

One-to-Two Millimeter Wave Spectra of TCl and TBr†

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The $J=0 \rightarrow 1$ rotational transitions of TCl and TBr have been measured at 1.36-mm and 1.74-mm wavelengths, respectively. These measurements, with α_e and D from infrared data, yield the following constants:

	For tritium chloride, TCl ³⁵	TCl ³⁷
$\nu_0(0 \rightarrow 1)$	222 143.78 \pm 0.4 Mc/sec	221 195.40 \pm 0.4 Mc/sec
B_0	111 075.76 Mc/sec	110 601.53 Mc/sec
B_e	112 032.0 Mc/sec	111 550.6 Mc/sec
r_0	1.28003A	1.28002A
r_e	1.27456A	1.27456A
$eQq(\text{Cl})$	67.0 \pm 0.6 Mc/sec	53.0 \pm 0.6 Mc/sec

	For tritium bromide, TBr ⁷⁹	TBr ⁸¹
$\nu_0(0 \rightarrow 1)$	172 499.05 \pm 0.3 Mc/sec	172 343.23 \pm 0.4 Mc/sec
B_0	86 252.24 Mc/sec	86 174.33 Mc/sec
B_e	86 947.2 Mc/sec	86 868.8 Mc/sec
r_0	1.42012A	1.42011A
r_e	1.41443A	1.41442A
$eQq(\text{Br})$	530 \pm 2 Mc/sec	443 \pm 2 Mc/sec

From the TBr measurements and similar measurements on DBr made previously in this laboratory, the mass ratio $m_T/(m_D) = 1.49747$ was obtained.

INTRODUCTION

THE present work represents a part of a program to measure precisely the spectra of light simple molecules which have their first rotational lines occurring in the shorter millimeter or upper sub-millimeter range. The hydrogen halides DBr and DI have already been measured.^{1,2} In the present paper results on TCl and TBr are reported. The latter isotopic forms, to our knowledge, have not previously been investigated with optical spectroscopy although the hydrogen and deuterium species have been thoroughly studied with infrared spectroscopy.

EXPERIMENTAL RESULTS

The methods of generating, detection, and measurement of millimeter wave frequencies are essentially the same as those already described in papers from Duke University.³

A dc bias on the multiplier crystal was used to advantage in some of the present observations. Although no improvement over the optimum unbiased performance was obtained, the bias proved to be helpful in arriving more rapidly at the optimum performance. It is of greatest advantage when the klystron output is below that needed for best multiplication.

For the TBr measurements, the seventh harmonic from a 2K33 klystron was employed while for TCl the ninth harmonic of the same tube was used. Frequency measurements were made at the fundamental output with a secondary frequency standard monitored by Station WWV.

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¹ C. A. Burrus and W. Gordy, Phys. Rev. **92**, 1437 (1954).

² W. Gordy and C. A. Burrus, Phys. Rev. **93**, 419 (1954).

³ W. C. King and W. Gordy, Phys. Rev. **90**, 319 (1953); **93**, 407 (1954).

The advantages of the shorter millimeter wave spectroscopy for the study of radioactive gases are demonstrated by the present measurements made with a G-band wave-guide cell 15 cm in length. The total volume of the cell was only 0.2 cc. Figure 1 shows the $J=0 \rightarrow 1$ lines of TCl³⁷ observed in this cell. A crystal video detector with a wide band (10-kc) amplifier and a 60 cps sweep was employed. These lines could, of course, be recorded with a narrow-band amplifier at a signal-to-noise ratio better than 10 times that shown. The concentration of TCl³⁷ in the sample is normal, 25 percent, and the pressure is of the order of 10^{-2} mm of Hg. Collisions with the cell walls probably broaden the lines here.

The samples of tritium chloride and tritium bromide were prepared in the Oak Ridge National Laboratory by the action of ultraviolet light on mixtures of tritium gas and the halide.

TRITIUM CHLORIDE

The first rotational line of TCl falls at 1.3 mm, and is split into two sets of three components by the Cl isotopic shift and by the Cl nuclear quadrupole interaction. Table I gives the measured frequencies. From an analysis of the spectrum, unperturbed rotational frequencies, ν_0 , and nuclear quadrupole couplings,

TABLE I. $J=0 \rightarrow 1$ transition of tritium chloride.

