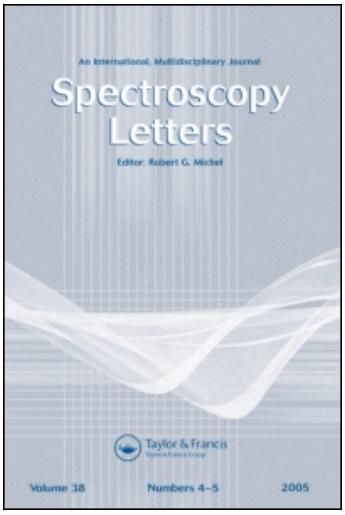

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The Infrared Spectrum of Crystalline Methyl Formate

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THE INFRARED SPECTRUM OF CRYSTALLINE METHYL FORMATE*

Keywords: Methyl Formate, Polarized Infrared Spectra

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The vibrational spectra of methyl formate have been recorded and analyzed by many workers[1]. As a result, the vibrational assignment and molecular conformation is well known. None of these workers have reported the infrared spectra of crystalline methyl formate, however, and only one group[1] has reported the Raman spectrum of the crystalline compound. In addition, there appears to be no report in the literature concerning the crystal structure of methyl formate by diffraction or other methods. This is perhaps not surprising in view of the compounds low melting point (-99°C). Since methyl formate is the first and simplest member of the ester class, it seemed desirable to have some data on the infrared spectra of the crystal even though the detailed analysis of such data, in the absence of a reported cyrstal structure, is difficult and uncertain. Nevertheless, it is often possible to draw some con-

clusions concerning the nature of the crystalline material, particularly if an oriented sample can be obtained so that polarized radiation can be used.

Samples of crystalline methyl formate were obtained by cooling capillary films of the liquid between alkali halide windows in a CTi Model 20 Cryostat and in a conventional low temperature Dewar type infrared cell cooled with liquid nitrogen. It has been shown[2,3] that such a procedure can yield oriented polycrystalline samples which may be studied with polarized radiation. The methyl formate was distilled three times prior to obtaining the crystal films. The infrared spectra were recorded on a Perkin-Elmer Model 180 Infrared Spectrophotometer using the standard wire grid polarizer accessory. Great difficulty was encountered in obtaining the crystal films due to the extreme volatility of methyl formate. The sample chamber must be evacuated to prevent condensation of moisture on the windows at low temperatures and methyl formate is quite volatile even at temperatures near its freezing point. In addition, crystalline methyl formate appears to have a rather large vapor pressure, since attempts to observe spectra near the melting point invariably result in rapid loss of sample. As a result, the cyrstal film must be cooled rapidly to well below the freezing point of methyl formate if they are to be retained for study.

A number of samples were cooled and their spectra recorded. Although there were no obvious differences in the procedures used, we obtained two quite different spectra, evidence that two different crystalline forms of methyl formate were obtained. Typical spectra

of the two forms are reproduced in Figures 1 and 2 and the observed band frequencies are listed in Table 1. The frequencies listed for Form II in Table 1 are the average frequencies noted in two spectra obtained from the same sample when the polarizer was rotated by 90°. This difference in observed frequencies and band shapes observed upon rotation of the polarizer indicates that the sample is rather highly oriented. Differences in frequency are small at

