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The Far-Infrared Laser Magnetic Resonance Spectrum of Vibrationally Excited C_2H[1]

JOHN M. BROWN

The Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, England

AND

KENNETH M. EVENSON

National Bureau of Standards, Boulder, Colorado 80303

Some previously observed but unassigned lines in the laser magnetic resonance spectrum of the F + CH_4 flame at 490.4 μm have been assigned to the $N = 7 \leftarrow 6$, $+ \leftarrow -$ transition of the C_2H radical in its (010) vibrational level. The spectrum is an interesting example of a magnetic resonance spectrum of a radical displaying Hund's case (b) coupling and arises because the laser frequency is very close to the zero-field molecular frequency. The measured resonances are combined with recently available millimeter-wave observations of C_2H in the same vibrational level to give an improved set of molecular parameters. Some of these parameters provide quantitative information on the extent of the mixing of the $\tilde{X}^2\Sigma^+$ state with the low-lying $\tilde{A}^2\Pi$ state of C_2H.

1. INTRODUCTION

The C_2H radical is now known to be a significant constituent of several chemical systems, both in the laboratory (*1–3*) and in the interstellar medium (*4, 5*). Partly for this reason, it has been subjected to intensive study by a wide variety of spectroscopic techniques. These include electron spin resonance (ESR) (*6, 7*), matrix isolation infrared (*8, 9*), far-infrared laser magnetic resonance (LMR) (*10*), microwave spectroscopy (*11–13*), color-center laser spectroscopy (*14–17*), and diode laser spectroscopy (*18*). Despite all this work, many characteristics of the low-lying $\tilde{A}^2\Pi$ state of C_2H including its precise location still await determination. Even the C–H stretching frequency of C_2H in its ground $^2\Sigma^+$ state has not been measured at the time of writing. Any additional information on C_2H is certain to be useful.

The present paper is an extension of a previous study of C_2H by far-infrared LMR (*10*). In the earlier paper, partially resolved resonances were observed at very low flux densities (<20 mT) with the 490.4-μm line at 611.3 GHz and assigned to the $N = 7 \leftarrow 6$ rotational transition of C_2H in its ground vibrational level. A series of weak doublets lying at higher fields were observed at the same time but were not assigned by Saykally *et al.* (*10*). Following the work of Curl *et al.* (*15*), we were able to assign

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these resonances to the $N = 7 \leftarrow 6$ transition of C_2H in the (010) level which lies some 370 cm^{-1} above the ground state (*19*). Lower N rotational transitions of C_2H in the same vibrational level have been observed very recently by two independent groups using millimeter-wave techniques (*20, 21*). The availability of these additional frequencies makes it worthwhile to analyze the magnetic resonance data quantitatively. This paper describes the assignment of the LMR spectrum and its analysis along with the zero-field frequencies. The observations provide a good example of a magnetic resonance spectrum of a molecule close to the limit of Hund's case (b) coupling, a rather unusual occurrence.

2. EXPERIMENTAL DETAILS AND RESULTS

The far-infrared LMR spectrum of the C_2H radical was recorded in the NBS laboratories at Boulder, Colorado, with an optically pumped LMR spectrometer which has been described previously (*22*). The spectrometer consists of two sections, a far-infrared gain cell pumped transversely by a CO_2 laser with a single-line output power of about 35 W and an intracavity sample cell, which is located between the pole pieces of a 38-cm electromagnet capable of producing flux densities up to 2.0 T. The gain cell and sample region are separated by a rotatable, polypropylene beam splitter which determines the polarization of the laser radiation relative to the static magnetic field. The C_2H radical was generated in the sample region in the same way as before (*10*) by the reaction of F atoms with CH_4 in a flow system. A 5% mixture of F_2 in He was passed through a microwave discharge at a pressure of 110 Pa and the products reacted with about 3 Pa of CH_4. The absorption signals were modulated at 5 kHz by a set of Helmholtz coils. The output of the laser was coupled into a He-cooled Ge bolometer by a 45° cylindrical copper mirror. After suitable amplification and phase-sensitive detection, the signal was displayed on a chart recorder as the first derivative of an absorption lineshape.