	$F \rightarrow F'$	Frequency in Mc/sec	
		Observed	Calculated*
TCl ³⁵	3/2 \rightarrow 3/2	222 130.32 \pm 0.4	222 130.38
	3/2 \rightarrow 5/2	222 147.23 \pm 0.4	222 147.13
	3/2 \rightarrow 1/2	222 160.50 \pm 0.4	222 160.53
TCl ³⁷	3/2 \rightarrow 3/2	221 184.82 \pm 0.4	221 184.80
	3/2 \rightarrow 5/2	221 198.00 \pm 0.4	221 198.05
	3/2 \rightarrow 1/2	221 208.69 \pm 0.4	221 208.65

* Calculated with the ν_0 and coupling constants listed in Table II.

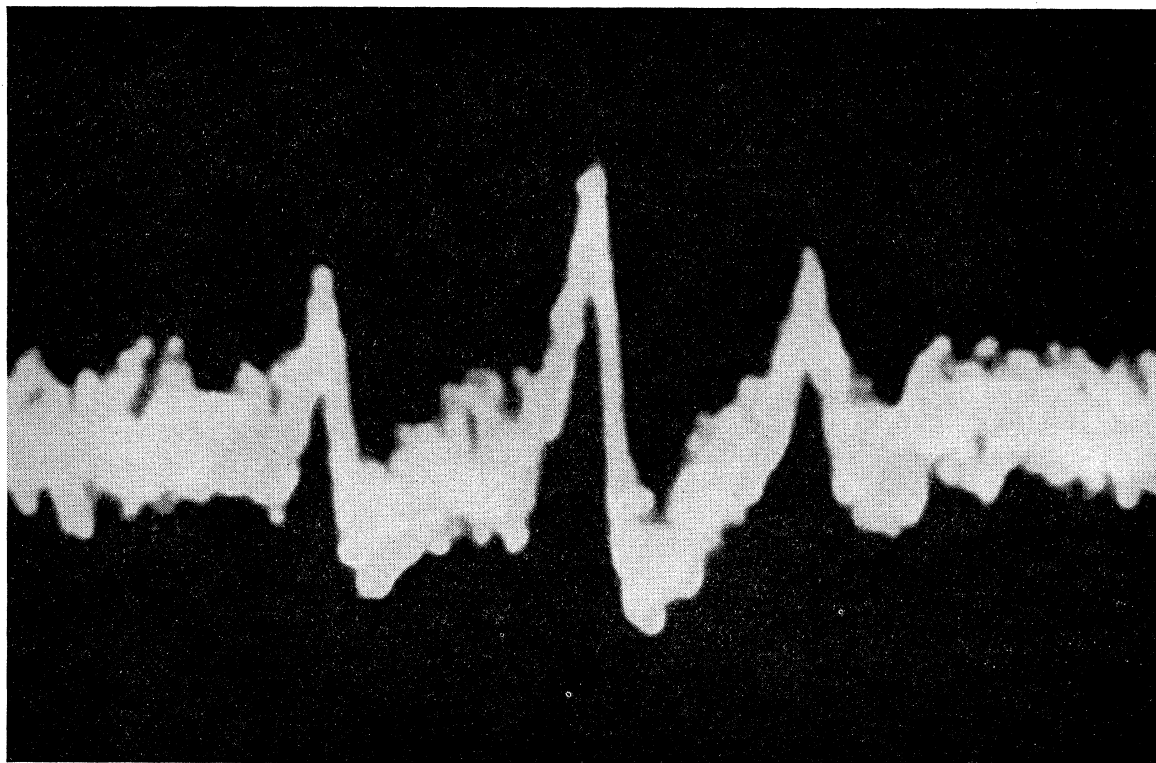


FIG. 1. Oscilloscope tracing of the $J=0 \rightarrow 1$ rotational transition (1.36-mm wavelength) of TCl^{37} with Cl^{37} in its natural abundance of 25 percent. The absorption cell employed was of 15 cm length and 0.2 cc total volume.

eQq , listed in Table II were obtained. These were then used to calculate a comparative spectrum for showing the degree of consistency of the results. Methods of analysis of such a spectrum are described in detail elsewhere⁴ and will not be repeated here.

