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Experimental Evidence of Restricted Rotation in CH3–C≡C–CF3

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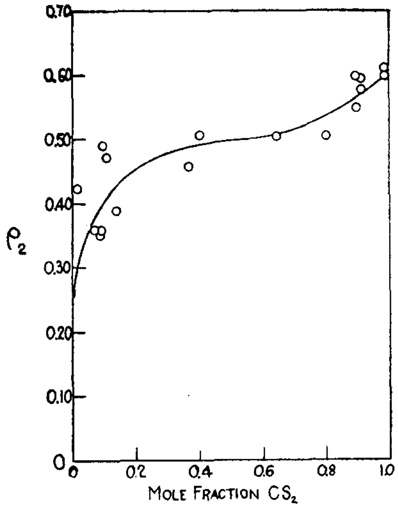

FIG. 3. The variation of the calculated depolarization of the carbon disulfide, ρ_2, in a solution with carbon tetrachloride with mole fraction of carbon disulfide.

The value of ρ_2 at infinite dilution corresponds to that for a carbon disulfide molecule completely surrounded by symmetrical carbon tetrachloride molecules. It is of interest to compare this value with $\rho = 0.115$ for carbon disulfide in the gaseous state.[7] Any difference occurring between these two values would apparently result from the polarization field of the dipoles induced in the carbon tetrachloride, and is analogous to the difference between dipole moments measured in the gaseous phase and in solution at infinite dilution.[8]

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† This work is part of a senior honors research problem conducted by Mr. Powers as partial fulfillment of the requirements for a degree of B.S. in Chemistry at the University of Massachusetts. The work was partially supported by a contract with the U. S. Office of Naval Research.

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‡ The CCl_4 was Eastman Spectro Grade. The CS_2 was Mallinckrodt Analytical Reagent Grade.

* Further purification by filtering did not result in a greater reduction of turbidity.

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Experimental Evidence of Restricted Rotation in $CH_3-C\equiv C-CF_3$

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THE problem of demonstrating the presence of potential barriers in molecules and, if possible, finding the barrier height has successfully been attacked by means of microwave technique[1–4] which has thus proved to be useful as a supplement to existing thermodynamic and spectroscopic methods.

So far, the microwave spectroscopists have concentrated their efforts on molecules like CF_3CH_3,[1–3] SiH_3CH_3,[4] and CH_3OH.[5,6] In all these cases the groups that are supposed to interact are at close distances to each other (1.50–2.00A). In order to enlarge the experimental background for the current theoretical discussion on the origin of potential barriers it seemed interesting to investigate molecules of the general type $CX_3-C\equiv C-CY_3$ in which the distance between the end groups is roughly 4–4.5A. $CH_3-C\equiv C-CH_3$ belongs to such molecules. Heat capacity measurements[7,8] have shown a practically complete absence of hinderence to the rotation of the methyl groups. Studies of the infrared spectrum under high resolution[9] seemed to show that the barrier must be very low if not zero. Recently, the temperature variation of the dipole moment of $CH_2Cl-C\equiv C-CH_2Cl$ *in solution*[10] was determined. The rotation was shown to be restricted but the result was not too conclusive because of the presence of the solvents. In a microwave experiment with some gas at a low pressure this difficulty is circumvented.

Because of lack of dipole moment $CH_3-C\equiv C-CH_3$ is unsuited for microwave investigation. It was decided to investigate $CH_3-C\equiv C-CF_3$ because none of its nuclei have spins differing from 0 or 1/2. Therefore, the complications which might arise from a spin hyperfine structure in the spectrum are avoided. If, furthermore, the potential barrier in $CH_3-C\equiv C-CH_3$ is small the introduction of three fluorine atoms instead of hydrogen probably means an amplification of the phenomenon to be studied.