The observations described in this paper were made using the 490.4-μm laser line of vinyl bromide (*23*), pumped by the $10P(16)$ line of the CO_2 laser. This is the same laser line that was used in the earlier work to study C_2H in its ground vibrational level (*10*). The previous observations, between 0 and 0.02 T, were reproduced with slightly better signal-to-noise ratios. The spectrum for π (that is, parallel or $\Delta M_J = 0$) polarization is shown in Fig. 1. The features attributable to the vibrational ground state occur at very low fields. Here we are concerned with the progression of doublet resonances running out to higher fields. Laser pulling experiments allowed the sign of the tuning rate ($\partial\nu/\partial B$) to be determined. The two members of each doublet tuned in opposite directions, the lower field member with a negative sign and the higher field with a positive sign. This observation strongly suggests that the doubling is not caused by nuclear spin hyperfine effects. By reducing the pressure and modulation amplitude, it was just possible to resolve a further doubling of the first two members of the progression. This is discernible in the spectrum of Fig. 1. Subsequent analysis showed that the larger doubling is attributable to electron spin (fine structure) effects and the smaller doubling, to the proton hyperfine splitting in C_2H.

The magnetic field was controlled with a rotating coil magnetometer. This magnetometer was subsequently calibrated at slightly higher fields against a proton NMR

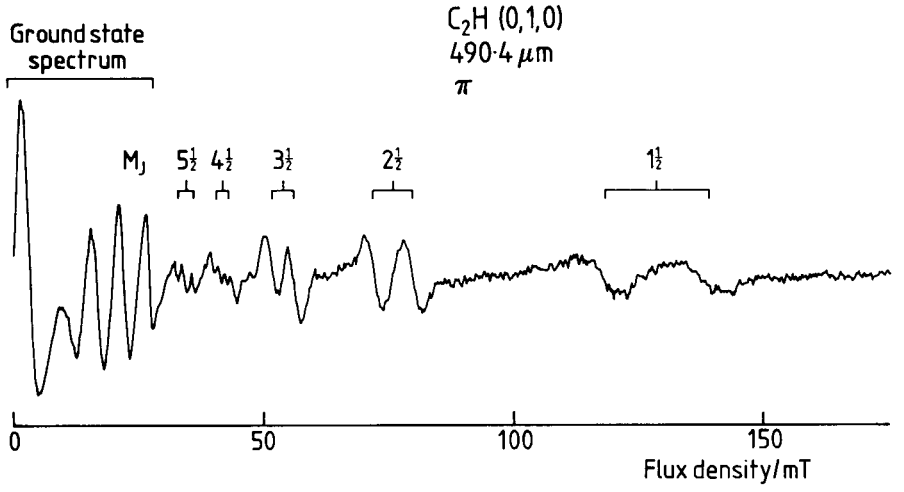

FIG. 1. The 490.4-μm spectrum of the C_2H radical between 0.0 and 0.15 T recorded in the π (parallel or $\Delta M_J = 0$) polarization. The first five resonances arise from the $N = 7 \leftarrow 6$ transition of C_2H in its ground vibrational level and have been analyzed in previous work (*10*). The other resonances at higher fields form a series of doublets and are associated with the $N = 7 \leftarrow 6$ transition of C_2H in the (010) excited vibrational level. The doubling arises from the electron spin fine structure. An additional, smaller doubling is just visible on the first two members of this series and arises from proton hyperfine effects. Frequency pulling experiments show that the tuning rate $\partial\nu/\partial B$ for the first member of each doublet is negative whereas that for the second member is positive.

fluxmeter. The uncertainty in a single measurement is ±0.2 mT. The results for the spectrum recorded in both parallel and perpendicular polarizations are given in Table I.

After the assignment of the 490.4-μm spectrum was completed as described in the following section, other near coincidences between far-infrared laser lines and rotational transitions of C_2H in the (010) level were predicted. Detailed calculation of the magnetic resonance spectrum in each case suggested that the resonances would occur at fields when the electron spin was significantly decoupled and would consequently be very weak. Searches were made with the best candidates (the 694.2- and 570.6-μm lines of CH_3OH and the 432.1-μm line of HCOOD) but no signals were observed.