For molecules rotating at the high frequencies of the one-to-two millimeter wave range, the centrifugal stretching effects are not entirely negligible even in the $J=1$ state. Because only one rotational line was observed, we could not measure the stretching constant D_J . Fortunately, D_J can be calculated from the infrared values for HCl or DCl to the accuracy needed to correct for the small stretching in the $J=1$ state. Similarly, the zero point vibration effects which could not be measured in the present work are calculable from the infrared results. The B_0 value for a $J=0 \rightarrow 1$ transition is connected to the ν_0 by

$$B_0 = \frac{1}{2}\nu_0 + 2D_J.$$

Pickworth and Thompson⁵ give for DCl^{35} , $D_J = 1.371 \times 10^{-4} \text{ cm}^{-1}$ and for DCl^{37} , $D_J = 1.363 \times 10^{-4} \text{ cm}^{-1}$ which in Mc/sec are 4.110 and 4.086, respectively. We convert these to the TCl values of 1.934 and 1.917 Mc/sec by multiplication with the square of the

reduced mass ratios $[\mu(\text{DCl})/\mu(\text{TCl})]^2$. The equilibrium value, B_e , is given by

$$B_e = B_0 + \frac{1}{2}\alpha_e.$$

To obtain α_e , we converted the values 0.1123 cm^{-1} and 0.1118 cm^{-1} , respectively, of DCl^{35} and DCl^{37} , (from Pickworth and Thompson⁵) to the corresponding TCl values by multiplication with the factor $[\mu(\text{DCl})/\mu(\text{TCl})]^{\frac{1}{2}}$. The B_e values which we give are limited by the α_e values thus obtained to six or perhaps five significant figures. The internuclear distances calculated from the B_0 and B_e values are given in Table II. The r_e value, 1.274_6 \AA , in DCl measured by Pickworth and

TABLE II. Characteristic constants of tritium chloride.^a

	TCl^{35}	TCl^{37}
$eQq(\text{Cl})$	$67.0 \pm 0.6 \text{ Mc/sec}$	$53.0 \pm 0.6 \text{ Mc/sec}$
$\nu_0(0 \rightarrow 1)$	$222\,143.78 \pm 0.4 \text{ Mc/sec}$	$221\,195.40 \pm 0.4 \text{ Mc/sec}$
B_0	$111\,075.76 \text{ Mc/sec}$	$110\,601.53 \text{ Mc/sec}$
D	1.93_4 Mc/sec^b	1.91_7 Mc/sec^b
α_e	1912 Mc/sec^b	1898 Mc/sec^b
B_e	$112\,032.0 \text{ Mc/sec}$	$111\,550.6 \text{ Mc/sec}$
r_0	1.28003 \AA	1.28002 \AA
r_e	1.27456 \AA	1.27456 \AA

^a Masses used for calculations: $\text{H} = 1.008145 \text{ amu}$; $\text{D} = 2.014741 \text{ amu}$; $\text{T} = 3.016997 \text{ amu}$; $\text{Cl}^{35} = 34.980064 \text{ amu}$; $\text{Cl}^{37} = 36.977675 \text{ amu}$.

^b Values of D and α_e are calculated from the corresponding values for DCl obtained by infrared spectroscopy by H. W. Thompson and J. Pickworth, Proc. Roy. Soc. (London) A218, 37 (1953).

⁴ Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953).

⁵ J. Pickworth and H. W. Thompson, Proc. Roy. Soc. (London) A218, 37 (1953).

Thompson is in excellent agreement with the microwave value.

Perhaps the information of most interest obtained in the present work is the Cl nuclear quadrupole coupling in TCl (which will, of course, be essentially that in HCl). Hydrogen chloride has intermediate ionic character whereas most simple diatomic molecules for which couplings have been observed have either very low ionic character or almost completely ionic character. Furthermore, the complication of possible double bond character is out for bonds to hydrogen.

From Heitler-London theory, with various amounts of hybridization assumed for the Cl orbital, Schatz⁶ has predicted that the Cl³⁵ coupling in HCl may be of the order of 110 Mc/sec. The measured value, 67 Mc/sec, is more nearly in agreement with that, 61 Mc/sec, predicted⁷ from a simple ionic character-electronegativity relation⁸ derived empirically from nuclear quadrupole coupling data with all hybridization effects neglected. The solid state value 53.3 Mc/sec obtained from the pure quadrupole spectrum⁹ of HCl is 20 percent lower. A lower value is expected for the solid because of the increased ionic character caused by the dipole-dipole interaction of the closely spaced molecules of the solid.