The hitherto unknown molecule $CH_3-C\equiv CF_3A$ was prepared by mixing CF_3J(0.005 mole) and $CH_3-C\equiv CH$(0.01 mole) at room temperature in a sealed-off Pyrex tube (30 cc) which was afterwards irradiated by mercury light for ten days. A pure compound (I) (vp = 39.5 mm Hg at 20.5°C) was isolated by careful, repeated destillations. Yield: 0.001 mole. Presumably the compound is $CH_3-CJ=CH(CF_3)$ since Haszeldine[11] prepared $CHJ=CH(CF_3)$ by a similar reaction. In the present case the compound $CH_3-C(CF_3)=CHJ$ (II) may also be formed. However, the pure compound next obtained (III) by refluxing (I) over dry KOH in a sealed-off tube at 150°C for 60 hours[12] consisted of symmetric top molecules as shown by the appearance of the microwave spectrum. Therefore, (II) has not been formed, or (II) and its reaction products have been discarded at one of destillations which finally resulted in (III). Yield: 0.0003 mole. The pure compound (III) had vp = 12 mm Hg at −46.0°C. Under the influence of KOH (I) may split off HJ in two different ways forming either (*A*) or $CF_3-CH=C=CH_2$ (*B*). Since *B*-molecules are far from being symmetric tops we conclude that (III) is mainly the compound we want, $CH_3-C\equiv C-CF_3$.

If the possible barrier in $CH_3-C\equiv C-CF_3$ is high (2–3 kcal/mole) the microwave spectrum must be similar to e.g., that of CF_3CH_3,[1–3] i.e., it will consist of a few (3–5 or so) isolated lines spread over a 0–200 Mhz range. These lines correspond to molecules in torsionally excited levels.

If there is no barrier the *energy level diagram* certainly deviates from what it would be for a perfectly rigid rotor but due to the selection rules the spectra will be identical ($\Delta K_1 = \Delta K_2 = 0$), i.e., the spectrum must consist of single lines separated by $2B$, where B is the rotational constant corresponding to rotation about an axis perpendicular to the axis of symmetry. For $CH_3-C\equiv C-CF_3$ this separation will be about 2600 Mhz.

The microwave spectrum, studied in the 21670–25830 Mhz region by means of Stark modulation technique, proved to represent an intermediate between the two possibilities sketched above. Two groups of lines, *the groups being of very similar structure*, were found. One group extended from 21900–22130 Mhz, the other from 24650–24890 Mhz. Both groups were observable at low field intensities (300 volts/cm) at 0.06 and 0.01 mm gas pressure and dry ice temperature. Both groups were flanked by numerous Stark components (unresolved). This indicates almost with certainty that symmetric top molecules are present. Furthermore, if we assume that $d_{CF} = 1.38$, $d_{CH} = 1.09$, $d_{C-C} = 1.54$, and $d_{C\equiv C} = 1.20$A and that the valence angles are tetrahedral (whether this is perfectly correct or not) we find that the $J = 7 \rightarrow 8$ transition of a perfectly rigid $CH_3-C\equiv C-CF_3$ molecule will cause microwave absorption at 20752 Mhz, the $J = 8 \rightarrow 9$ transition at 23346 Mhz. The ratio of these frequencies is $9/8 = 1.125$. The ratio of the frequencies corresponding to the centers of the two domains of microwave absorption, is $\frac{24770}{22015} = 1.125$. Therefore, the two groups of lines found represent absorption due to $J = 7 \rightarrow 8$ and $J = 8 \rightarrow 9$ transitions, complicated by the presence of restricted rotation.

Both groups of lines consist of 6 subgroups, each subgroup extending over a 15–20 Mhz range. We interpret each subgroup as consisting of several unresolved lines since a microwave line width of 15–20 Mhz would be something very exceptional. Indeed, we doubt at present that it will be possible to resolve the spectrum using ordinary Stark technique because probably the "quadratic" Stark components of some lines coincide with unperturbed lines.

The presence of hindered rotation in $CX_3-C\equiv C-CY_3$ compounds is thus firmly established. The barrier height is certainly less than for e.g., CH_3SiH_3 where it is about 1200 cal/mole.[3] Further studies of the spectra of $CH_3-C\equiv C-CF_3$ are planned in order to try to fix the approximate magnitude of the potential barrier.

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The Infrared Spectrum of Dimethyltriacetylene

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DIMETHYLTRIACETYLENE (octa-2,4,6,-triyne) has been synthesized by Jones[1,2] and co-workers,[3] who have described its chemical and physical properties. Cook *et al.*[4] have obtained the infrared absorption spectra of $CH_3-(C\equiv C)_n-CH_3$ ($n=2-6$) in CCl_4 solution with a Perkin-Elmer double-beam spectrometer with NaCl prisms and have reported the location of the $-C\equiv C-$ stretching band for this series of compounds.

