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The Microwave Spectrum and Molecular Constants of Trifluoromethyl Acetylene*

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Pure rotational transitions, $J=4\rightarrow5$, $6\rightarrow7$, and $8\rightarrow9$ have been measured for CF_3CCH and $J=5\rightarrow6$ and $8\rightarrow9$ for CF_3CCD. These yield for CF_3CCH, $B_0=2{,}877.948$ Mc/sec, $D_J=0.2_4$ kc/sec, $D_{JK}=6.3$ kc/sec, and for CF_3CCD, $B_0=2{,}696.073$ Mc/sec, $D_J=0.2_6$ kc/sec, $D_{JK}=6.2$ kc/sec. If $\angle FCF$ is tetrahedral, $d(C\equiv C)$ and $d(CH)$ are assumed to be 1.207A and 1.056A, respectively, then the bond lengths $d(CF)=1.330$A and $d(C-C)=1.493$A are obtained. Rotational frequencies of molecules in excited bending vibration modes have been measured and found to agree with Nielsen's theory of l-type doubling.

I. INTRODUCTION

TRIFLUOROMETHYL acetylene is a new compound prepared the first time in 1950 by Haszeldine.[1] Consequently, little is known of its physical properties. The present study was undertaken in the hope of determining its molecular structure. This has been only partly achieved, since measurements on only two isotopic species have been made. As expected, its microwave spectrum is that characteristic of a symmetric top rotator. The moments of inertia, I_B, and centrifugal stretching constants of the forms CF_3CCH and CF_3CCD have been obtained. Rotational transitions of molecules in excited bending vibration states have been measured and found to agree with Nielsen's theory of l-type doubling.

II. EXPERIMENTAL PROCEDURE

The absorption lines were observed with a video detection sweep spectroscope,[2] and were measured with a frequency standard[3] monitored by comparison with station WWV. Measurements were made at dry ice temperature with pressures of about 10^{-3} mm of Hg.

The sample of trifluoromethyl acetylene was prepared by the method devised by Haszeldine.[1] Trifluoromethyl acetylene-d was obtained by exchange with a solution of sodium carbonate in heavy water. The completeness of the conversion was indicated by failure to detect lines caused by CF_3CCH in the CF_3CCD sample.

III. RESULTS FOR THE GROUND VIBRATIONAL STATE

Table I lists the measured frequencies of CF_3CCH and CF_3CCD for the ground vibrational state. Rotational constants calculated from these appear in Table II. For the calculation of I_B the value of Planck's constant used was $h=6.62373\times10^{-27}$ ergsec.

If the CF_3 group is assumed to be tetrahedral and $d(C\equiv C)=1.207$A and $d(CH)=1.056$A, as in methyl acetylene,[4] the lengths obtained for the other bonds are

$$d(C-F)=1.330\text{A},\quad d(C-C)=1.493\text{A}.$$

TABLE I. Observed frequencies for the rotational transitions of trifluoromethyl acetylene and trifluoromethyl acetylene-d in the ground vibrational state.

Species	Transition		Frequency[a] Mc/sec
CF_3CCH	$J=4\rightarrow5$	$K=0\rightarrow0$ $K=1\rightarrow1$	28,779.31
		$K=2\rightarrow2$	27,779.14
		$K=3\rightarrow3$	27,778.76
		$K=4\rightarrow4$	27,778.32
	$J=5\rightarrow6$	$K=0\rightarrow0$ $K=1\rightarrow1$	34,535.09
		$K=2\rightarrow2$	34,534,86
		$K=3\rightarrow3$	34,534.47
		$K=4\rightarrow4$	34,533.91
		$K=5\rightarrow5$	34,533.23
	$J=8\rightarrow9$	$K=0\rightarrow0$ $K=1\rightarrow1$	51,802.26
		$K=2\rightarrow2$	51,801.90
		$K=3\rightarrow3$	51,801.32
		$K=4\rightarrow4$	51,800.54
		$K=5\rightarrow5$	51,799.56
		$K=6\rightarrow6$	51,798.26
		$K=7\rightarrow7$	51,796.78
		$K=8\rightarrow8$	51,795.10
CF_3CCD	$J=5\rightarrow6$	$K=0\rightarrow0$ $K=1\rightarrow1$	32,352.62
		$K=2\rightarrow2$	32,352.36
		$K=3\rightarrow3$	32,352.01
		$K=4\rightarrow4$	32,351.47
		$K=5\rightarrow5$	32,350.82
	$J=8\rightarrow9$	$K=0\rightarrow0$ $K=1\rightarrow1$	48,528.42
		$K=2\rightarrow2$	48,528.08
		$K=3\rightarrow3$	48,527.56
		$K=4\rightarrow4$	48,526.74
		$K=5\rightarrow5$	48,525.74
		$K=6\rightarrow6$	48,524.54
		$K=7\rightarrow7$	48,523.08
		$K=8\rightarrow8$	48,521.44