3. ANALYSIS

(i) Effective Hamiltonian for the (010) Level of C_2H

Previous studies of C_2H in the (010) vibrational level by color-center laser spectroscopy (*15*) have shown that the rotational levels can be described by a $^2\Pi$ electronic Hamiltonian with a spin–orbit coupling constant A equal to -0.35 cm^{-1}. This value is smaller than the rotational constant B (1.45 cm^{-1}) and consequently the levels conform to a Hund's case (b) coupling scheme (*24*). On the other hand, this value is very large in comparison with the expectations for an isolated level of a $^2\Sigma$ electronic state which is vibrationally Π in character. The explanation, as Curl *et al.* point out (*15*), is that the (010) level of the $\tilde{X}\,^2\Sigma^+$ state of C_2H is perturbed by levels of the

TABLE I

Observed Transitions in the Rotational Spectrum of C_2H in the (010) Level of the $\tilde{X}^2\Sigma^+$ State

(a) Far Infrared LMR Spectrum 490.4 μm

N	F_i	Parity	M_J	ν/MHz	Flux Density/mT	(Obs-calc) /MHz
7 ← 6	F_1	+ ← −	5½ ← 5½	611333.6	33.8	1.5[a]
	F_2		5½ ← 5½		35.9	-2.1
	F_1		4½ ← 4½		40.2	-1.4
	F_2		4½ ← 4½		42.4	2.8
	F_1		3½ ← 3½		52.4	0.8
	F_2		3½ ← 3½		56.0	0.2
	F_1		2½ ← 2½		71.7	-0.3
	F_2		2½ ← 2½		79.6	-0.0
	F_1		1½ ← 1½		115.3	-0.6
	F_2		1½ ← 1½		136.0	0.2
	F_1		-½ ← ½		42.0	-0.5
	F_2		-½ ← ½		46.7	0.0
	F_1		-1½ ← -½		54.8	0.0
	F_2		-1½ ← -½		62.1	-0.5
	F_1		-2½ ← -1½		77.8	-0.0
	F_2		-2½ ← -1½		91.1	-0.4
	F_1		6½ ← 5½		104.8	0.3
	F_2		6½ ← 5½		112.9	-0.2

(b) Millimeter-wave spectrum (20)

N	J	Parity	F	Frequency (MHz)	(obs-calc) /kHz
2 ← 1	1½ ← ½	+ ← −	1 ← 0	170885.841 (82)[b]	4[a]
		+ ← −	2 ← 1	170887.030 (29)	10
		+ ← −	1 ● 1	170897.890 (42)	-6
		− ← +	1 ← 0	172246.787 (46)	-4
		− ← +	2 ← 1	172249.761 (20)	-2
		− ← +	1 ← 1	172263.532 (38)	2

[a] Calculated values obtained using the parameter values given in Table II.

[b] Authors' estimate of experimental uncertainty, in units of the last quoted decimal place.

[c] Proton hyperfine splitting unresolved.

TABLE I—*Continued*

N	J	Parity	F	Frequency (MHz)	(obs-calc) /kHz
	2½ ← 1½	+ ← −	3 ← 2	174215.440 (26)	24
		+ ← −	2 ← 1	174219.435 (42)	−25
		− ← +	3 ← 2	175575.067 (95)	28
		− ← +	2 ← 1	175578.769 (41)	−34
3 ← 2	2½ ← 1½	− ← +	c	259152.150 (38)	−14
		+ ← −	c	261196.725 (38)	−4
	3½ ← 2½	− ← +	4 ← 3	260447.247 (32)	−1
		− ← +	3 ← 2	260448.876 (35)	−30
		+ ← −	4 ← 3	262487.823 (20)	−34
		+ ← −	3 ← 2	262489.430 (24)	59
4 ← 3	3½ ← 2½	+ ← −	c	346249.035 (50)	9
		− ← +	c	348974.523 (54)	6
	4½ ← 3½	+ ← −	c	346928.993 (37)	10

same vibronic symmetry in the low-lying $\tilde{A}^2\Pi$ state. In consequence, some of the orbital angular momentum is transferred from the $\tilde{A}$ to the $\tilde{X}$ state and the parameters such as the spin–orbit constant A or the Λ-doubling constant p become quite large in magnitude. Such parameters are therefore valuable sources of information on the extent of the vibronic coupling and are well worth determining.

