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PRERESONANCE RAMAN STUDY OF FURAN

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ABSTRACT

This work reports an investigation of the intensity variation with excitation wave number in the preresonance Raman spaectra of some normal modes of vibration of Furan. The purpose of this study is to relate the intensity behaviour to the position symmetry and oscillator strength of the absorption band at wave number shift $|\tilde{\upsilon}| = 1384$ cm^{-1} associated with electronic transition of the scattering molecule.

INTRODUCTION

Furan, C_4H_4O has the molecular structure shown in Figure (1). Borino, 1938, has suggested that the molecule belongs to molecular point group C_{2v}. The molecular vibrations of the molecule are distributed among the sysmmetry classes as follows:

$$8a_1 + 3a_2 + 3b_1 + 7b_2$$

The axis convention used for this assignment by Shimanovchi, 1972 requires that the z-axis corresponds to the two-fold axis and the x-axis is perpendicular to the molecular plane.

A full normal co-ordinate analysis and vibrational assignment of the infrared and Raman spectrum of furan has been made by Pickett, 1940. A strong polarized band at 1390 cm^{-1} was assigned to a C-C stretching vibration with some contribution to the vibration from the C-O stretch and the C-C-H in plane bending.

The depolarized ratio of this totally symmetric vibration was measured as $\rho\left(\frac{\bar{n}}{2}\right) = 0.33$ by Sidorov and Kalashmikova, 1968. Such a deplorization ratio suggests the dominance of one on-diagonal element of the transition polarizibility tensor. The preresonance Raman intensity of such a band should be interpretable in terms of an Alberecht-Hutley $F_A{}^2$ expression, 1961, 1970 and 1971.

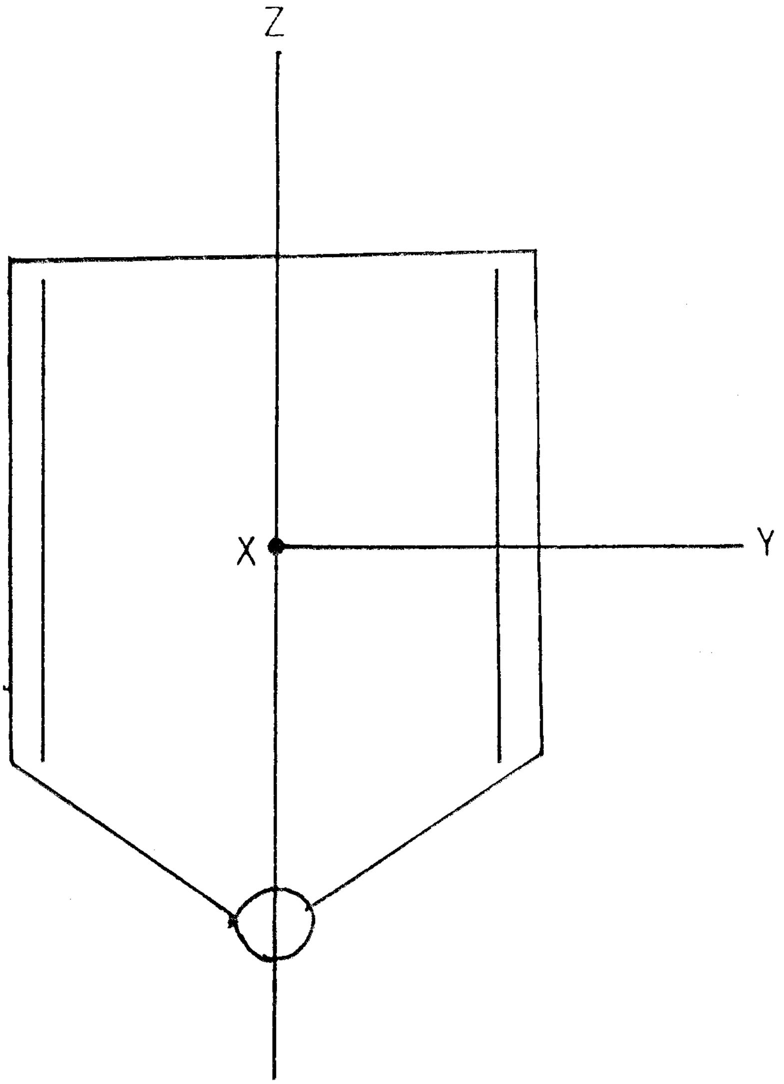

Figure 1. The chemical structure of furan (C_4H_4O)

