# LETTERS TO THE EDITOR

## ELECTRONIC TRANSITION MOMENT VARIATION IN AlO ($A^2\Sigma^+$–$X^2\Sigma^+$) BAND SYSTEM

PRECISE knowledge of the variation of electronic transition moment ($R_e$) with internuclear distance ($r$) is needed for the study of transition probabilities in the band systems of diatomic molecules. The dependence of $R_e$ on $r$ is generally determined by the following expression,

$$I_{v'v''} = KN_{v'} \nu^4_{v'v''} R_e^2(\bar{r}_{v'v''}) \left| \int \psi_{v'} \psi_{v''} dr \right|^2$$

or

$$(I_{v'v''}/q_{v'v''} \nu^4_{v'v''})^{1/2} = (KN_{v'})^{1/2} R_e(\bar{r}_{v'v''}) \quad (1)$$

where, $I_{v'v''}$ is the intensity of an emission band, $q_{v'v''} = \left| \int \psi_{v'} \psi_{v''} dr \right|^2$ is the Franck-Condon (FC) factor, and the other symbols carry their usual[1] meaning. Since $N_{v'}$ is a constant for a particular progression, equation (1) can be written as,

$$R_e(\bar{r}_{v'v''}) \propto (I_{v'v''}/q_{v'v''} \nu^4_{v'v''})^{1/2}.$$

Using this relation Nicholls and Jarmain[2] have proposed that the dependance of $R_e$ on $r$ can be studied by plotting a graph of $(I_{v'v''}/q_{v'v''} \nu^4_{v'v''})^{1/2}$ against $\bar{r}_{v'v''}$. These plots for different $v''$-progressions are scattered due to the fact that $N_{v'}$ is constant only for a given $v''$-progression. The rescaling procedure due to Turner and Nicholls[3] is usually adopted to bring these plots on the same scale. However, there is an inherent drawback in this procedure since all the measured intensities of the bands cannot be used. Therefore, the method of regression due to Cunio and Johnson[4] is to be used for the evaluation of $R_e$ as a function of $r$. In this method all the measured intensities of the bands are used. The present note reports the dependance of $R_e$ on $r$ for the (A–X) transition of AlO molecule using the said method of regression. Recently reported[5] R-K-R-V FC-factors and $r$-centroids for this transition are used along with the available[6,7] band intensities in different spectral sources and the $R_e$-$r$ relations are derived. The resulting linear and quadratic expressions are given in Table I. These expressions are valid for the range of $r$ between 1·519 Å to 1·772 Å.

TABLE I

| Sl. No. | Spectral Source | $R_e - r$ relations |
|---|---|---|
| 1. | Low pressure arc | $R_e = k(1 - 0{\cdot}482\, r)$ |
| | | $R_e = k(1 - 1{\cdot}759\, r + 0{\cdot}623\, r^2)$ |
| 2. | Shock tube | $R_e = k(1 - 0{\cdot}391\, r)$ |
| | | $R_e = k(1 - 1{\cdot}298\, r + 0{\cdot}392\, r^2)$ |
| 3. | Exploding wire | $R_e = k(1{\cdot} - 0{\cdot}473\, r)$ |
| | | $R_e = k(1 - 1{\cdot}431\, r = 0{\cdot}002\, r^2)$ |

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## INFRARED SPECTRA OF METHYL BENZOATE AND BENZYL BENZOATE

METHYL BENZOATE and benzyl benzoate are mono-substituted benzenes wherein one hydrogen atom in each of the molecules are replaced by $-COOCH_3$ and $-COOCH_2C_6H_5$ respectively in the position '1' of the benzene ring. The Raman spectra of methyl benzoate and ethyl benzoate were earlier studied by Biswas[1], Matsuno[2], Kohlrausch *et al.*[3]. Since a complete assignment of the observed infrared bands of methyl benzoate (MB) and benzyl benzoate (BB) has not been given by any of the earlier workers[5–8]. A study of the infrared spectra of these molecules in the liquid phase was undertaken to obtain detailed information about the fundamental vibrations in the ground state.

The infrared spectra of MB and BB, contained in a cell, has been recorded in the liquid phase in the region 4000–250 $cm^{-1}$ on a Perkin Elmer double beam Infrared Spectrophotometer. The thickness of the cell was 0·025 mm. The chemicals (by B.D.H., England) were of pure quality and were used as such. The observed bands are analysed in terms of various ground state vibrations.

Molecules of MB and BB are assumed under $C_{2v}$ symmetry where the thirty normal modes of vibrations

can be divided into 11, $a_1$ type; 3, $a_2$ type; 10, $b_1$ type and 6, $b_2$ type modes of vibrations. Along with this there will be some internal vibrations due to substituents. The analysis of bands and the assignment of fundamental frequencies have been proposed on the basis of comparison with those of similar molecules. The assignment of the fundamental modes are given in Table I.