[a] Absolute frequencies are accurate to ±0.10 Mc/sec.

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[1] R. N. Haszeldine, Nature **165**, 152 (1950). We are indebted to Dr. Haszeldine for furnishing us details of this preparation.

[2] W. Gordy and M. Kessler, Phys. Rev. **72**, 644 (1947).

[3] R. R. Unterberger and W. V. Smith, Rev. Sci. Instr. **19**, 580 (1948).

[4] R. Trambarulo and W. Gordy, J. Chem. Phys. **18**, 1613 (1950).

The assumptions made appear to be reasonable. The CC triple bond length is quite insensitive to conjugation effects and has been found to be 1.21A in a large number of similar molecules, and the $\equiv C-H$ distance has not been found to vary significantly from molecule to molecule. The greatest error is caused by the assumption of the angle.

Measurement of lines with C^{13} in each of the three carbon positions would allow a complete determination of the structure. The video detection spectrometer used did not have quite enough sensitivity to detect lines of the molecules with C^{13} in natural abundance. An attempt was made to detect these on a Stark modulation spectrograph. With this method the weak C^{13} lines were so obscured by the many Stark components of the C^{12} lines that identification was uncertain. We expect to detect them later with a superheterodyne receiver.

The cathode-ray scope display of a part of the $J=8\rightarrow 9$ rotational transition of CF_3CCH shown in Fig. 1 illustrates the separation by centrifugal distortion of the lines of different K in a symmetric top molecule as well as the effects of nuclear spin on the relative intensities of these lines. The $K=0$, 1, and 2 lines were not well resolved and are omitted. The relative intensities of the $K=3$ and $K=6$ lines compared with the intensities of the others are those predicted with a spin of $\frac{1}{2}$ for F^{19}. This photograph, therefore, provides objective confirmation by microwave spectroscopy of the F^{19} spin.

TABLE II. Rotational constants for the ground vibrational states of trifluoromethyl acetylene.

Species	B_0 (Mc/sec)	D_J (kc/sec)	D_{JK} (kc/sec)	$I_B(\times 10^{+40}$ g-cm²)
CF_3CCH	2877.948	0.2_4	6.3	291.4_{94}
CF_3CCD	2696.073	0.2_6	6.2	311.1_{58}

IV. ROTATIONAL SPECTRA FOR AN EXCITED VIBRATIONAL STATE

Two groups of lines, weaker than those for the ground vibrational state, were found centered about 28,834 Mc/sec and 51,902 Mc/sec. Each group consisted of a number of closely spaced lines approximately midway between two more widely spaced lines. The patterns were typical of the rotational spectra resulting from an excited degenerate bending vibration. These lines were interpreted as the $J=4\rightarrow 5$ and $8\rightarrow 9$ rotational transitions of CF_3CCH for the first excited $C-C\equiv C$ bending mode.

The method of treatment for the interaction of degenerate vibrations with rotation has been set forth by Nielsen,[5] and the term values for $J=1$ and $J=2$ calculated by him. The order of the secular equation of the submatrix is $4J+2$, and for high values of J the solution by direct methods becomes prohibitive. Nevertheless, since only the levels corresponding to the same angular momentum of the framework interact, the secular equation may be factored by inspection. The rotational term values for the vibrational quantum numbers $v=1$ and $l=\pm 1$ are

$$\begin{aligned}F_v(J,K,l)=&B_vJ(J+1)-(B_v-C_v)K^2-2C_vKl\xi\\&-D_JJ^2(J+1)^2-D_{JK}J(J+1)K^2-D_KK^4\\&+2\{(2D_J+D_{JK})J(J+1)+(2D_K+D_{JK})K^2\}Kl\xi\\&+P(J,K,l),\end{aligned}$$

