Raman Spectrum of Tropolone

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Introduction

Infra-red absorption of tropolone (cycloheptatrienolone) has been reported by several authors,[1,2,3] while its Raman data are not published yet. Just as with any other compound these two sets of information are indispensably needed in attempting to analyze and interpret the vibrational structure in the near ultra-violet absorption spectrum of tropolone vapor, which we also are investigating. In this paper are reported the results of our observation on the Raman spectrum of tropolone, one of the prototypes of seven-membered ring hydrocarbons.

Experimental

The spectrograph used is one constructed in this laboratory having three dense flint glass prisms of side lengths 6 cm. or more, and heights 4.5 cm. or more. The camera lens is a photographic objective of 21 cm. focal length and *F*/2.6 relative aperture, while the collimator lens is an achromat of 45 cm. focus and *F*/5 relative aperture. The spectrum is photographed on a strongly curved film strip placed at the focal surface of the instrument. The reciprocal dispersion of this spectrograph in the vicinity of Hg 4359 Å line is 39 Å per mm.

The scatterer was a solution of 5 g. tropolone in white crystalline powder form prepared in Prof. Nozoe's laboratory at Tohoku University, Sendai, dissolved in pure benzene, the concentration being about 1.6 mol. per litre. The solution was put into a Wood's tube of 1 cm. bore and 15 cm. length, and was irradiated sidewise with two glass mercury lamps, each consuming about 10 amp. current. Kodak "Super XX" panchromatic film was used and the time of exposure was 10 hr. For the calibration of wave-lengths iron arc spectrum was photographed in juxtaposition on the scattered spectrum.

Nine Raman scattered lines in all were observed, all being excited by the Hg 4359 Å and no line originating from the Hg 4047 Å was recorded. This is due to the strong absorption of tropolone lying in the region expected for the appearance of the latter lines. The measured wave-number shifts of the nine Raman lines are given in the 1st. column of Table I, along with their estimated intensities in brackets, the highest of which is assigned to grade number 5.

The tropolone solution was colorless at the start of the exposure, but soon began to turn yellow on irradiation, and the whole sample ultimately became a reddish-brown viscous fluid. This photochemical change accompanied by strong coloration made further continuation of the exposure almost meaningless, and a rather premature termination of the experiment was inevitable, although it was not favorable for satisfactorily recording weaker lines. The same photo-chemical coloration was experienced by us in photographing the vapor absorption spectrum of tropolone, but in that case the colored product remained in the liquid phase, not affecting the vapor phase absorption, provided pure tropolone still remained.

Discussion

Comparing our results with those of infra-red absorption reported by Shimanouchi et al., and given in the 2nd. column of our Table*, the agreement of wave-numbers is generally good, and the intensities go parallel. As we see in the Table three new low frequencies are found in Raman effect which were not measured in infra-red absorption, while counterparts of the two strong infra-red peaks at 1480 cm.$^{-1}$ and 1560 cm.$^{-1}$ could not be clearly confirmed on our film, owing to the approximate coincidence of positions of these lines with the strong scattered lines due to benzene.

In a Raman spectrum shifted lines with overtone or combination frequencies are not normally observed, so that our nine frequencies observed with not insignificant intensities, even under the unfavorable condition stated above, are to be considered all of fundamentals. From this standpoint the reported infra-red frequencies 770 cm.$^{-1}$, 880 cm.$^{-1}$, and 1050 cm.$^{-1}$ may very probably be interpreted as combinations and an overtone, $357+436$ cm.$^{-1}$, 2×436 cm.$^{-1}$, and $357+679$ cm.$^{-1}$, respectively, for which, naturally, Raman lines are not observed.

In the 3rd. column of the Table are given some of the fundamental vibration frequencies of tropolone in its electronically unexcited state, which are determined in the vibrational analysis of the near ultra-violet absorption bands of the vapor.[4] The agree-

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* Shimanouchi et al. (ref. 3) have not reported the numerical value of frequencies and the intensities of the infra-red absorption peaks. The values given in our Table are those estimated from their published absorption curve.

