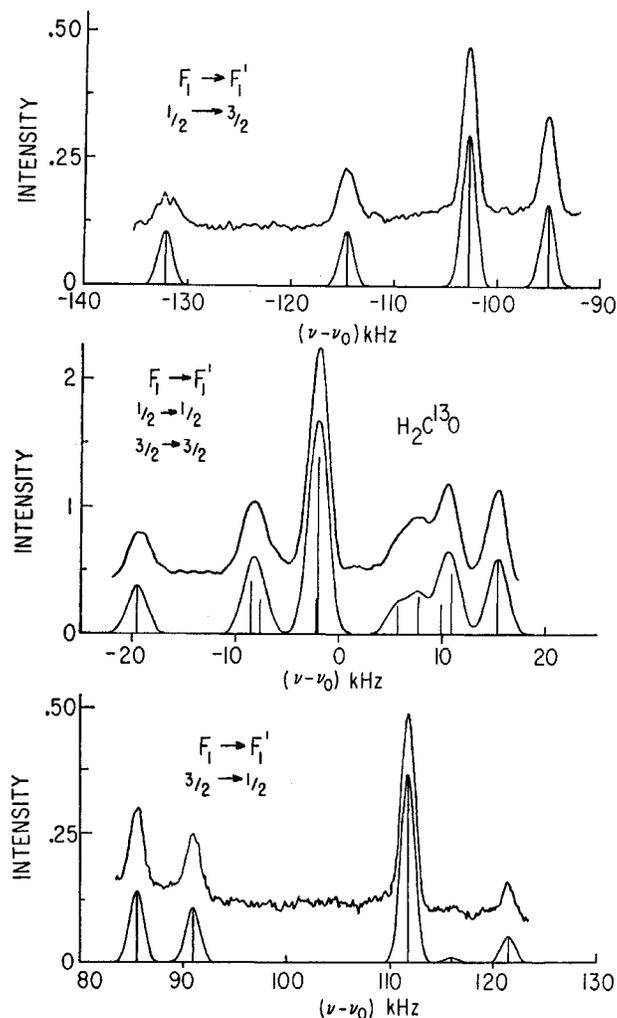


FIG. 4.—Observed (*upper spectra*) and theoretical (*lower spectra*) hfs of the 1_{10} - 1_{11} transition of H_2^{13}CO .

The best-fit theoretical spectrum, again calculated from the expressions in TKL, is shown below the observed spectrum in Figure 4; the rms deviation of the theoretical from the observed frequencies is only 130 Hz.

The hfs of the 1_{10} - 1_{11} H_2^{13}CO transition can be understood qualitatively as follows: a large ^{13}C ($I_C = \frac{1}{2}$) spin-rotation interaction splits each rotational level into two well-spaced sublevels, each of which is then further split by the small spin-rotation and spin-spin interactions of the protons, and by the small spin-spin interaction between the ^{13}C nucleus and the protons. Six independent parameters determine the hfs (cf. TKL), namely, $C_C(1_{10})$, $C_C(1_{11})$, $C_H(1_{10})$, and $C_H(1_{11})$, the spin-rotation constants of the ^{13}C and the protons, and $\langle r_{\text{HC}}^{-3} \rangle$ and $\langle r_{\text{HH}}^{-3} \rangle$, where r_{HC} and r_{HH} are the indicated internuclear distances, and the average indicated by the brackets is over the ground vibrational state. The values of these constants, determined from the best-fit theoretical spectrum, are given in Table 2. The curve showing the frequency of the peak intensity of the hyperfine manifold as a function of line width is plotted in Figure 5.

TABLE 3
 MEASURED HYPERFINE FREQUENCIES OF THE $\text{H}_2^{13}\text{CO } 1_{10} \rightarrow 1_{11}$
 TRANSITION, WITH RESPECT TO $\nu_0 = 4593088.54 \pm 0.06$ kHz