where

$$P=\pm J(J+1)B_e^2a/\omega_s \quad \text{for} \quad K=\pm 1, \quad l=\pm 1;$$

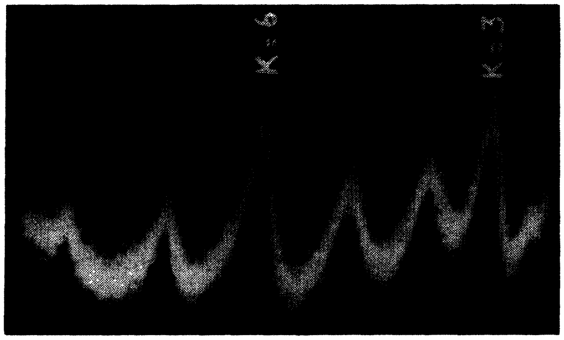

FIG. 1. Part of the $J=8\rightarrow 9$ rotational transition of CF_3CCH showing lines for $K=3$ to 8.

TABLE III. Frequencies and assignments for the $J=4\rightarrow 5$ and $8\rightarrow 9$ rotational transitions of CF_3CCH for the excited bending vibration $V_{10}=1$.

J	Transition K	l	Observed freq. (Mc/sec)[a]	Calculated freq. (Mc/sec)
4→5	±1	±1	28,816.48 28,852.61	28,816.52 28,852.72
	0	±1	28,835.26	28,835.31
	±1	∓1	28,834.45	28,834.65
	±2	±1	28,833.81	28,833.78
	±2	∓1		28,833.94
	±3	±1	28,834.20	28,834.12
	±4	±1		28,834.03
	±3	∓1	28,833.22	28,833.19
	±4	∓1	28,832[b]	28,832.48
8→9	±1	±1	51,869.14 51,934.48	51,869.10 51,934.20
	0	±1	51,906.64	51,906.69
	±1	∓1	51,903.42	51,903.55
	±2	±1	51,896.86	51,896.89
	±2	∓1	51,901.68	51,901.87
	±3	±1	51,899.44	51,899.26
	±5	±1		51,899.42
	±3	∓1	51,899.99	51,900.36
	±4	±1		51,899.68
	±4	∓1	51,898.61	51,898.77
	±6	±1		51,898.74
	±5	∓1	...	51,896.06
	±6	∓1	51,894.95	51,895.04
	±7	±1	51,897.63	51,897.72
	±7	∓1	51,892.88	51,892.71
	±8	±1	...	51,896.39
	±8	∓1	51,890.62	51,890.42

[a] All frequencies except that marked [b] are accurate to ±0.20 Mc/sec.
[b] Frequency accurate to ±1 Mc/sec.

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[5] H. H. Nielsen, Phys. Rev. 77, 130 (1950).

and

$$P=\pm\frac{\{J(J+1)-K(K\mp1)\}\{J(J+1)-(K\mp1)(K\mp2)\}}{2(K\mp1)\{(1-\xi)C_v-B_v\}}\times\left(\frac{B_e^2a}{\omega_s}\right)^2$$

for K other than ±1 and $l=\pm1$, the upper sign being taken for $l=+1$ and the lower for $l=-1$. This holds for K different from ±1 only when P is small. The frequencies of the transitions are then

$$\nu=2B_v(J+1)-4D_J(J+1)^3-2D_{JK}(J+1)K^2+4(2D_J+D_{JK})(J+1)Kl\xi+\Delta P(J,K,l),$$

where

$$\Delta P=\pm2(J+1)B_e^2a/\omega_s \quad \text{for} \quad K=\pm1, \quad l=\pm1$$

$$\Delta P=\pm\frac{(J+1)\{(J+1)^2-(K\mp1)^2\}}{(K\mp1)\{(1-\xi)C_v-B_v\}}(B_e^2a/\omega_s)^2,$$

for K other than ±1 and $l=\pm1$. As before, the upper sign is taken for $l=+1$ and the lower for $l=-1$.

