RAMAN SPECTRUM OF ACETONITRILE

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Received October 10, 1964

(Communicated by Professor R. S. Krishnan, F.A.SC.)

1. INTRODUCTION

THE acetonitrile (methyl cyanide, CH_3CN) molecule belongs to the point group C_{3v} and as such it has eight distinct modes of vibrations ν_1, ν_2, ν_3, ν_4, ν_5, ν_6, ν_7 and ν_8, 4 of which come under the A_1 class and the remaining 4 under the E class. All these eight modes are active in Raman effect and in infra-red absorption. Although in infra-red absorption eight principal absorption maxima corresponding to ν_1 to ν_8 have been recorded (Venkateswarlu, 1951, 1952, Nakagawa and Shimanauchi, 1962 and Millegan and Jacose, 1962), in Raman effect the line corresponding to the mode ν_7 has not been recorded so far (Evans and Bernstein, 1955). The Raman spectrum of acetonitrile (liquid) has therefore been reinvestigated using the very intense helical arc of Toronto type constructed in our Laboratory. The λ 4046 radiation of the arc was suppressed by using a filter containing a saturated solution of $NaNO_2$. With the Hilger two-prism spectrograph exposures of the order of 36 hours were given to get an intense spectrogram.

2. RESULTS AND DISCUSSION

An enlarged photograph of the Raman spectrum of acetonitrile is reproduced in Fig. 1 (*a*) and the corresponding microphotometer record in Fig. 1 (*b*). 19 distinct Raman lines have been recorded for this substance and their frequency shifts have been entered in Table I. The lines with frequency shifts 483, 1178 and 1244 cm.$^{-1}$ which are marked on the microphotometer record are the intense modes ν_1 and ν_2 excited by λ 4046 radiation. In the second and third columns of the same table are entered the frequency shifts of the Raman lines reported by Evans and Bernstein (1955) and frequencies of infra-red absorption maxima observed by P. Venkateswarlu (1952). There is a very close correspondence between the Raman effect data of the present author and the infra-red absorption data of Venkateswarlu. This is what should be expected for the molecule belonging to C_{3v} point group.

TABLE I

Raman spectrum of acetonitrile

Sl. No.	Author	Evans and Bernstein	Infra-red	Mode	Class	Assignment
	Wing upto 120 $cm.^{-1}$					
1	380	379	379	ν_8	E	C—C ≡ N bending
2	674	674	..	..	..	..
3	754	750	749	$2\nu_8$	$A_1 + E$	Octave
4	920	919	917	ν_4	A_1	CC stretching
5	1044	..	1047	ν_7	E	CH_3 rocking
6	1378	1371	1376	ν_3	A_1	CH_3 deformation
7	1414	..	..	$\nu_7 + \nu_8$	..	Combination
8	1449	1443	1443	ν_6	E	CH_3 deformation
9	1558	..	..	..	..	..
10	2197	..	2204	$2\nu_4 + \nu_8$	..	..
11	2248	2248	2254	ν_2	A_1	C≡N stretching
12	2289	2289	2293	$\nu_3 + \nu_4$	..	..
	..	..	2411	..	..	..
13	2460	..	2482	$\nu_6 + \nu_7$	..	Combination
	..	..	2628	$\nu_2 + \nu_8$	..	Combination
14	2644	..	2674	..	..	..
15	2736	..	..	$2\nu_3$	A_1	..
16	2841	..	..	$\nu_3 + \nu_6$	..	Combination
17	2887	2882	2859	$2\nu_6$	..	Octave
18	2942	2941	2944	ν_1	A_1	Symmetric C—H stretching
19	2999	3001	3002	ν_5	E	Asymmetric C—H stretching