Transition* ($F_1F \rightarrow F'_1F'$)	Relative Intensity (Theoretical)	$\nu - \nu_0 \dagger$ (kHz)
1/2, 1/2 \rightarrow 3/2, 1/2.....	1.05	-132.22 \pm 0.14
1/2, 1/2 \rightarrow 3/2, 3/2.....	1.06	-114.78 \pm 0.14
1/2, 3/2 \rightarrow 3/2, 1/2.....	0.04	-112.65 \pm 0.25 \ddagger
1/2, 3/2 \rightarrow 3/2, 5/2.....	2.98	-102.87 \pm 0.09
1/2, 3/2 \rightarrow 3/2, 3/2.....	1.62	-95.19 \pm 0.14
1/2, 1/2 \rightarrow 1/2, 1/2.....	0.37	-39.16 \pm 0.16
1/2, 3/2 \rightarrow 1/2, 1/2.....	3.83	-19.57 \pm 0.07
1/2, 1/2 \rightarrow 1/2, 3/2.....	4.18	-8.59 \pm 0.25 \ddagger
3/2, 1/2 \rightarrow 3/2, 1/2.....	2.74	-7.39 \pm 0.10
3/2, 3/2 \rightarrow 3/2, 1/2.....	2.84	-2.16 \pm 0.25 \ddagger
3/2, 5/2 \rightarrow 3/2, 5/2.....	14.00	-2.00 \pm 0.05
3/2, 5/2 \rightarrow 3/2, 3/2.....	2.31	+5.70 \pm 0.15
3/2, 3/2 \rightarrow 3/2, 5/2.....	3.02	+7.58 \pm 0.15
3/2, 1/2 \rightarrow 3/2, 3/2.....	2.44	+9.97 \pm 0.15
1/2, 3/2 \rightarrow 1/2, 3/2.....	4.86	+10.89 \pm 0.25 \ddagger
3/2, 3/2 \rightarrow 3/2, 3/2.....	5.90	+15.37 \pm 0.11
3/2, 1/2 \rightarrow 1/2, 1/2.....	1.40	+85.54 \pm 0.10
3/2, 3/2 \rightarrow 1/2, 1/2.....	1.07	+90.93 \pm 0.10
3/2, 5/2 \rightarrow 1/2, 3/2.....	3.69	+111.78 \pm 0.08
3/2, 1/2 \rightarrow 1/2, 3/2.....	0.09	+116.04 \pm 0.25 \ddagger
3/2, 3/2 \rightarrow 1/2, 3/2.....	0.51	+121.38 \pm 0.20

* F_1F refers to the upper level of the transition and F'_1F' to the lower level.

\dagger Quoted uncertainties represent standard deviations of from six to ten measurements.

\ddagger Calculated from frequency closure.

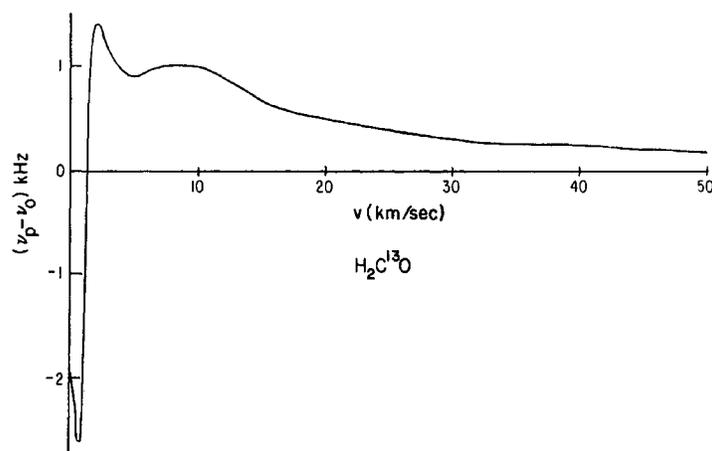


FIG. 5.—Peak frequency of the hyperfine envelope for H_2^{13}CO as a function of line width

d) $\text{H}_2\text{C}^{18}\text{O}$

The 1_{10} - 1_{11} transition of $\text{H}_2\text{C}^{18}\text{O}$ has been studied in the laboratory by Oka, Hirakawa, and Shimoda (1960), but with considerably less precision and resolution than is attainable in our spectrometer. We used the nozzle-beam source to observe this transition in a beam of natural formaldehyde, where the fractional abundance of $\text{H}_2\text{C}^{18}\text{O}$ is only 0.2 percent. The observed spectrum is the upper curve in Figure 6. Line widths are about 2 kHz, and the signal-to-noise ratio for the strongest line is about 15 with a 3-s time constant.

