CHEMISTRY LETTERS, pp. 1091-1096, 1973. Published by the Chemical Society of Japan

DEPENDENCE OF RAMAN INTENSITIES OF PYRROLE, FURAN AND THIOPHENE UPON EXCITATION WAVELENGTH

Shoichi TAKAMIZAWA and Mitsuo ITO
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

The intensities of some totally symmetric Raman lines of pyrrole, furan and thiophene have been measured with 5145 A and 3371 A excitations. The Raman lines due to the stretching vibrations of two equivalent C-C bonds of the ring having greater double bond characters showed greater wavelength dependence of the intensities. The intermediate states mainly responsible to these Raman lines are low lying π, π^* electronic excited states. The results support the theoretical prediction about connection between the vibrational mode of the Raman line and the molecular geometry in the electronic excited state.

The intensities of vibrational Raman lines are known to be closely related with the electronic excited states of molecule. The experimental study of dependence of Raman intensities on the wavelength of incident light is one of the most useful approaches to clarify the relationship between the Raman intensities and electronic excited states, and several works 1-4) along this line have recently been attempted for relatively simple molecules whose electronic absorptions lie in visible or near ultraviolet region. In order to get the explicit wavelength dependence, various exciting lights covering a wide range of wavelength are required. Addition of N_2 gas laser of 3371 A to He-Ne and Ar lasers hitherto used expanded covering region to ultraviolet 5,6). In the present paper, we report the Raman spectra of three five-membered heterocyclic ring compounds, pyrrole, furan and thiophene excited by Ar and N_2 lasers.

The Raman spectra were measured with the same method as that reported before 5). Exciting lights used were an Ar ion laser of 5145 A and a pulsed N_2 laser of 3371 A. All the samples used were purified by distillations prior to the spectral measurements. The absorption spectra and the positions of the exciting frequencies used are shown in Fig. 1.

A typical example of the spectra excited at different wavelengths is shown in Fig. 2 for furan. A considerable difference in relative intensities between the two spectra excited at 5145 A and 3371 A is seen. Similar spectral changes were found also for pyrrole and thiophene. In order to evaluate the intensity change quantitatively, a constant amount of benzene was dissolved in each sample and 990 cm^{-1} Raman line of benzene was used as an internal intensity standard. The relative intensities, which were evaluated from the areas of the individual Raman lines recorded in a chart in an expanded scale and corrected for photomultiplier

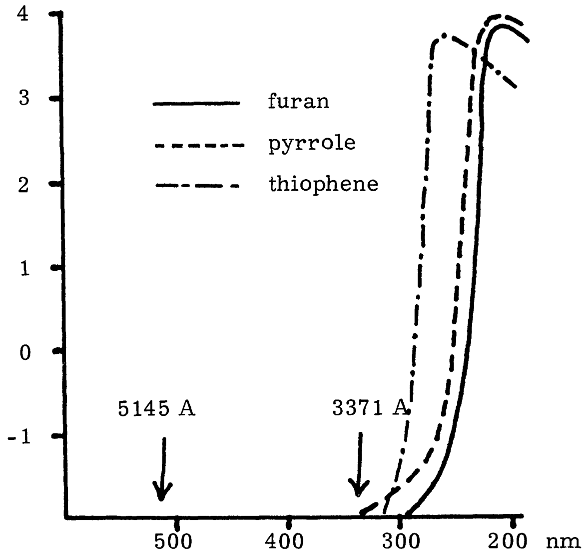

Fig. 1. The absorption spectra of furan, pyrrole and thiophene in cyclohexane : Arrows shows the positions of excitation wavelengths.