By comparison with infra-red data and the assignments given by the earlier workers, all the eight fundamental modes have been identified (Table I). The mode ν_7 which was missing in the Raman spectra recorded by the earlier workers can be seen very clearly in the microphotometer record at 1044 cm.$^{-1}$ [*see* Fig. 1 (*b*)]. It is comparatively a weaker line. There is also a continuous background which extends from 0 cm.$^{-1}$ up to about 1200 cm.$^{-1}$ with the intensity falling off as one proceeds away from the exciting line. Besides, there is the usual intense rotational wing accompanying the Rayleigh which extends up to 120 cm.$^{-1}$ The presence of the continuous background has made 1044 line scarcely visible on the photograph. The intensity of the 1044 line is definitely less than the intensity of some of the octaves and combinations. It is surprising to note that all the fundamental modes except ν_7 appear with considerable intensity in Raman effect. The modes ν_1, ν_2, ν_3 and ν_4 which come under symmetric A_1 class are more intense and sharper than the degenerate modes ν_5, ν_6, ν_7 and ν_8.

The Raman spectrum exhibits eleven lines belonging to the second-order spectrum. Nine of them have been explained as octaves and combinations (summations) of the fundamental modes.

3. SUMMARY

Raman spectrum of acetonitrile has been re-examined. 19 Raman lines have been recorded which include all the eight fundamental modes, three octaves and six summations. The fundamental mode ν_7 which has not been recorded before appears very weakly in the Raman spectrum.

4. ACKNOWLEDGEMENT

The author wishes to express his sincere thanks to Professor R. S. Krishnan for his guidance and encouragement.

5. REFERENCES

1. Evans, J. C. and Bernstein, H. J. *Can. Jour. Chem.*, 1955, **33**, 1746.
2. Millegan, D. E. and Jacose, M. E. *Jour. Mole. Spectroscopy*, 1962, **8**, 126.
3. Nakagawa, I. and Shimanauchi, T. *Spectrochimica Acta*, 1962, **18**, 513.
4. Venkateswarlu, P. .. *Jour. Chem. Phys.*, 1951, **19**, 293 and 1952, **20**, 923.

EXPLANATION OF PLATE VI

FIG. 1 (*a*) Raman spectrum of acetonitrile taken with λ 4358 excitation and two-prism spectrograph.

(*b*) Microphotometer record of the above.

(b)

(a)

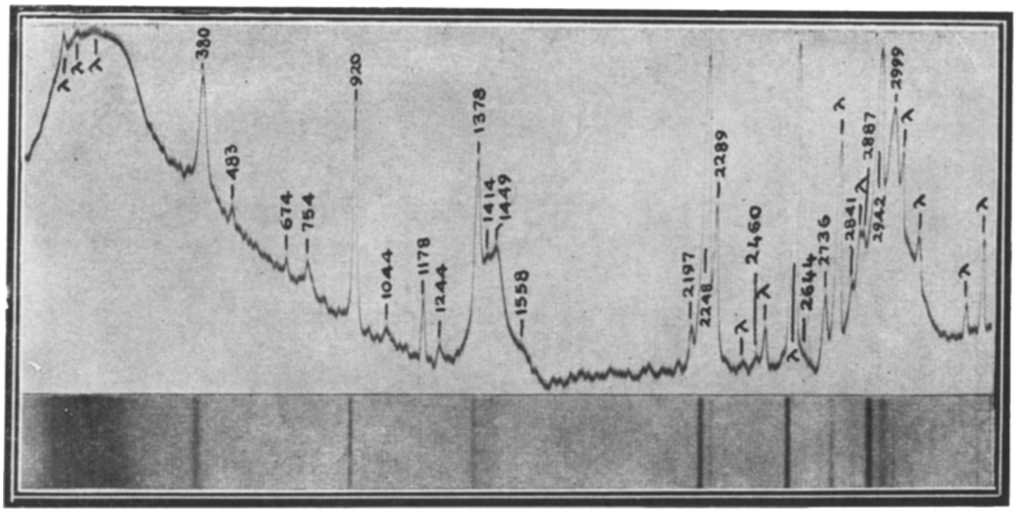

FIG. 1 (a) Raman Spectrum of Acetonitrile taken with λ 4358 Excitation and Two-Prism Spectrograph.

(b) Microphotometer Record of the above.