Since the ^{18}O nucleus, like that of ^{16}O , has zero spin, the hfs of the 1_{10} - 1_{11} transition of $\text{H}_2\text{C}^{18}\text{O}$ closely resembles that of ordinary formaldehyde. The measured frequencies of the hyperfine transitions are given in Table 4. As in the case of H_2CO , the hyperfine

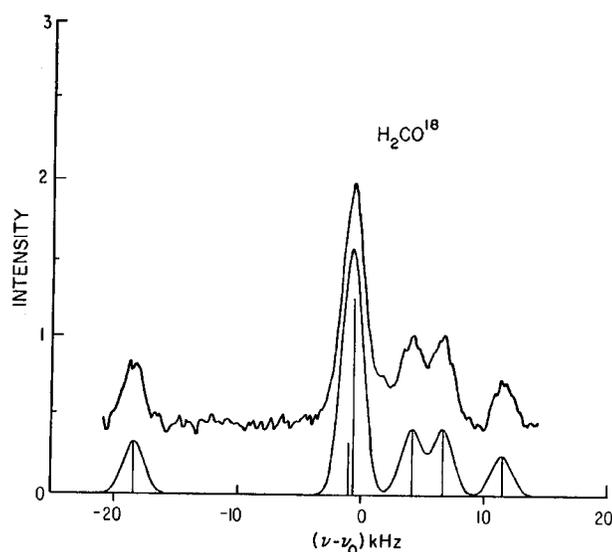


FIG. 6.—Observed and theoretical hfs of the 1_{10} - 1_{11} transition of $\text{H}_2\text{C}^{18}\text{O}$

TABLE 4
MEASURED HYPERFINE FREQUENCIES OF THE
 $1_{10} \rightarrow 1_{11}$ $\text{H}_2\text{C}^{18}\text{O}$ TRANSITION, WITH RESPECT
TO $\nu_0 = 4388796.98 \pm 0.12$ kHz

Transition* $F \rightarrow F'$	Relative Intensity (Theoretical)	$\nu - \nu_0$ † (kHz)
1→0.....	4	-18.43 ± 0.14
0→1.....	4	- 1.02 ± 0.30‡
2→2.....	15	- 0.68 ± 0.08
2→1.....	5	+ 4.09 ± 0.10
1→2.....	5	+ 6.56 ± 0.17
1→1.....	3	+11.45 ± 0.13

* F refers to the upper level of the transition and F' to the lower level.

† Quoted uncertainties represent the standard deviations of ten measurements.

‡ Not resolved, therefore calculated from the hyperfine constants.

spectrum is determined by the three parameters $C_H(1_{10})$, $C_H(1_{11})$, and $\langle r_{HH}^{-3} \rangle$. The best-fit theoretical spectrum is shown in Figure 6, and the values of the hyperfine constants determined from the fit are given in Table 2. The shift of the peak of the hyperfine envelope with line width is shown in Figure 3.

e) HDCO

The only previous measurement of the 6-cm transition of HDCO was also by Oka *et al.* (1960) in a conventional absorption spectrometer. Since the natural abundance of deuterium is only 0.015 percent, we used an enriched sample of para-formaldehyde containing 90 percent HDCO to obtain the spectrum. The observed hyperfine spectrum, shown in Figure 7, was obtained with the crinkly-foil beam source, driven at a pressure some 10 times lower than normal in order to conserve the sample.

The best-fit theoretical spectrum shown in Figure 7 reproduces the observed hfs to within 100 Hz; the full width at half-maximum of the Gaussian line shape has been taken to be 1.5 kHz. Slight discrepancies between the theoretical and experimental intensities are discernible and again can be attributed to state selection. Most of the HDCO hyperfine transitions are not well enough resolved to be measured individually, so their exact frequencies must be determined from the fit. The best-fit frequencies, listed in Table 5, are designated by the upper and lower values of the quantum numbers F_1 and F , defined by the coupling scheme

$$J + I_D = F_1, \quad F_1 + I_H = F,$$

where I_D is the deuteron spin, I_H is the proton spin, and J is the total angular momentum of the molecule excluding nuclear spins.