Since there is considerable interest in the spectra of polyacetylenic compounds,[5,6] we are investigating the vibrational spectra of dimethyltriacetylene (DMTA). Table I shows the infrared bands of DMTA obtained in CS_2 and CCl_4 solution with a Perkin-Elmer Model 21 double-beam spectrometer with NaCl optics and a Beckman IR-2 spectrometer with KBr optics, in juxtaposition to the results communicated by Jones.[7] Except for three low wave number skeletal vibrations, all allowed infrared fundamentals have been identified. The remaining bands have not been assigned as yet pending an investigation of the Raman spectrum. Table II lists some of the more prominent infrared absorption bands of the series of molecules $CH_3-(C\equiv C)_n-CH_3$ for $n=2$ to $n=6$ as communicated by Jones.[7] An investigation of the Raman spectrum and work on the normal coordinate treatment is in progress. The sample of DMTA was supplied through the courtesy of Professor E. R. H. Jones. Thanks are due to Dr. R. B. Bernstein of the Chemistry Department for placing the Perkin-Elmer spectrometer at our disposal. The authors also appreciate the assistance of the Office of Ordnance Research, U. S. Army; the Research Corporation; and the American Academy of Arts and Sciences for partial support of this research.

TABLE I. Infrared spectral data for dimethyltriacetylene ($CH_3-C\equiv C-C\equiv C-C\equiv C-CH_3$).[a]

ν(cm^{-1}) PR	I	J	Description	ν(cm^{-1}) PR	I	J	Description
443	w			1378	vs	1380	$-CH_3$
604	w			1428	s	1432	$-CH_3$
654	vvw			1466	w		
674	vvs		$\equiv C-C\equiv$	1807	w		
764	m			1956	w		
808	m			2036	m	2038	
853	vw			2221	vvs	2222	$-C\equiv C-$
932	m		$\equiv C-C\equiv$	2396	w		
1020 1033	m	1019	$-CH_3$	2445	w		
				2724	w		
1067	vvw			2835	m	2837	
1118	w			2912	s	2913	$-C-H$
1177	w			2955	m	2960	$-C-H$
1247	vvw			3022	m		
1290	w			3064	vvw		
1326	vvw			3080	w		
1363	vvw			3283	vw		

[a] PR = Present Results; I = estimated relative intensity (v = very, w = weak, m = medium, s = strong); J = Jones, reference 7.

TABLE II. Infrared spectral data for some dimethylpolyacetylenes [$CH_3-(C\equiv C)_n-CH_3$, $n=2, 3, 4, 5, 6$].[a]

$n=2$	$n=3$	$n=4$	$n=5$	$n=6$
2961	2960	2915	2932	
2915	2913			
2845	2837	2840	2855	
2725				
2216	2222	2237	2221	2207
2156				
2050	2038			
		1704		
1437	1432	1419	1466	
1370	1380	1374	1379	
		1280	1261	
			1092	
1025	1019	1019	1012	

[a] Private communication, reference 7. All values are in cm^{-1}. The spectra were obtained in CCl_4 solution with a Perkin-Elmer double-beam instrument with NaCl optics.

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Raman Spectrum of Oxalyl Chloride

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RECENTLY a paper by Ziomek, Meister, Cleveland, and Decker[1] on the Raman and infrared spectrum of oxalyl chloride has appeared in which doubts are cast on some of the experimental results obtained by Saksena and Kagarise.[2]

The discrepancies in question are not large and undoubtedly can be explained, but not in the manner proposed by ZMCD. The criticisms advanced by ZMCD are based on the contention that the experimental methods used by SK were inadequate in three respects: (1) polarization method, (2) resolving power, and (3) filtering technique.

It is possible to see the detail referred to by SK by reference to their Fig. 1. However, the reproductions are too small and the quality of the paper is inadequate to show the excellence of the polarization technique and resolution of the instruments used. We should like the reader to compare Fig. 1 of a paper by Rank, Saksena, and Shull[3] with Fig. 2 of Cleveland's[4] paper describing his polarization method. As a test of our supposedly inadequate resolution, Figs. 1 and 2 of a paper by Kagarise and Rank[5] may be consulted. The results of SK were obtained by the same methods and instruments which produced the plates from which the figures referred to above were prepared.

The 15-ft grating spectrograph has resolved sharp Raman lines of less than 3-cm^{-1} separation and has a linear dispersion of 3.5A/mm in contrast to ZMCD's dispersion of 33A/mm. Our prism spectrograph has a dispersion of 19A/mm and resolving power limited only by the grain size of the type 1 photographic