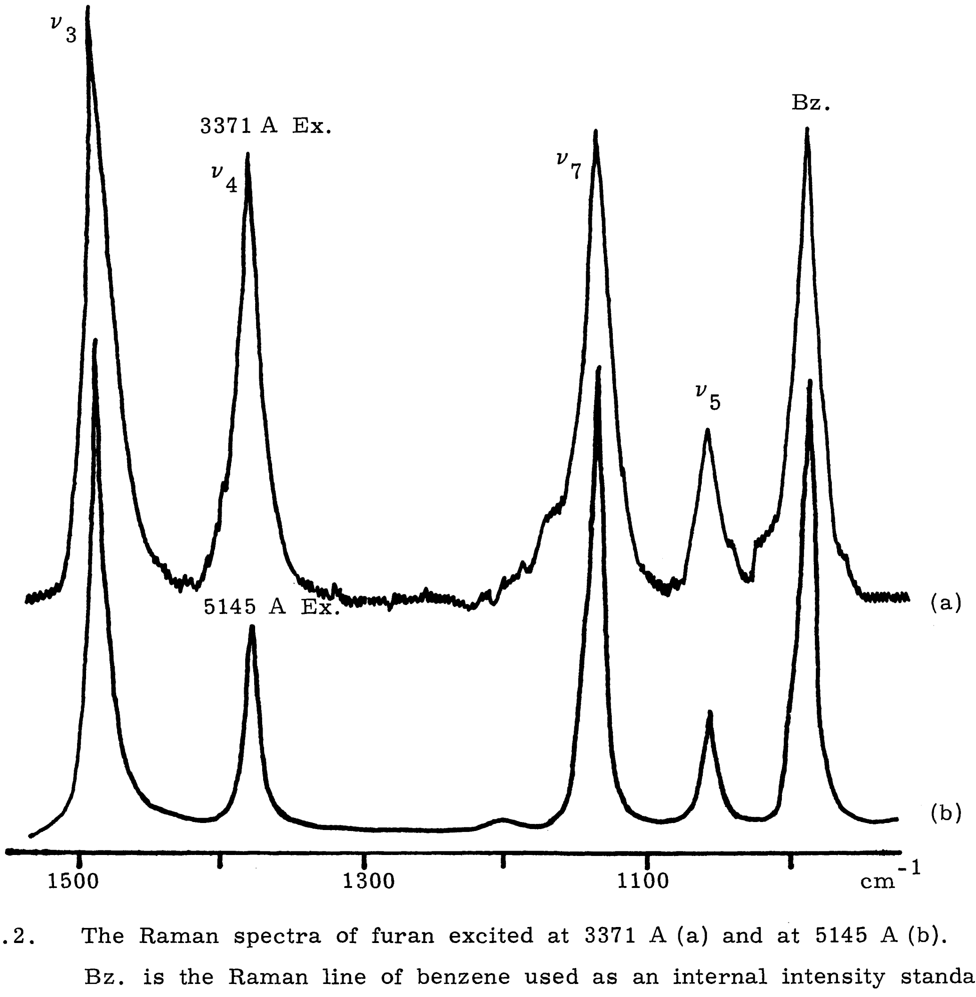

Fig. 2. The Raman spectra of furan excited at 3371 A (a) and at 5145 A (b). Bz. is the Raman line of benzene used as an internal intensity standard.

sensitivity, were normalized for the intensity of 990 cm^{-1} line of benzene. The intensity ratios of the individual Raman lines of 3371 A excitation to those of 5145 A excitation are given in Table 1 under the columns of R obs. The symmetry species and approximate vibrational modes of the Raman lines 7) are given in the first column of the table. According to our recent study of absolute Raman intensity 8), the absolute intensity of the Raman line of benzene of 990 cm^{-1} increases by 1.8 apart from the ν^4 dependent factor when the excitation wavelength is changed from 5145 A to 3371 A. Therefore, 1.8 should be multiplied to the observed ratios and the values thus corrected are listed under the columns of R correct. in the table. Accuracy of the ratios is believed to be within 10%.

Recently, Albrecht and Hutley 1) have developed a theory for dependence of vibrational Raman intensity on the wavelength of incident light and applied the results to the preresonance Raman effect of p-nitroaniline in benzene solution. According to their theory, the cross section of the Raman line of a totally symmetric vibration is proportional to dimensionless frequency factor

$$F_A = \nu^2 (\nu_e^2 + \nu_o^2) / (\nu_e^2 - \nu_o^2)^2$$

where ν_o is the exciting frequency, $\nu = \nu_o - \nu'$, ν' being the Raman frequency. Subscript e refers to virtual electronic states with eigen frequencies at ν_e. Pyrrole and furan have similar electronic absorptions due to π-π* transitions : the absorptions at 6.77 ev ($^1A_1 \leftarrow {}^1A_1$) and 5.87 ev ($^1B_1 \leftarrow {}^1A_1$) for pyrrole 9) and at 6.47 ev ($^1A_1 \leftarrow {}^1A_1$) and 5.88 ev ($^1B_1 \leftarrow {}^1A_1$) for furan 10). Thiophene is reported to possess three π-π* absorption bands 11) at 6.80 ev