The unbalanced *p* electron number, U_p , of Cl in gaseous HCl can be obtained with the aid of the coupling per unbalanced *p* electron —110 mc/sec, obtained from atomic beam experiments.¹⁰ It is $U_p = 67/110 = 0.61$. If hybridization and overlap charge effects are neglected, the ionic character of the HCl bond is determined by the U_p as 39 percent. The ionic character estimated from electronegativity is 45 percent if the Pauling χ values, 2.1 and 3.0, are employed for H and Cl, or 42.5 percent if the values 2.13 and 2.98 derived from force constants¹¹ are used.

TRITIUM BROMIDE

Table III gives the calculated and observed lines of the $J=0 \rightarrow 1$ transition of TBr⁷⁹ and TBr⁸¹. In Table IV, the rotational constants and other information is

TABLE III. $J=0 \rightarrow 1$ transition of tritium bromide.

	$F \rightarrow F'$	Frequency in Mc/sec	
		Observed	Calculated ^a
TBr ⁷⁹	3/2 \rightarrow 1/2	172 366.65 \pm 0.3	172 366.55
	3/2 \rightarrow 5/2	172 472.43 \pm 0.3	172 472.55
	3/2 \rightarrow 3/2	172 605.06 \pm 0.3	172 605.05
TBr ⁸¹	3/2 \rightarrow 1/2	172 232.46 \pm 0.3	172 232.53
	3/2 \rightarrow 5/2	172 321.11 \pm 0.3	172 321.13
	3/2 \rightarrow 3/2	172 430.85 \pm 1.0	172 431.83

^a Calculated with the ν_0 and force constants listed in Table IV.

⁶ P. N. Schatz, J. Chem. Phys. **22**, 695 (1954).

⁷ W. Gordy, J. Chem. Phys. **22**, 1417 (1954).

⁸ W. Gordy, J. Chem. Phys. **19**, 792 (1951).

⁹ R. Livingston, see tabulation in reference 4, p. 366.

¹⁰ V. Jaccarino and J. G. King, Phys. Rev. **83**, 471 (1951).

¹¹ W. Gordy, J. Chem. Phys. **14**, 305 (1946).

TABLE IV. Characteristic constants of tritium bromide.^a

	TBr ⁷⁹	TBr ⁸¹
$eQq(\text{Br})$	530 \pm 2 Mc/sec	433 \pm 2 Mc/sec
$\nu_0(0 \rightarrow 1)$	172 499.05 \pm 0.3 Mc/sec	172 343.23 \pm 0.4 Mc/sec
B_0	86 252.24 Mc/sec	86 174.33 Mc/sec
D	1.36 Mc/sec ^b	1.36 Mc/sec ^b
α_e	1390 Mc/sec ^b	1389 Mc/sec ^b
B_e	86 947.2 Mc/sec	86 868.8 Mc/sec
r_0	1.42012A	1.42011A
r_e	1.41443A	1.41442A
m_T/m_D	1.497471 ^c	1.497464 ^c

^a Values of D and α are calculated from the corresponding values for HBr obtained by infrared spectroscopy by Thompson, Williams, and Callomon, Spectrochim. Acta **5**, 311 (1952).

^b The B_e 's employed for DBr were obtained from the B_0 of reference 2 and the α 's calculated from HBr data of reference 12.

^c Masses used for calculations: hydrogen—see Table II; Br⁷⁹ = 78.94438 amu; Br⁸¹ = 80.94228 amu.

TABLE V. Comparison of nuclear quadrupole coupling in gaseous TBr and DBr.

Nucleus	Coupling in Mc/sec	
	TBr	DBr
Br ⁷⁹	530 \pm 2 ^a	533 \pm 3 ^b
Br ⁸¹	443 \pm 2 ^a	445 \pm 3 ^b

^a This work.

^b W. Gordy and C. A. Burrus, Phys. Rev. **93**, 419 (1954).

summarized. The auxiliary constants, α_e and D_J , were calculated from infrared data as described for TCl.

In Table V, the nuclear quadrupole couplings are compared with those of DBr previously obtained. Through an error in transcription, the eQq for Br⁸¹ in DBr was listed as 455 Mc/sec in the earlier work rather than as 445 mc/sec, the value which was obtained from the spectrum. The TBr couplings are slightly smaller for both Br⁷⁹ and Br⁸¹ than are those of DBr. The differences are, however, within the experimental error and may not be significant.