We have used the same model as Curl *et al.* (*15*) for the levels of the (010) state of C_2H in our analysis, adopting the N^2 formulation of the $^2\Pi$ Hamiltonian (*25*). This allows the use of the same computer program employed in the analyses of the LMR spectra of diatomic species such as CH (*26*) and OH (*27*). The detailed definition of the molecular parameters is given in these references.

(ii) Zeeman Patterns and Assignments

In order to understand the 490.4-μm magnetic resonance spectrum, it is necessary to appreciate how the individual M_J components of a rotational transition in C_2H vary with magnetic flux density. The relative positions, intensities, and tuning rates of these components constitute the Zeeman pattern. In a near Hund's case (b) molecule like C_2H in its $\tilde{X}^2\Sigma^+$ state, the electron spin is quite easily decoupled from the molecular framework by the magnetic field and the energy levels show a Paschen–Back effect. In this situation, the Zeeman pattern depends markedly on the size of the mismatch between the laser frequency and the molecular transition frequency at zero field. The range of patterns which can arise for a given molecule can be best appreciated by plotting the dependence of a transition frequency on magnetic field (*28, 29*). A mag-

netic resonance spectrum then corresponds to a (horizontal) cut through the diagram at a particular frequency. This procedure works because it is almost always possible to make a reasonably reliable estimate of the magnetic moment of a molecule in any given rotational level. It has been used successfully in the analyses of a wide range of magnetic resonance spectra, for example, CH_2 (*22*).

The rotational transition of C_2H in the (010) level involved in the 490.4-μm spectrum is $N = 7 \leftarrow 6$. The rotational levels of this vibrational state show l-type doubling; the spectrum is concerned with the higher-frequency component of the l-type doublet ($+ \leftarrow -$). At zero magnetic field, there are four spin components associated with this transition: $J = 7\frac{1}{2} \leftarrow 6\frac{1}{2}$ (or $F_1 \leftarrow F_1$) and $J = 6\frac{1}{2} \leftarrow 5\frac{1}{2}$ ($F_2 \leftarrow F_2$), both of which are strong; $J = 6\frac{1}{2} \leftarrow 6\frac{1}{2}$ ($F_2 \leftarrow F_1$) which is allowed but considerably weaker; and $J = 7\frac{1}{2} \leftarrow 5\frac{1}{2}$ ($F_1 \leftarrow F_2$) which is forbidden at zero field but can acquire a low intensity in the presence of a magnetic field. The dependence of the transition frequencies of the individual M_J components of these four transitions in π polarization with magnetic field is shown in Fig. 2. The $F_1 \leftarrow F_1$ and $F_2 \leftarrow F_2$ transitions tune very little as the field increases but they retain their full electric dipole intensity. The $F_1 \leftarrow F_2$ and $F_2 \leftarrow F_1$ transitions on the other hand tune very strongly but rapidly lose such electric dipole intensity as they possess with increasing field. This behavior is simply a manifestation of electron spin decoupling (*28*).

For C_2H in the (010) level, the 490.4-μm laser frequency lies almost exactly midway between the $F_1 \leftarrow F_1$ and $F_2 \leftarrow F_2$ zero-field frequencies. The relevant part of the transition frequency diagram is shown with an expanded scale in Fig. 3. The relative positions and intensities of the observed lines allow the transition frequency to be located in one of two positions on this diagram, equidistant about the center line. The observed signs of the tuning rates remove this final ambiguity in the assignment and show that the laser frequency is slightly above the midpoint of the Zeeman diagram where the $F_1 \leftarrow F_1$ and $F_2 \leftarrow F_2$ transitions cross over. The positions of the observed lines in the spectrum of Fig. 1 are marked in Fig. 3. The quantum number assignment follows immediately.

(iii) Fit of the Observed Data for the (010) Level of C_2H

The 490.4-μm LMR spectrum of C_2H in the (010) level depends on the zero-field rotational frequency, the spin–rotation splitting of the levels $N = 6$ and 7, and the molecular magnetic moments (g factors). There is insufficient information to determine all the molecular parameters for this vibrational level. However, the measurement of lower rotational transition frequencies by millimeter-wave spectroscopy (*20, 21*) enlarges the data set considerably and makes a fit to a molecular Hamiltonian worthwhile.