TABLE I

*Vibrational frequencies (in $cm^{-1}$) and assignment*

| Raman frequencies of $C_6H_5X$ $X = COOCH_3$ | Infrared frequencies of $C_6H_5X$ $X = COOCH_3$ | $X = COOCH_2C_6H_5$ | Assignment |
|---|---|---|---|
| 218 (5) D | 258 (4, s) | 263 (4, s) | $b_1$ $\phi$ (c–X) |
| | 335 (7, vs) | 330 (3) | $b_1$ $\phi$ (c–C) |
| 360 (4) P | 359 (5, s) | 355 (3) | $a_1$ $\alpha$ (c–C) |
| | 475 (4) | 454 (4, s) | $b_1$ $\phi$ (c–C) |
| | 519 (2) | 595 (5, vs) | $a_1$ $\alpha$ (c–c) |
| 679* (2) $P^1$ | 685 (9, vs) | 705 (10, b) | $b_1$ $\phi$ (c–c) |
| 808 (0) | 802 (5, s) | 800 (5, s) | $b_1$ ($\gamma$ c–H) |
| 826 (6) P | 820 (9, vs) | 820 (4, s) | $b_2$ or $b_1$ $\gamma$ (c–H) |
| 850 (0) | 845 (3) | 840 (3, s) | $b_1$ $\gamma$ (c–H) |
| 942** | 932 (5, s) | 880 (3, s) | $b_1$ $\gamma$ (c–H) |
| 969 (1) | 965 (8, vs) | 908 (7, vs) | $b_2$ or $b_1$ $\gamma$ (c–H) |
| 1003 (10) P | 1000 (4, s) | 1000 (6, s) | $a_1$ $\nu$ (c–c) |
| 1028 (4) P | 1025 (9, vs) | 1021 (10, vs) | $a_1$ $\beta$ (c–H) |
| 1064 (2) | 1070 (9, vs) | 1065 (10, vs) | $a_1$ $\beta$ (c–H) |
| 1111* (3) $P^1$ | 1110 (10, b) | 1100 (10, b) | $a_1$ $\beta$ (c–H) |
| 1160 (3) D | 1175 (9, s) | 1172 (9, vs) | $a_1$ $\beta$ (c–H) |
| 1277 (8) P | 1280 (10, b) | 1260 (10, b) | $a_1$ $\beta$ (c–H) |
| 1311 (3) P | 1313 (10, s) | 1310 (10, vs) | $a_1$ $\nu$ (c–c) |
| 1452* (2) $D^1$ | 1450 (10, s) | 1450 (10, vs) | $a_1$ $\nu$ (c–c) |
| 1495 (2) | 1490 (7, vs) | 1495 (8, vs) | $a_1$ $\nu$ (c–c) |
| 1591 (1) | 1580 (7, s) | 1582 (7, vs) | $a_1$ $\nu$ (c–c) |
| 1603 (10) D | 1600 (9, vs) | 1600 (8, vs) | $a_1$ $\nu$ (c–c) |
| | 3000 (6, s) | 3005 (7, vs) | $a_1$ $\nu$ (c–H) |
| | 3033 (6, 5) | 3030 (7, vs) | $a_1$ $\nu$ (c–H) |
| 3073 (5 b) P | 3063 (6, s) | 3064 (7, s) | $a_1$ $\nu$ (c–H) |
| | 3090 (6) | 3090 (5, s) | $a_1$ $\nu$ (c–H) |

*Note*: Values in parenthesis refer to the relative intensities. $\nu$ = stretching, $\beta$ = in-plane bending, $\gamma$ = out-of-plane bending, $\alpha$ = in-plane deformation, $\phi$ = out-of-plane deformation, s = sharp, vs = very sharp, b = broad, * = polarisation data taken from Biswas, ** = frequency taken from Biswas.

*C–C Ring Deformation Frequencies*: Amongst the C = C stretching, frequencies 1000 $cm^{-1}$ in both the compounds are identified as ring breathing frequency. Along with this, the frequencies 1313, 1450, 1490, 1580, 1600 $cm^{-1}$ and 1310, 1450, 1495, 1582, 1600 $cm^{-1}$ are assigned as the other carbon stretching frequencies for MB and BB, and correspond to 1585 ($e_{2g}$), 1485 ($e_{1u}$) and 1310 ($b_{2u}$) modes of benzene.

*C–H Stretching Frequencies*: Sharp and very sharp infrared bands appearing at 3000, 3033, 3063, 3090 $cm^{-1}$ and 3005, 3030, 3064, 3090 $cm^{-1}$ have been considered due to C–H stretching for MB and MB respectively.

*C–H Bending Vibrations*: There are four very sharp, sharp and broad bands for both the compounds at 1025, 1070, 1110, 1175 $cm^{-1}$ in MB and at 1021, 1065, 1100, 1172 $cm^{-1}$ in BB which may correspond to C–H in-plane bending vibrations. The bands observed at 802, 820, 845, 932, 965 $cm^{-1}$ and 800, 820, 840, 880, 908 $cm^{-1}$ may correspond to the C–H out-of-plane bending vibrations for the respective compounds.

*C–C Bending Vibrations*: The infrared bands at 335, 475, 685 $cm^{-1}$ and 330, 454, 705 $cm^{-1}$ are assigned as carbon out-of-plane bending vibration. Moreover the in-plane carbon bending vibrations may be identified at 359, 519 $cm^{-1}$ in MB and at 355, 595 $cm^{-1}$ in MB.

Present authors assign tentatively the sharp bands 258 $cm^{-1}$ and 263 $cm^{-1}$ due to C–$COOCH_3$ and C–$COOCH_2C_6H_5$ out-of-plane bending vibrations for the MB and BB. Internal vibrations of the substituents were not observed due to the limitations of the instrument.

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