Electronic emission spectra of \( o- \) and \( m- \)fluorobenzaldehyde vapours

M K HAQUE* and S N THAKUR
Department of Physics, Banaras Hindu University, Varanasi 221 005, India
*Present address: Department of Physics, T.N.B. College, Bhagalpur 812 007, India

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Abstract. The high resolution \( n^* \) electronic emission spectra of \( o- \) and \( m- \)fluorobenzaldehyde vapours in the region 365-560 nm excited in a discharge are reported for the first time. The spectra of both the compounds consist of the \( \tilde{A} \, ^1A'' - \tilde{X} \, ^1A' \) fluorescence as well as the \( \tilde{a} \, ^3A' - \tilde{X} \, ^1A' \) phosphorescence bands. In the case of \( o- \)isomer, all the eleven out-of-plane vibrations have been observed in the fluorescence and the phosphorescence, though weakly in the latter, whereas in the case of \( m- \)isomer, only ten have been observed in the fluorescence and nine in the phosphorescence. It is found that the most intense bands in both the fluorescence and the phosphorescence spectra of these molecules belong to the trans-\( O \) rotamer.

Keywords. Fluorescence; phosphorescence; rotamer; isomer; emission spectra.

1. Introduction

The electronic spectra of \( o- \) and \( m- \)fluorobenzaldehyde were studied in the region 365-560 nm both in absorption (Padhey and Viladker 1966; Chandra and Sharma 1967; Srivastava 1968) and in emission (Srivastava 1968), but these workers made an erroneous interpretation of the observed bands as belonging to only one electronic system. The emission bands observed under high resolution in the present investigation can be differentiated into two types on the basis of their-rotational contours. As in the case of benzaldehyde (Hollas and Thakur 1973) and \( p- \)fluorobenzaldehyde (Haque and Thakur 1978), here also the sharp bands have been attributed to the \( \tilde{a} - \tilde{X} \) (phosphorescence) system and the diffuse bands to the \( \tilde{A} - \tilde{X} \) (fluorescence) system. There may be two different forms of \( o- \) and \( m- \)fluorobenzaldehyde called the trans-\( O \) and the cis-\( O \) rotamers, and although the problem of rotational isomerism in these molecules has been studied by a number of workers both experimentally and theoretically (Miller et al 1967; Drakenberg et al 1975; Green and Harrison 1976; Crowder and Northam 1969; Wasylishen and Schaefer 1971; Bock and Tomchuk 1972; Aw et al 1972; Bruce et al 1974), the study of this phenomenon in the electronic spectra has been made for the first time by Haque and Thakur (1979). It has been found that most of the prominent vibronic bands can be explained as due to the trans-\( O \) rotamer in both the molecules.
2. Experimental Details

The samples of o- and m-fluorobenzaldehyde used in the present investigation were obtained from Koch Light Co. (U.K.) and were used without further purification. The experimental details for recording and measuring the emission spectra were the same as described earlier (Haque and Thakur 1978). The absorption spectra were photographed on a 1.5 m Baush and Lomb grating spectrograph and the intensity variations were studied in the temperature range 80°C–240°C. The experimental details are given in Haque (1979).

3. Description of observed spectra

3.1 o-Fluorobenzaldehyde

The 00° band of $A^1A'' - X^1A'$ fluorescence emission is the strongest band in this system and lies at 26333.3 cm$^{-1}$ in good agreement with its position at 26333.1 cm$^{-1}$ in the absorption spectrum. There are two main peaks in its rotational contour with a separation of about 9 cm$^{-1}$ and the lower wavenumber peak is the stronger of the two (figures 1a and 2a). The relative separations of all the bands in the spectrum have been obtained from the stronger peak. A sequence interval of $+27$ cm$^{-1}$ is the next most prominent feature in the neighbourhood of the 00° band followed by the sequence intervals of $-10$ and $-9.7$ cm$^{-1}$ in order of decreasing intensities. The rotational peaks of the 00° band group have a width of about 2 cm$^{-1}$ (full width at half of the maximum intensity, FWHM) which is the same as in benzaldehyde (Hollas and Thakur 1973) and p-fluorobenzaldehyde (Haque and Thakur 1978). The 00° band group contains about 80% of the total intensity of the fluorescence and the rest is spread over the remaining weak vibronic bands among which the band at 25626.1 cm$^{-1}$ is relatively intense. The rotational contours of the weaker bands are not as clearly defined as those of the 00° band, and the assignments have been made by considering the separation of the most intense feature of the band group in question from the 00° band. There are two features at $-52.9$ and $-59.4$ cm$^{-1}$ from the 00° band which appear very prominently in the fluorescence emission but do not appear as prominently in the vapour absorption and do not show an appreciable change in their intensities as compared to that of the 00° band on increasing the temperature of the absorption cell.

The 00° band of the $A^3A'' - X^3A'$ system has been identified at 24603.5 cm$^{-1}$ in good agreement with the liquid phase absorption at 24670 cm$^{-1}$ (Vander Donckt and Vogels 1972). The rotational contour of this band also consists of two peaks with a separation of about 7 cm$^{-1}$ with the lower frequency peak showing more intensity (figures 1b and 2b). Positive sequence intervals of 16.9, 26.8, 33.7, and 42.5 cm$^{-1}$ appear with a gradual decrease in intensity. Three negative sequence intervals of $-25.4$, $-34.6$, and $-41.6$ cm$^{-1}$ also appear with appreciable intensities and each can be observed up to two members. A band at 24545.9 cm$^{-1}$ appears with a rotational contour different from that of the 00° band and stands out amongst the bands in this region.