Molecular orbital calculations on this conjugated system have been made by Wheland and Pauling, 1935. Between 1898 and 1938 various workers, Hartly and Dobbie, 1898, Henri and Foster have studied the u.v. absorption spectrum of furan at wavenumbers above 47620 cm^{-1} (below 210 nm). These studies were made both in vapour phase and the solution phase. All workers are in agreement that the band in this region are weak and are likely to be of the forbidden type.

Peckett, 1940, has studied the u.v. absorption spectrum of furan in the region 220–255 nm. The region shows three distinct band systems of high intensity

A vibrational analysis was made of one of these band systems. The 0–0 band associated with this transition occurred at 52230 cm^{-1} (191.5 nm). The analysis revealed three prominent totally symmetric vibrations at 1395, 848 and 1068 cm^{-1}. The 1384 band of furan was found in the system associated with an 0–0 transition at 52083 cm^{-1} (192 nm). Thus furan has electronic absorptions due to $\pi-\pi^*$ transitions at 52184 cm^{-1} with symmetry $^1A_1$ and at 47425 cm^{-1} with symmetry $^1B_2$.

Ito, 1973 measured the relative intensity of the 1384 cm^{-1} band in the Raman spectrum at two excitation wave numbers 19435 cm^{-1} (514.5 nm) and 29665 cm^{-1} (337.1 nm) in order to obtain support for the theoretical prediction of Shorygin, 1953, Svanine, 1965, Verlan, 1966 and Hirakawa et. al. 1972, about the connection between the vibrational mode associated with the Raman band and the molecular geometry in the excited state. For each excitation wavenumber the intensity was measured relative to the 991 cm^{-1} band of benzene as internal intensity standard. The two possible electronic states of furan which could be involved in the Raman enhancement occur at 47425 cm^{-1} (210 nm), $^1B_2$ (–*) and 52184 cm^{-1} (192 nm) $^1A_1$ $(\pi-\pi^*)$.

The calculated relative Raman intensity of 1384 cm^{-1} band at these two wavenumbers, namely;

$$I_{29665}cm^{-1}\ (1384\ cm^{-1})\ /\ I_{19435}\ cm^{-1}\ (1384\ cm^{-1})$$

based on an Albrecht–Hutley, 1961, $F_A{}^2$ expression was 4.95 if the $^1B_2$ $(\pi-\pi^*)$ transition was involved and 3.54 if the $^1{}_{A1}$ $(\pi-\pi^*)$ transition was involved. The measured value of Ito (1973) of 4.81 suggested that the state involved in the Raman enhancement of the 1384 cm^{-1} band was the $^1B_2$ $(\pi-\pi^*)$ state at 47425 cm^{-1} (210 nm). The disadvantages of this study by Ito, 1973, are: that the relative intensities were measured at only two excitation wavenumbers, and consequently the errors are inevitably large; the correction factor for the intensity dependence on excitation wavenumbers of the 991 cm^{-1} band of benzene is large; and also no apparent spectrum calibration was made.

In this study we have measured the relative intensitites of the 1384 cm^{-1} band at eight excitation wavenumbers in the range 19435–22002 cm^{-1}.

EXPERIMENTAL

The sample of furan used in this study was purified by distillation and was also treated with animal charcoal in order to minimise fluorescence due to small amounts of impurity. A spinning cell was used to reduce thermal decomposition.

The Raman spectra in the present study was excited with radiation from an argon ion (CW) gas laser, spectra–physics model 165. The output power of the laser used for Raman excitation was between 80–300 mw in order to save the sample from photo–decomposition and from heating effects.

The scattering radiation from the sample was dispersed with a spex double monochromator model 1401 which is of the Czerny–Turnur type and has a linear wavenumber scan drive.