The assignments of the excited vibrational lines, the observed frequencies, and the calculated positions of the lines are given in Table III. The parameters used to give the calculated line positions are: $B_v=2883.46$ Mc/sec, $D_J=0.2$ kc/sec, $D_{JK}=7.0$ kc/sec, $\xi=1.5$, $B_e^2a/\omega_s=1.81$ Mc/sec, and $(B_e^2a/\omega_s)^2/\{(1-\xi)C_v-B_v\}=7.0$ kc/sec. The parameters listed are those which gives the best fit to the data. Although the upper limit for ξ is $+1$ from theoretical considerations, it is not possible to fit the observed data using values of $\xi\leq+1$. From the value of B in the ground state and this excited state, $\alpha_{10}=-6.51$ Mc/sec.

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The Effective Range of Nuclear Forces. Effect of the Potential Shape

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Corrections to the theory of the effective range, which take account of the shape of the neutron-proton potential, are discussed. The following quantities are calculated for a Yukawa, exponential, and square well potential: (*a*) various triplet ranges compatible with the value obtained for $\rho_t(0,-\epsilon)$ from the latest experiments, $(1.72\pm0.035)\times10^{-13}$ cm. (*b*) The singlet effective range r_{0s} from neutron-proton scattering cross sections at energies up to 6 Mev. (*c*) r_{0s} from neutron absorption cross sections by hydrogen. (*d*) Photoelectric and photomagnetic disintegration cross sections for the deuteron for various γ-rays.

It is shown that a comparison of the values obtained for r_{0s} from (*b*) and (*c*) could, with a slight increase in experimental accuracy, give an estimate of the potential shape. Present, very tentative, indications are for a short-tailed potential and a value for r_{0s} of about $(2.7\pm0.5)\times10^{-13}$ cm.

I. INTRODUCTION

In a previous paper[1] (quoted as **B**) Bethe developed formulas for nuclear scattering using the theory of the effective range. In a second paper[2] (quoted as **BL**) Bethe and Longmire applied the effective range theory to the photodisintegration of the deuteron. Throughout this paper we use, wherever possible, the same notation as in these references. In these two papers and in a paper[3] (quoted as **BJ**) by Blatt and Jackson it was shown that the effect of the shape of the nuclear potential on the various quantities which can be calculated from experiments is small; these effects were masked completely by the experimental inaccuracies in the results available at that time. In the meantime, many of the relevant experimental determinations have been repeated with greatly increased accuracy; notably the measurements of the deuteron binding energy, the coherent neutron-proton scattering amplitude, and the neutron-proton scattering cross section for neutron energies up to 5 Mev. It therefore seemed worthwhile to calculate the deviations from the simple formulas obtained on the effective range theory (quoted as *ERT*) for the various potential shapes.

In this paper we derive formulas for the evaluation of the effective singlet range r_{0s} for a neutron-proton potential of Yukawa, exponential-well, and square-well shape from two independent experimental measurements: (i) neutron-proton scattering cross sections for neutron energies up to 5 Mev. (ii) Cross section for the capture of slow neutrons by protons. We also derive expressions for the photomagnetic and photoelectric disintegration cross sections of the deuteron, for γ-rays of "classical" energies, for the potential shapes mentioned above.

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[1] H. A. Bethe, Phys. Rev. **76**, 38 (1949), to be referred to as **B**.

[2] H. A. Bethe and C. Longmire, Phys. Rev. **77**, 647 (1950), to be referred to as **BL**.

[3] J. M. Blatt and J. D. Jackson, Phys. Rev. **76**, 18 (1949), to be referred to as **BJ**.

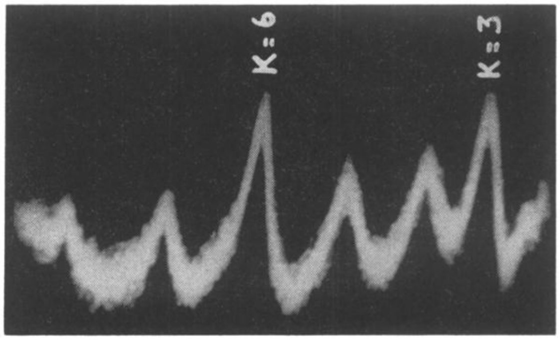

FIG. 1. Part of the $J=8\rightarrow9$ rotational transition of CF_3CCH showing lines for $K=3$ to 8.