All the available measurements on C_2H in the (010) level were included in the fit; they are collected in Table I. Each datum was weighted inversely as the square of the experimental uncertainty. This uncertainty is given for each of the millimeter-wave measurements in Table Ib and that for each of the LMR measurements was taken as 0.5 MHz. The model used in the fit was the electronic $^2\Pi$ Hamiltonian (*27*). Because the levels involved are vibronically $^2\Pi$, all the parameters determined must be regarded as effective to a greater or lesser extent. The rotational Hund's case (a) basis set was truncated at $\Delta J = \pm 1$. The result of the least-squares fit is given in the form of residuals

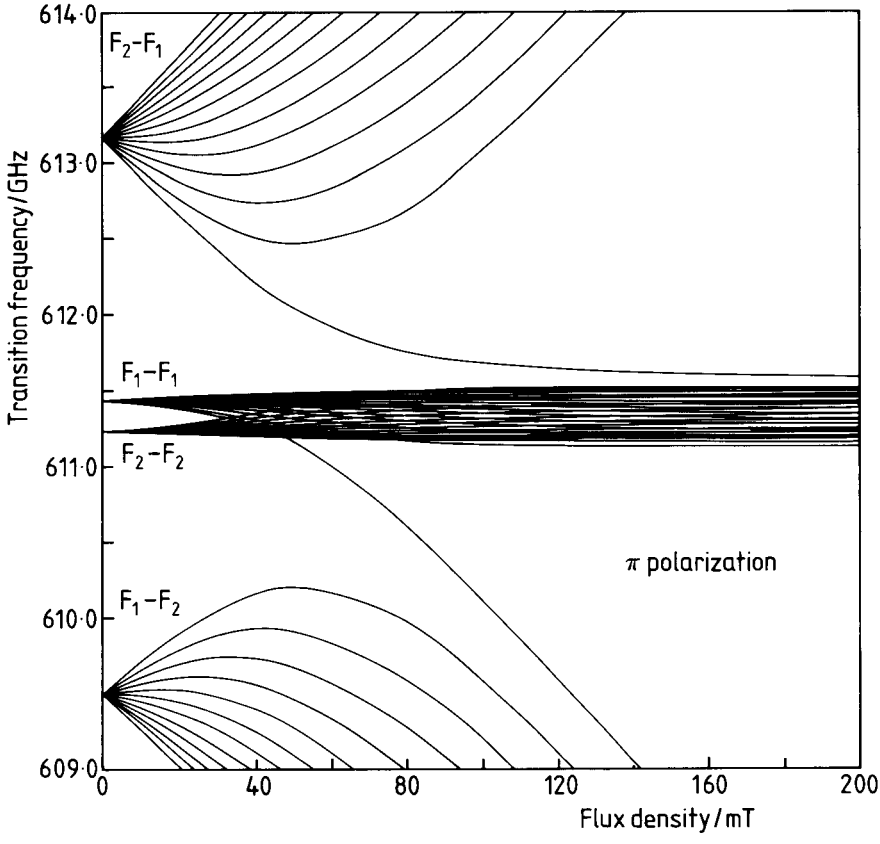

FIG. 2. The behavior of the transition frequencies of the four spin components of the $N = 7 \leftarrow 6$ transition of C_2H in the (010) level of its $\tilde{X}\,^2\Sigma^+$ state with varying magnetic field in π polarization. The F_1–F_1 and F_2–F_2 transitions become independent of field as it increases but retain their full electric dipole intensity. The F_2–F_1 and F_1–F_2 transitions, on the other hand, tune rapidly with the magnetic field but lose their electric dipole intensity as the field increases. This is a manifestation of the decoupling of the electron spin (which provides the magnetic moment) from the rotating molecular framework (with which the electric dipole transition moment is associated).