RESULTS

Figure (2) shows a typical trace of the stokes Raman spectrum in the range 1350–1420 cm^{-1} together with a trace of the 802 cm^{-1} band of cyclohexane on the same scale. Figure (3) shows the stokes Raman spectra in the same range of figure (2) at each of the eight excitation wavenumbers. Table (1) lists I_{OBS} (with errors) together with $I_{CALC.}$ base on a Albrecht–Hutley $F_A{}^2$ expression with $\tilde{\upsilon}_{ri}{}^* = 47500 / cm^{-1}$ for the 1384 cm^{-1} band for various excitation wavenumbers in the range 19435–22002 cm^{-1}. Figure (4) shows a plot of $I_{OBS.}$ of the 1384 cm^{-1} band (single points with error bars) and $I_{CALC.}$ (solid curve) against excitation wavenumber.

DISCUSSION

Verlan, 1966, has found that the band 1384 cm^{-1} is the stokes Raman spectra of furan arises from a totally symmetric ring vibration. The table shows that this band is strongly resonance enhanced relative to the intensity of 802 cm^{-1} band of cyclohexane as the excitation wavenumber increases. It can be seen from Figure (4) that there is an excellent agreement between $I_{OBS.}$ and $I_{CALC.}$ where $I_{CALC.}$ has been determined by an Albrecht–Hutley $F_A{}^2$ expression with $\tilde{\upsilon}_{ri} = 47500$ cm^{-1}.

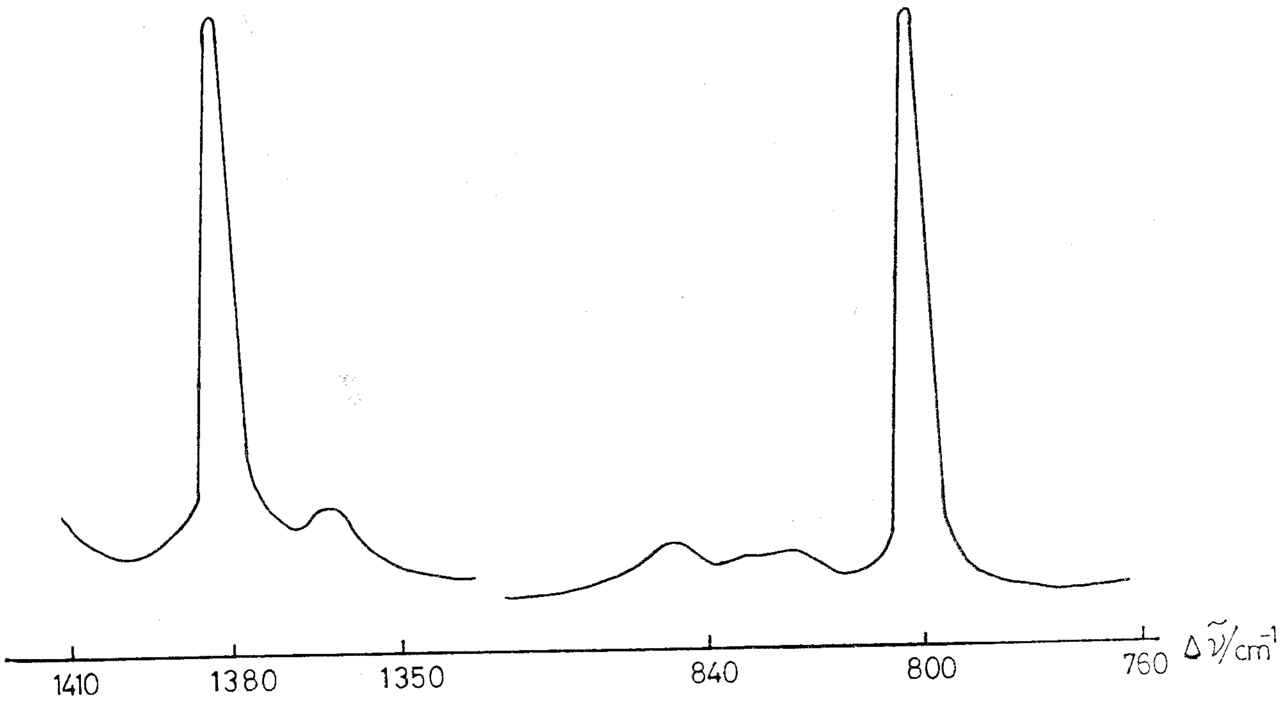

Figure 2. **A typical trace showing the Raman band of the internal standard cyclohexane at 802 cm^{-1}** together with the Raman bands of furan in the wavenumber shift range 1350–1410 cm^{-1}.