Hyperfine structure in HDCO is produced by the electric-quadrupole interaction of the deuteron ($I_D = 1$) with the molecular electric field, and by the smaller magnetic interactions of the proton and deuteron. The hyperfine spectrum is then determined by seven parameters (cf. TKL), namely, $C_D(1_{10})$, $C_D(1_{11})$, $C_H(1_{10})$, and $C_H(1_{11})$, the spin-rotation constants of the deuteron and the proton; $\langle r_{HD}^{-3} \rangle$, where r_{HD} is the distance between the proton and the deuteron; V_{aa} , the electric-field gradient along the a inertial axis; and V_{bb} , the field gradient along the b inertial axis (the gradient in the direction

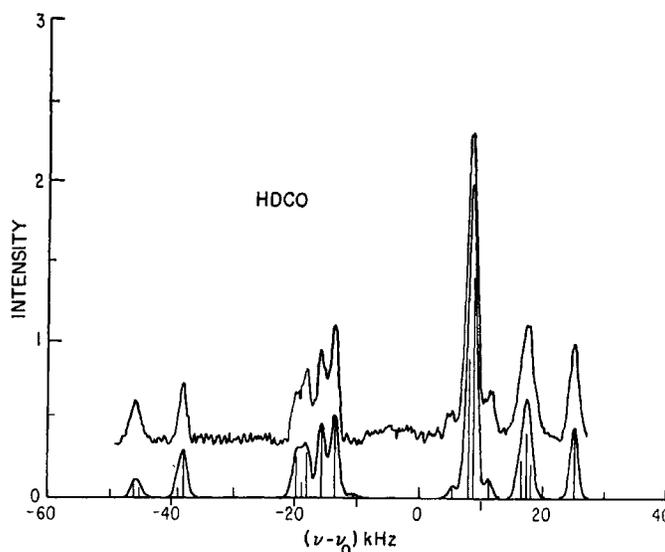


FIG. 7.—Observed and theoretical hfs of the 1_{10} - 1_{11} transition of HDCO

perpendicular to the plane of the molecule is determined from V_{aa} and V_{bb} by Laplace's equation). The best-fit values of the hyperfine constants are given in Table 2. The peak intensity of the hyperfine manifold as a function of line width is plotted in Figure 8.

IV. DISCUSSION

Although a systematic interpretation of the hyperfine coupling constants is beyond the scope of this article, it is an interesting check on the accuracy to which the formaldehyde HFC has been measured and analyzed to note how well certain derived parameters, notably internuclear distances, and the electric-field gradients at the hydrogen nucleus, agree among themselves and with the results of previous work.

a) Internuclear Distances

Table 6 lists the internuclear distances $\langle r^{-3} \rangle^{-1/3}$ obtained from the spin-spin constants of Table 2; it can be seen that all the hydrogen-hydrogen distances, both H-H

TABLE 5
BEST-FIT HYPERFINE FREQUENCIES OF THE $1_{10} \rightarrow 1_{11}$ HDCO TRANSITION,
WITH RESPECT TO $\nu_0 = 5346141.59 \pm 0.09$ kHz

Transition* ($F_1F \rightarrow F'_1F'$)	Relative Intensity (Theoretical)	$\nu - \nu_0 \dagger$ (kHz)	Transition* ($F_1F \rightarrow F'_1F'$)	Relative Intensity (Theoretical)	$\nu - \nu_0 \dagger$ (kHz)
$1_{1/2} \rightarrow 1_{1/2}$	0.89	-46.07	$2_{3/2} \rightarrow 1_{3/2}$	0.27	-11.14
$1_{3/2} \rightarrow 1_{1/2}$	0.65	-45.17	$2_{5/2} \rightarrow 2_{3/2}$	0.80	+ 5.38
$1_{1/2} \rightarrow 1_{3/2}$	0.67	-39.00	$2_{3/2} \rightarrow 2_{3/2}$	0.89	+ 7.92
$1_{3/2} \rightarrow 1_{3/2}$	2.76	-38.10	$2_{5/2} \rightarrow 2_{5/2}$	14.00	+ 8.62
$1_{1/2} \rightarrow 2_{3/2}$	2.66	-19.93	$2_{3/2} \rightarrow 2_{5/2}$	1.24	+11.17
$1_{3/2} \rightarrow 2_{3/2}$	0.96	-19.03	$1_{1/2} \rightarrow 0_{1/2}$	2.44	+16.44
$2_{3/2} \rightarrow 1_{1/2}$	2.91	-18.22	$1_{3/2} \rightarrow 0_{1/2}$	4.21	+17.34
$1_{3/2} \rightarrow 2_{5/2}$	4.76	-15.78	$0_{1/2} \rightarrow 1_{1/2}$	2.21	+18.03
$2_{5/2} \rightarrow 1_{3/2}$	5.20	-13.71	$0_{1/2} \rightarrow 1_{3/2}$	4.44	+25.11