in Table I and the parameters determined are given in Table II. In these calculations, the magnetic moment was assumed to arise from the electron spin only; i.e., $g_S = 2.002$ and $g_L = 0.0$. In view of the other evidence of vibronic coupling, this is almost certainly not correct. However, because the observed resonances occur at low magnetic fields, the Zeeman effect does not need to be modeled very accurately. All the other parameters in the $^2\Pi$ Hamiltonian, including A_D, were constrained to zero. The K-type doubling of the levels of C_2H in the (010) state is determined primarily by the parameter q; in other words, the splitting is predominantly a manifestation of l-type doubling (*15*). The sign of this parameter is therefore known from vibration–rotation theory. If the level were being treated as a vibrational Π level, the parameter q would be positive. However, there is an inconsistency between the sign convention used for l-type doubling and that for Λ-type doubling parameters (*30*). Since we are using an electronic $^2\Pi$

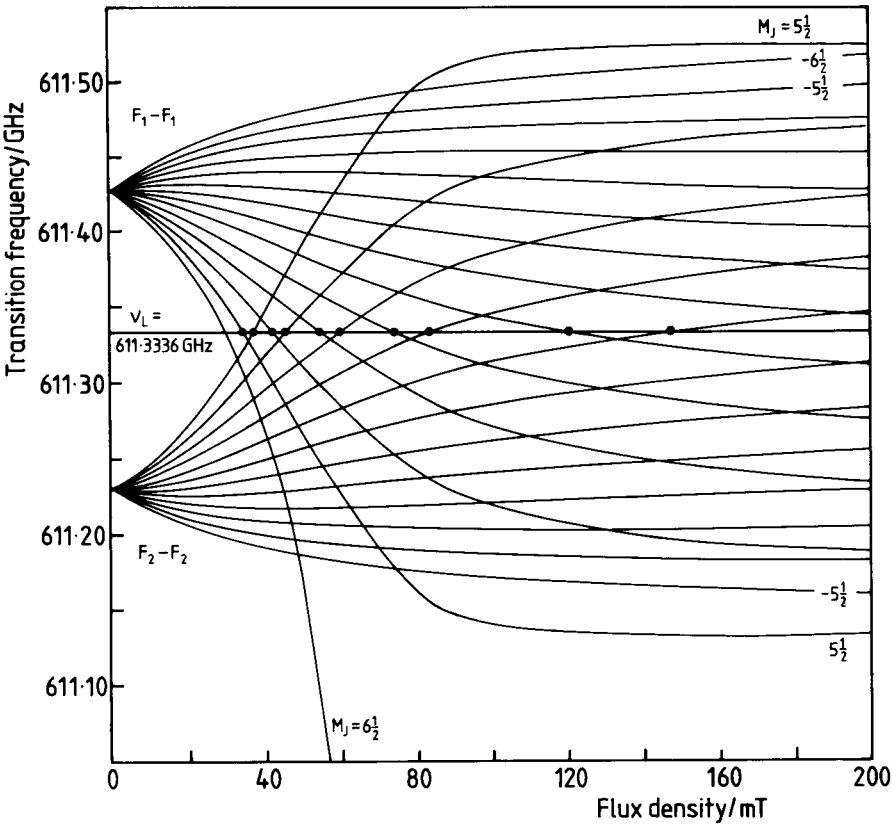

FIG. 3. An enlarged portion of the transition frequency diagram of Fig. 2, showing the frequencies close to that of the 490.4-μm far-infrared laser. The positions of the observed resonances in the π spectrum, shown in Fig. 1, are marked with black dots. Note that the pattern is almost symmetrical about its midpoint and that any given spectrum could equally well be assigned to a frequency below this value as above it. The information obtained on the signs of the tuning rates, $\partial\nu/\partial B$, allows this ambiguity to be resolved.

Hamiltonian, q is a Λ-doubling parameter and is taken to be negative. Irrespective of which description is adopted, the f levels lie above the e levels in the (010) state of C_2H.

The parameters determined in the fit are compared in Table II with those reported by Woodward *et al.* (*20*) from their fit of the microwave data set by itself. There is good agreement between the two sets of values. The inclusion of the LMR data somewhat improves the determination of the rotational parameters B and D.