The earlier work on DBr combined with the present measurement on TBr allow an evaluation of the mass ratio of tritium and deuterium. The reduced mass ratios are inversely proportional to the B_e values, from which the mass ratio,

$$m_T/m_D = 1.49747,$$

is readily derived. The greatest error in this evaluation arises from the α_e values obtained from infrared data. Nevertheless, the good agreement with the ratio,

$$m_T/m_D = 1.497462,$$

from other sources indicate that the infrared values of α_e are very good. Two sources of α_e are available, one from the HBr results of Thompson, Williams, and Callomon¹² and the other from the DBr results of Keller and Nielsen.¹³ Values from the two sources are

¹² Thompson, Williams, and Callomon, Spectrochimica Acta **5**, 311 (1952).

¹³ F. L. Keller and A. H. Nielsen, Phys. Rev. **91**, 235 (1953).

in good agreement. The mass of tritium, so far as we know, has not been measured directly, but it has been calculated with high accuracy from nuclear reaction energies. The $m_D = 2.014741(\pm 3)$ value which we used here is given by Ogata and Matsuda,¹⁴ and the $m_T = 3.016997(\pm 11)$ is that given by Whaling, Fowler, and Lauritsen.¹⁵ This value m_D with our mass ratio

leads to the spectroscopy value $m_T = 3.01700_8$ for the tritium mass.

After our measurements on TBr were complete we received the Progress Report from the Columbia Radiation Laboratory dated October 30, 1954 which states that A. H. Nethercot and B. Rosenblum¹⁶ have also made measurements on the $J=0 \rightarrow 1$ transition of TBr.

¹⁴ K. Ogata and H. Matsuda, Phys. Rev. **89**, 27 (1953).

¹⁵ Whaling, Fowler, and Lauritsen, Phys. Rev. **83**, 512 (1951).

¹⁶ Note added in proof.—The work of Nethercot and Rosenblum has now been published [Phys. Rev. **97**, 84 (1955)].

Fermi Resonance in the Microwave Spectrum of Linear XYZ Molecules*

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Measurements of the rotation-interaction constants α_i for the various vibrational states in the microwave spectrum of OCS and OCSe show little consistency. These discrepancies are explained within experimental accuracy as being due to interaction between adjacent vibrational levels with quantum numbers v_1, v_2, v_3 and v_1-1, v_2+2, v_3 . Resonance of this type, called Fermi resonance, has also been found in ICN but the interaction constant is very much smaller.

THE rotational frequency for any vibrational state of a linear XYZ molecule is given to a first approximation by

$$\nu_{J-1 \rightarrow J} = 2JB_v - 4D_v(J^3 - l^2J), \quad (1)$$

$$B_v = B_e - \alpha_1(v_1 + \frac{1}{2}) - \alpha_2(v_2 + 1) - \alpha_3(v_3 + \frac{1}{2}),$$

where B_e is the rotational constant, assuming the nuclei to be in their equilibrium positions, and is inversely proportional to the moment of inertia of the molecule; D_v is the centrifugal distortion coefficient in the vibrational state v ; J is the quantum number of the total angular momentum; v_i the quantum number of the i th vibrational mode; and q is the l -type doubling constant.

In this type of molecule, the centrifugal distortion is usually small compared to the effects to be considered and can be neglected. The second vibrational mode v_2 , the bending mode, is degenerate. Owing to vibration-rotation interaction this degeneracy is lifted and is split into two levels, called l -type doublet, and is designated by $v_2^{l_1}$ and $v_2^{l_2}$, respectively. The l -type splitting is appreciable only when $l=1$ and is given by $\Delta\nu = 2qJ$.¹ The l -type coupling constant varies slightly with J by an amount of the order of $q(B/\omega)J(J+1)$.²

The rotation-vibration constants α_i depend in a complex way on the potential function, on the moment

of inertia, and on the vibrational frequencies ω of the molecule. Experimentally, one can determine the values of α by measuring the frequency difference between the ground state and the excited vibrational states or between adjacent vibrational states. Thus, for example, the frequency difference between the ground state (000) and the center of the l -type doublet excited vibrational state (010) in the $J=1 \rightarrow 2$ transition should equal $4\alpha_2$.