[1] Scott and Tarbell, *J. Am. Chem. Soc.*, **72**, 240 (1950).

[2] Doering and Knox, *J. Am. Chem. Soc.*, **73**, 828 (1951).

[3] K. Kuratani, M. Tuboi and T. Shimanouchi, This Blletin **25**, 250 (1952).

[4] MS. in preparation.

ment between these and the corresponding Raman values is very satisfactory. The largest discrepancy, 6 cm.$^{-1}$ between the 1262 cm.$^{-1}$ Raman and the 1256 cm.$^{-1}$ ultra-violet frequencies is probably due to change of bond forces concerned in the respective phases of aggregation, revealed specifically pronouncedly in this particular mode of vibration, even though the magnitude itself is quite small. In the near ultra-violet absorption spectrum we have found that the wave-number difference 643 cm.$^{-1}$ constitutes the key frequency, solely giving rise to many long band progressions, meaning that it is the excited state value of a totally symmetrical vibration frequency in the tropolone molecule with respect to its symmetry. In its spectral behaviour this frequency is entirely analogous to the 923 cm.$^{-1}$ excited state frequency of the benzene molecule. Now, the strong Raman shift 743 cm.$^{-1}$ in tropolone can plausibly be identified with the ground state value of the above 643 cm.$^{-1}$ Accordingly, we interpret 743 cm.$^{-1}$ as belonging to the totally symmetrical breathing vibration of the heptatriene ring, analogous to the 992 cm.$^{-1}$ frequency in benzene.

The three frequencies 1262, 1418 and 1610 cm.$^{-1}$, strongly observed in Raman and infrared, and partly confirmed in ultra-violet absorption, may collectively be assigned to the stretching vibrations of the C—O bonds in the molecule. If these bonds were normal single and double bonds as a conventional non-resonating structure formula would indicate, their stretching vibration frequencies should be much more differentiated (1030 cm.$^{-1}$ in methanol and 1760 cm.$^{-1}$ in acetone). Then, the actual values of these frequencies, being concentrated in a comparatively narrow intermediate frequency region, suggest that the carbon-oxygen bonds in tropolone are of a somewhat different nature from either of the ordinary single or double bond. From electron diffraction measurements the two C—O distances are reported to be 1.34 Å and 1.26 Å,5) values intermediate between Pauling's covalent radii sums 1.43 Å and 1.22 Å for the normal single and double C—O bonds. This may be understood as due mainly to the effect of resonance, and partly also to the influence of an intramolecular hydrogen bond bridging the two oxygen atoms in the molecule, an inference entirely compatible with the above-reported findings in the Raman spectrum.

By analogy to the benzen spectrum the frequencies 357, 436, 679, 743, 959 and 1208 cm.$^{-1}$ very probably belong to skeleton vibrations of the molecule, in which mainly the seven C atoms move. As we were not able to determine depolarization factors, the symmetry assignments of these fundamentals cannot be directly given now. However, we can at least see that the close parallelism thus found to exist between the skeleton vibration frequencies in benzene and tropolone simply reflects the close similarity of the ring forming valence forces, and hence of the electron structures of the two kinds of aromatic compounds.

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TABLE I

VIBRATION FREQUENCIES IN TROPOLONE

(cm.$^{-1}$)

Raman (present work)	Infra-red absorption3)**	Ultra-violet absorption
C_6H_6 solution	CS_2 and CCl_4 solutions	vapor
357 (2)		356
436 (1)		
679 (2)		678
743 (3)	735 (3)	741
	770 (2)	
	880 (2)	
	910 (1)	
959 (1)	950 (2)	
	1050 (2)	
1208 (2)	1200 (3)	
	1230 (4)	
1262 (4)	1260 (5)	1256
	1300 (4)	
1418 (5)	1415 (4)	
	1480 (4)	
	1560 (4)	
1610 (5)	1610 (4)	

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5) M. Kimura and M. Kubo, This Bulletin, **26**, 250 (1953).

** Regarding the frequency and intensity values for the infra-red absorption peaks see foot note * on p. 75.