NORMAL VIBRATIONS OF N, N-DIMETHYLFORMAMIDE AND N, N-DIMETHYLACETAMIDE

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ABSTRACT

Infrared and Raman frequencies of N, N-dimethylformamide and N,N-dimethylacetamide as recorded by the authors, in the region 3100 cm$^{-1}$ to 250 cm$^{-1}$ are given. The normal co-ordinate treatment of these molecules has been carried out using general quadratic force field and the potential energy distribution of the various modes of vibrations have been calculated to study the nature of absorption frequencies arising out of the in-plane vibrations. The assignments made by the authors in the region 3100 cm$^{-1}$ to 500 cm$^{-1}$ are compared with those of Lumley Jones who assigned the frequencies on the basis of band contour studies. These calculations have enabled the authors also to assign the frequencies in the region 500 cm$^{-1}$ to 250 cm$^{-1}$ to the various bending modes of vibrations. The C—N stretching frequency in tertiary amides is considerably different from that in primary and secondary amides.

I. INTRODUCTION

SPECTROSCOPIC studies of primary and secondary amides and the normal co-ordinate treatment of these molecules received considerable attention in recent times. Several authors$^{1-11}$ have studied the infrared spectra of primary amides like formamide, and acetamide and secondary amides like $N$-methylformamide and $N$-methylacetamide and of their deuterated species in various states of aggregation to investigate the nature of intermolecular associations in these molecules and Miyazawa et al., Suzuki, Puranik and Lalitha Sirdeshmukh and the authors$^{5-7,9-11}$ subjected these molecules to normal co-ordinate treatment in order to understand the nature of the absorption frequencies arising out of different modes of vibrations. The main result that emerges out of these studies is that in primary amides, the amide I, the amide II and the amide III bands are essentially due to $\nu(C=O)$, $\delta(NH_2)$ and $\nu(C-N)$ vibrations respectively. On the other hand, in secondary
amides, while the amide I band is essentially a C=O stretch, the amide II and the amide III bands have been shown to arise out of the combined contribution of \( \delta (\text{NH}) \) and \( \nu (\text{C—N}) \) vibrations. These results have been broadly supported from the spectra of N-methylacetamide and acetonilide obtained by Bradbury and Elliot\(^{12}\) and Soichi Hayashi\(^{13}\) who used polarised infrared radiation in these studies. Lumley Jones\(^{14}\) assigned the vibrational frequencies of some secondary and tertiary amides in the region 3500 cm.\(^{-1}\) to 500 cm.\(^{-1}\) on the basis of band contour studies of infrared absorption bands and Katon \textit{et al.}\(^{15}\) recorded the spectra of these compounds in the region 700 cm.\(^{-1}\) to 250 cm.\(^{-1}\). There is no earlier attempt to investigate the nature of the absorption frequencies arising out of the in-plane vibrations in tertiary amides on the basis of normal co-ordinate treatment. The authors have therefore chosen two simplest molecules of the tertiary amides—N, N-dimethylformamide and N, N-dimethylacetamide and subjected them to normal co-ordinate treatment by using the general quadratic force field.

II. EXPERIMENTAL AND RESULTS

The infrared spectra of N, N-dimethylformamide and N, N-dimethylacetamide in the region 3100 cm.\(^{-1}\) to 700 cm.\(^{-1}\) have been recorded using Perkin-Elmer Model 21 infrared spectrophotometer with NaCl optics. The spectra of the liquids were recorded using microfilms of unknown thickness and of solutions in CCl\(_4\) with matched cells of 0.1 mm. thickness with NaCl windows. The spectra of the pure amides were also recorded in the region 700 cm.\(^{-1}\) to 400 cm.\(^{-1}\) with Perkin-Elmer Model 337 grating spectrophotometer, and in the region of 400 cm.\(^{-1}\) to 250 cm.\(^{-1}\) with Perkin-Elmer Model 521 grating spectrophotometer. The Raman spectra of these substances were recorded with Fuess glass spectrograph and Hilger's Raman source unit and \( \lambda 4358 \) was used as the exciting radiation. The infrared and Raman frequencies, as recorded by the authors and the assignments are given in Tables I and II and the corresponding infrared and Raman spectra are shown in Figs. 1, 2, 3 and 4. The infrared bands at 1256 cm.\(^{-1}\) and 1259 cm.\(^{-1}\) in the two amides are strong whereas the bands at 865 cm.\(^{-1}\) and 738 cm.\(^{-1}\) are weak. But in Raman spectra, the frequencies at 866 cm.\(^{-1}\) and 743 cm.\(^{-1}\) are the strongest lines while the other two frequencies at 1230 cm.\(^{-1}\) and 1259 cm.\(^{-1}\) are relatively less intense. Similarly the Raman line at 960 cm.\(^{-1}\) which is assigned to \( \nu (\text{C—CH}_3) \) vibration in N, N-dimethylacetamide is fairly strong whereas the corresponding band in infrared is weak.