* F_1F refers to the upper level of the transition and F'_1F' to the lower level.

† Estimated uncertainty is ± 0.10 kHz.

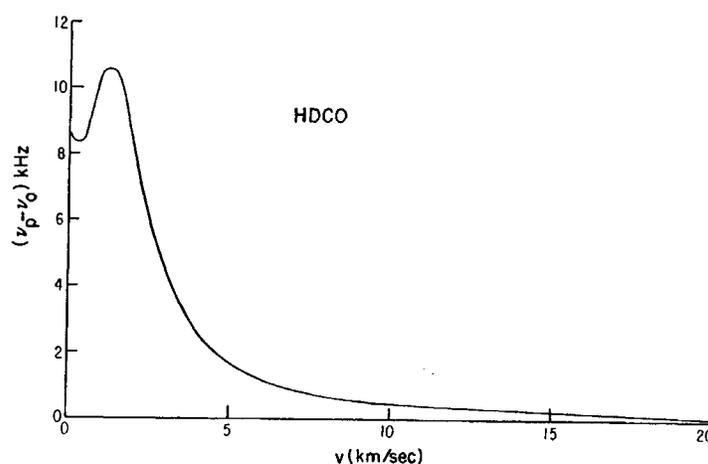


FIG. 8.—Peak frequency of the hyperfine envelope for HDCO

TABLE 6
INTERNUCLEAR DISTANCES

Molecule (1)	Nuclei (2)	$\langle r^{-2} \rangle^{-1/2}$ (Å) (3)	$\langle r^{-3} \rangle^{-1/3}$ (Å) (4)
H ₂ CO.....	H-H	1.89832 ± 0.00004*	1.894 ± 0.004
H ₂ ¹³ CO.....	H-H	1.89820 ± 0.00004*	1.900 ± 0.006
	H- ¹³ C	1.1161 ± 0.007*†	1.117 ± 0.003
H ₂ C ¹⁸ O.....	H-H	1.89826 ± 0.00008*	1.886 ± 0.009
HDCO.....	H-D	...	1.886 ± 0.023

* Takagi and Oka (1963).

† Value for H₂CO.

and H-D, are in excellent agreement with one another. The effects of zero-point vibration, which might be as large as ~ 0.3 percent, are apparently too small to be detected. Table 6 also gives, in column (3), the internuclear distances derived from the molecular "geometry"—i.e., from the rotation constants—and these are seen to agree with both the H-H and H-C distances derived from the spin-spin constants.

b) Electric-Field Gradient

If the deuteron quadrupole moment is taken to be $Q = 2.796 \times 10^{-27}$ cm² (Narumi and Watanabe 1964), the electric-field gradient along the C-D bond at the location of the D in HDCO is found from the data in Table 2 to be $V_{\xi\xi} = 8.25 \pm 0.25 \times 10^{14}$ statvolt cm⁻². This is in good agreement with the values 8.3×10^{14} and 8.45×10^{14} statvolt cm⁻² previously determined by, respectively, Thaddeus *et al.* (1964), and Flygare (1964). The asymmetry parameter $\eta = (V_{\xi\xi} - V_{xx})/V_{\xi\xi}$, a measure of the departure of the electric field from cylindrical symmetry about the C-D bond, is found to be $\eta = -0.013 \pm 0.04$, which agrees with the value $|\eta| < 0.15$ found by Thaddeus *et al.* but is considerably more accurate. This low value of η indicates that the electric field is indeed highly symmetric about the bond in formaldehyde at the location of the hydrogen nucleus.

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