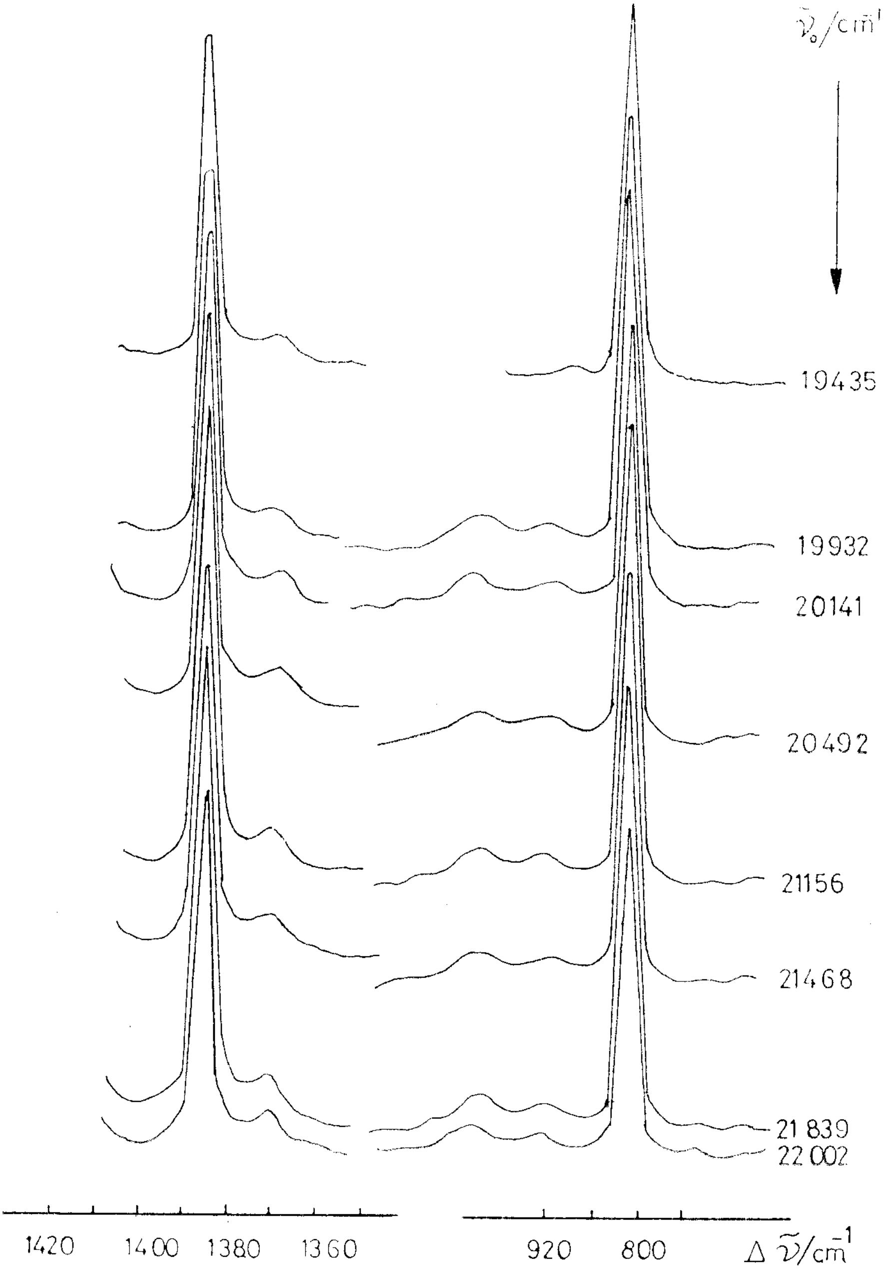

Figure 3. Raman spectra of furan (with cyclohexane as the internal standard) in the wavenumber shift regions 760–920 cm^{-1} and 1350–1420 cm for various excitation wavenumbers in the range 19435–22002 cm^{-1}.