4. DISCUSSION

The higher-field part of the 490.4-μm LMR spectrum of the C_2H radical has been assigned to the $N = 7 \leftarrow 6$ transition of the molecule in its (010) level. The assignment has been confirmed by fitting to a set of parameters consistent with other observations of the molecule by color-center laser (*15*) and millimeter-wave spectroscopy (*20*).

TABLE II

Molecular Parameters for CCH in the (010) Level of the $X^2\Sigma^+$ State

Parameter [a]	This work[b]		Woodward et al. (20)	
A	-10391.74	(42)[c]	-10391.58	(17)[d]
γ	-46.81	(11)	-46.800	(38)
B	43508.685	(11)	43508.6809	(76)
D	0.11464	(37)	0.11448	(32)
p	-4.36	(16)	-4.409	(91)
$10^3 p_D$	-0.49	(62)	1.8	(39)
q	-340.521	(16)	-340.5161	(98)
$10^2 q_D$	0.272	(69)	0.240	(53)
a	0.58	(22)	0.499	(84)
b_F	35.63	(32)	35.37	(12)
c	13.24	(35)	13.24	(13)
d	3.51	(19)	3.511	(68)

[a] Value in MHz.

[b] The following g factors were assumed: $g_L = 0.0$, $g_S = 2.002$.

[c] The numbers in parentheses are estimates of the standard deviation from the least-squares fit, in units of the last quoted decimal place.

[d] Authors' estimate of standard deviation.

The observation of a Hund's case (b) molecule by magnetic resonance techniques requires a very close near coincidence between the laser and the molecular transition frequency. Regrettably, there are at present no suitable laser lines to enable other rotational transitions for C_2H in the (010) level to be detected.

The parameters of an electronic $^2\Pi$ Hamiltonian have been fitted to the available rotational transition frequencies of C_2H in its (010) level. Some of the parameters determined (A, p, and the nuclear hyperfine parameter, a) would be expected to be zero if the (010) level was simply a vibrational level of a $^2\Sigma$ electronic state. The fact that they are not zero provides a quantitative measure of the perturbation of the $\tilde{X}^2\Sigma^+$ state by the $\tilde{A}^2\Pi$ state. For example, the spin–orbit constant for C_2H in a "pure" $\tilde{A}^2\Pi$ state is estimated to be -25 cm^{-1} (*16*). The value observed for C_2H in the (010) level of the $\tilde{X}$ state of -0.347 cm^{-1} implies that there is about 1.5% electronic Π character in this state. It would be very interesting to detect LMR transitions of C_2H in the $\tilde{A}^2\Pi$ state. Sensitivity considerations suggest that such observations would be quite possible. In particular, measurement of the orbital g factor g_L would provide a direct measure of the mixing between the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states since this parameter is rather easier to interpret than the spin-dependent parameters of the sort determined in the present study.

TABLE III

Calculated Pure Rotational Spectrum of C_2H in the (010) Level of the $\tilde{X}^2\Sigma^+$ State

N	Parity	F_1	F_2
2 ← 1	+ ← −	174216.09 MHz	170888.08 MHz
	− ← +	175575.54	172250.70
3 ← 2	− ← +	260447.57	259152.62
	+ ← −	262488.02	261197.32
4 ← 3	+ ← −	346928.80	346249.20
	− ← +	349649.87	348974.85
5 ← 4	− ← +	433487.70	433077.12
	+ ← −	436889.08	436483.33
6 ← 5	+ ← −	520071.44	519802.90
	− ← +	524152.78	523889.33
7 ← 6	− ← +	606658.21	606473.89
	+ ← −	611419.09	611240.18
8 ← 7	+ ← −	693236.72	693106.46
	− ← +	698676.68	698552.18
9 ← 8	− ← +	779799.95	779706.43
	+ ← −	785918.45	785831.09

The transition frequencies have been calculated using the parameter values given in Table II. The proton hyperfine splittings have been suppressed.

The positions of the lower rotational levels of C_2H in the (010) level of its $\tilde{X}^2\Sigma^+$ state are now very well defined. In Table III, we give the frequencies of the pure rotational transitions of C_2H in the (010) level with the nuclear hyperfine structure suppressed. The frequencies have been calculated using the parameter values given in Table II.

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