It has been the hope of microwave spectroscopists that rather exact nuclear mass ratios could be determined from the spectra of linear XYZ molecules with various isotopic substitutions by measuring the rotational frequencies and the values of the rotation-vibration constants to obtain the equilibrium moments of inertia of the various isotopic molecules. However, discrepancies have appeared in the measurement of the α 's from various vibrational states.³ These discrepancies are illustrated in Table I for OCS. Frequency shifts as high as 17 Mc/sec are found for some vibrational states in the $J=1 \rightarrow 2$ transition and similar shifts in the $J=2 \rightarrow 3$ transition. The (02⁰0) line, moreover, does not coincide with the center of the unsplit doublet (02⁰0), indicating that the perturbations depend not only on the energy of the vibrations but on their symmetry as well. Similar discrepancies have been observed for OCSe and smaller ones for ICN.

These anomalies may be explained as perturbations

* This work was supported jointly by the U. S. Signal Corps and the Office of Naval Research.

¹ H. H. Nielsen, Phys. Rev. **75**, 1961 (1949).

² C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., 1955), Chap. II has a detailed discussion on vibration-rotation interaction.

³ These discrepancies were reported for OCS by R. G. Shulman and C. H. Townes, Phys. Rev. **75**, 1318(A) (1949).

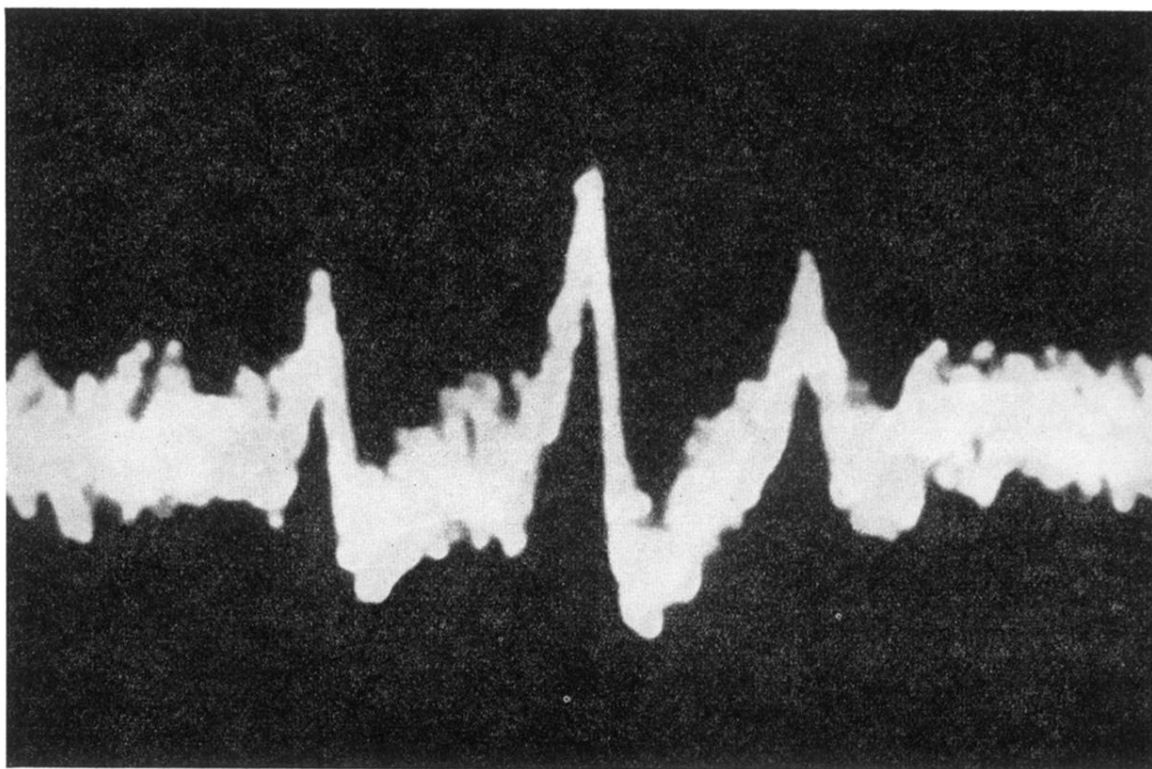


FIG. 1. Oscilloscope tracing of the $J=0 \rightarrow 1$ rotational transition (1.36-mm wavelength) of TCl^{37} with Cl^{37} in its natural abundance of 25 percent. The absorption cell employed was of 15 cm length and 0.2 cc total volume.