Table 1. The observed and corrected intensity ratios of the Raman lines excited by 3371 A to those excited by 5145 A. (R = I(3371 A) / I (5145 A))

	Furan			Pyrrole			Thiophene		
Approximate type of mode	ν (in cm^{-1})	R obs.	R correct.	ν (in cm^{-1})	R obs.	R correct.	ν (in cm^{-1})	R obs.	R correct.
$\nu_3(a_1)$ ring	1491	1.67	3.01	1467	1.91	3.44	1409	1.84	3.31
$\nu_4(a_1)$ ring	1384	2.67	4.81	1384	1.87	3.37	1360	1.70	3.06
$\nu_5(a_1)$ CH bend	1066	1.25	2.25	—	—	—	1083	1.28	2.30
$\nu_6(a_1)$ CH bend	—	—	—	—	—	—	1036	0.87	1.57
$\nu_7(a_1)$ ring	1140	1.05	1.89	1144	0.97	1.57	839	0.90	1.62

Table 2. The calculated ratios of the frequency factors $F_A(3371\ A)$ / $F_A(5145\ A)$ for ν_e of various π,π^* excited states

	Furan		Pyrrole		Thiophene	
	ν_e(ev)	$\frac{F_A(3371\ A)}{F_A(5145\ A)}$	ν_e(ev)	$\frac{F_A(3371\ A)}{F_A(5145\ A)}$	ν_e(ev)	$\frac{F_A(3371\ A)}{F_A(5145\ A)}$
${}^1B_1(\pi,\pi^*)$	5.88	4.95	5.87	4.98	5.15	9.90
${}^1A_1(\pi,\pi^*)$					5.90	4.88
${}^1A_1(\pi,\pi^*)$	6.47	3.54	6.77	3.11	6.80	3.08

(${}^1A_1 \leftarrow {}^1A_1$), 5.90 ev (${}^1A_1 \leftarrow {}^1A_1$), and 5.15 ev (${}^1B_1 \leftarrow {}^1A_1$). In Table 2, the ratios of the calculated frequency factors at 3371 A to those at 5145 A ($F_A(3371\ A)$ / $F_A(5145\ A)$) for various ν_e are given.

Comparison between the observed and calculated ratios in Tables 1 and 2 shows that all the Raman lines of 1300 ~ 1500 cm^{-1} region except for the Raman line of 1384 cm^{-1} of furan are roughly correlated with the electronic excited states of A_1 around 6.5 ~ 6.8 ev. The observed ratio of 4.81 for the Raman line of 1384 cm^{-1} of furan is rather close to the calculated value 4.95 associated with the B_1 electronic state at 5.88 ev. On the other hand, the observed ratios for the Raman lines of 800 ~ 1150 cm^{-1} region are much smaller than any calculated values. Thus, the totally symmetric Raman lines may be divided into two classes. The two Raman lines ν_3 and ν_4 of 1300 ~ 1500 cm^{-1} region belong to the first class which are correlated with the π,π^* electronic excited states of energies less than 7 ev, and the second class are the Raman lines (ν_5, ν_6 and ν_7) of 800 ~ 1150 cm^{-1} whose effective intermediate states should be much larger in energy than 7 ev. The two Raman lines ν_3 and ν_4 belonging to the first class are assigned to the in-plane ring vibrations 7). Although their detailed vibrational modes are not known, they are probably the modes involving largely the stretching of C-C bonds of the ring since their observed vibrational frequencies do not change very much from pyrrole or furan to thiophene despite of great change of mass of the hetero atom 12). It may be assumed also that the stretching of two equivalent C-C bonds of the ring contributes to the vibrational mode more than the stretching of remaining C-C bond. The two equivalent C-C bonds are known to have double bond characters greater than the remaining C-C bond 13). Thus, the high freqiencies of ν_3 and ν_4 seem to support the above modes.