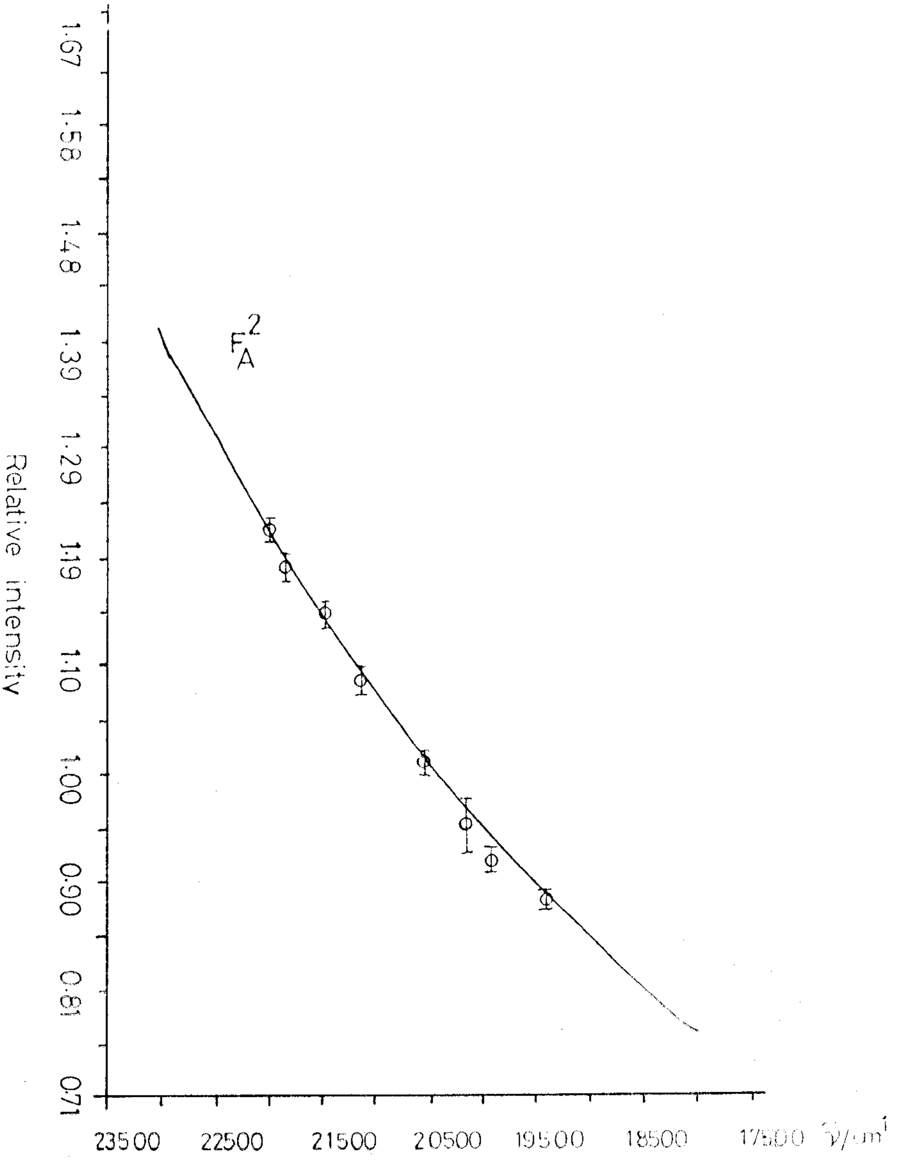

Figure 4. Comparison of $I_{OBS.}$ (individual points with error bars) and $I_{CALC.}$ (solid curve) using an Albrecht–Hutley $F_A{}^2$ expression with $\tilde{\nu}ri = 47.500$ cm^{-1} for the 1384 cm^{-1} band of furan.

This observation is in excellent agreement with that found by Ito et al, 1973, and shows that theband at 1384 cm^{-1} derives its Raman intensity from the low-lying $^1B_2$ (π–π^*) transition at 47425 cm^{-1}.

$\tilde{\upsilon}_{ri}{}^*$ wavenumber of the electronic absorbtion band.

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