According to literatures 7), among the Raman lines belonging to the second class, ν_7 is assigned also to the in-plane ring vibrations, while the remaining lines ν_5 and ν_6 are due to the in-plane C-H bending vibrations. As is shown by great decrease of the vibrational frequency of ν_7 from pyrrole or furan to thiophene, the mode of this vibration should involve a considerable movement of the heteroatom in constrast to the ring vibrations belonging to the first class.

The above may be roughly summarized as follows ; the Raman lines classified to the stretching of the equivalent C-C bonds having great double bond characters are correlated with the low-lying π,π^* electronic excited states, while the Raman lines of other vibrational modes are correlated with much higher excited states. According to the theory of Raman intensity[14)], a close connection is predicted between vibrational mode of a totally symmetric Raman line and change of molecular geometry between the ground state and the electronic excited state which plays a dominant role as an intermediate state for the Raman line in question. It is expected from a simple MO consideration that π-bond order of the two equivalent C-C bonds of the ring decreases very much in the π,π^* excited state. Therefore, a great geometrical change is expected between the ground and π,π^* excited states of molecules with respect to the distances of the two equivalent C-C bonds. The correlation between the vibrational mode and the expected geometrical change in the π,π^* excited state is now apparent, supporting the theoretical prediction.

It is not possible at the present time to associate the Raman lines belonging to the second class with particular electronic excited states. As desceibed before, the electronic excited states responsible to these Raman lines should be very high in energy and they are probably the states other than π,π^* involving great geometrical change in the molecule with respect to the C-H and C-S distances.

We thank Drs. K. Kaya, N. Mikami and Y. Udagawa for their valuable discussions.

References

1) A. C. Albrecht and M. C. Hutley, J. Chem. Phys. 55, 4438 (1971).

2) S. Koide, Y. Udagawa, N. Mikami, K. Kaya, and M. Ito, Bull. Chem. Soc. Japan 45, 3542 (1972).

3) M. Ito, I. Suzuka, Y. Udagawa, N. Mikami, and K. Kaya, Chem. Phys. Lett. 16, 211 (1972).

4) I. Suzuka, N. Mikami, Y. Udagawa, K. Kaya, and M. Ito, J. Chem. Phys. 57, 4500 (1972).

5) K. Kaya, N. Mikami, Y. Udagawa, and M. Ito, Chem. Phys. Lett. 13, 221 (1972).

6) K. Kaya, N. Mikami, Y. Udagawa, and M. Ito, Chem. Phys. Lett. 16, 151 (1972).

7) T. Shimanouchi, Tables of Molecular Vibrational Frequencies. Consolidated Volume I, p. 136-137, NSRDS-NBS 39, United States Department of Commerce and National Bureau of Standards, (1972).

8) Y. Udagawa, N. Mikami, K. Kaya, and M. Ito, J. Raman Spectroscopy, in press.

9) L. W. Pickett, N. E. Corning, G. M. Wieder, D. A. Semenow, and J. M. Buckley, J. Am. Chem. Soc. 75, 1618 (1953).

10) L. W. Pickett, N. J. Hoeflich and Thien-Chuan Liu, J. Am. Chem. Soc. 73, 4865 (1951).

11) W. C. Price and A. D. Walsh, Proc. Roy. Soc. A179, 201 (1941).

12) The frequency change is rather large for ν_3. But, it is much smaller compared with the frequency change for ν_7 which is also due to the ring vibration.

13) L. Orgel, T. Cottrell, W. Dick, and L. Sutton, Trans. Faraday Soc. 47, 113 (1951) ; S. Nagakura and T. Hosoya, Bull. Chem. Soc. Japan 25, 179 (1951).

14) P. P. Schorygin, Dokl. Akad. Nauk. USSR 87, 201 (1952) ; E. M. Verlan, Opt. Spectry. 20, 341 (1966) ; F. A. Savin, Opt. Spectry. 19, 308 (1965) and A. Hirakawa, H. Obanawa, and M. Tsuboi, the paper 6C24 presented at the Symposuim on Molecular Structure, Sendai, October, 1972.

(Received July 30, 1973)