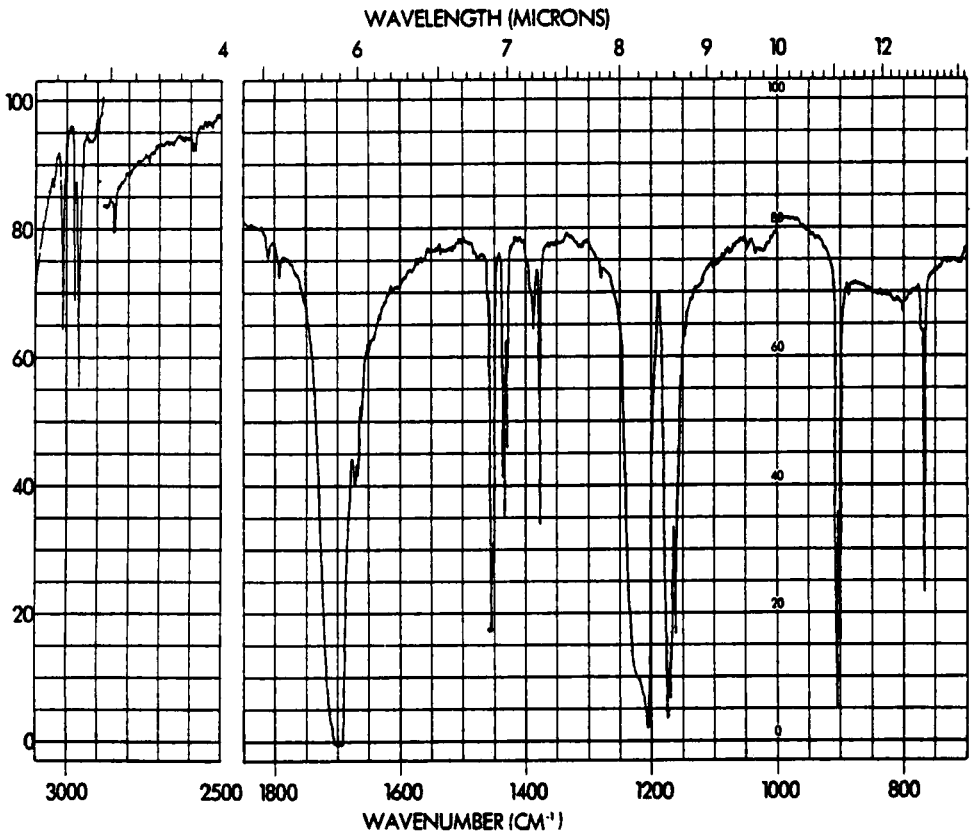

FIG. 1. The Partial Infrared Spectra of Form I of Crystalline Methyl Formate.

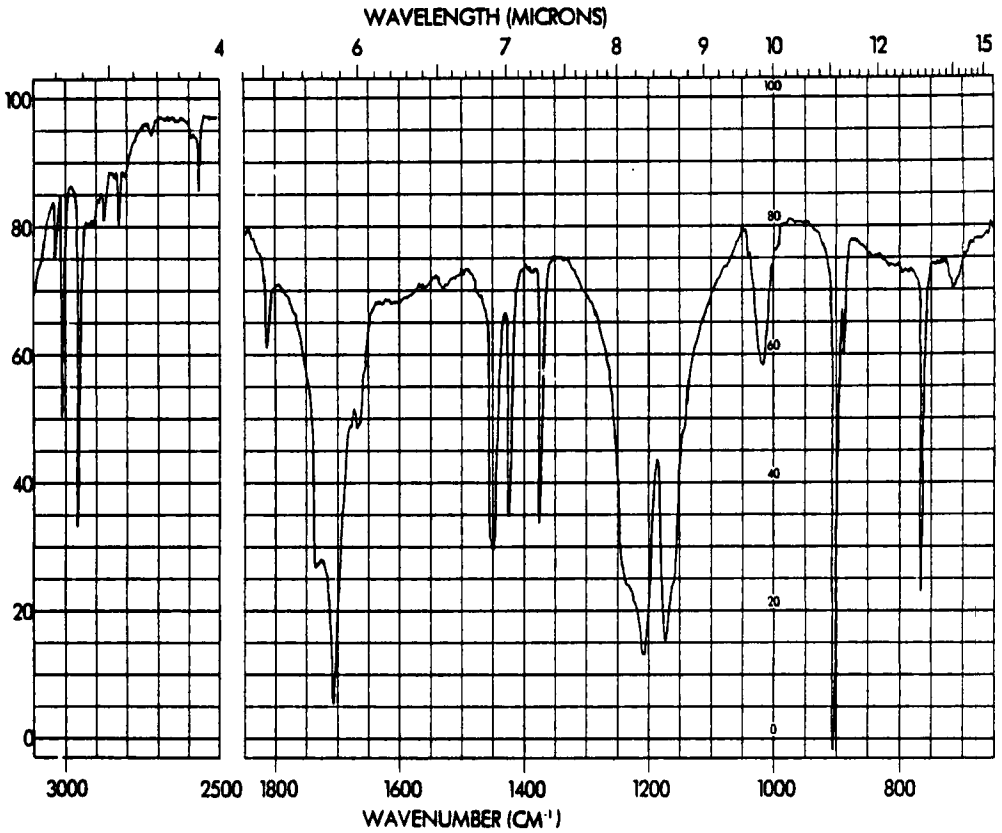

FIG. 2. The Partial Infrared Spectrum of Form II of Crystalline Methyl Formate.

the two polarizer settings (1-2 cm^{-1}) and are typical of factor group components observed in crystal spectra.

On the other hand, Form I shows no indication of orientation. Spectra recorded with polarizer settings differing by 90° are essentially identical. This indicates that Form I is either a randomly oriented sample or has a very special crystal structure. Although the postulate that Form I is randomly oriented is an

TABLE 1

Observed Infrared Absorption Bands of Two Forms of Crystalline Methyl Formate (in cm^{-1}).

Form I	Form II
	3040 w
	3014 m
3009 s	
2973 m	
2959 s	2959 s
1740 s, sh	1734 s, sh
1710 vs	1708 vs
1458 s	
1454 s	1455 s
1439 m	
1436 m	
1431 m	1431 s
1386 w	
1379 m	1380 s
	1235 s, sh
1216 vs	
1209 vs	1206 vs
1177 s	
	1172 vs
1165 s	
	1159 s, sh
	1023 w-m
908 s	909 s
902 s	
	897 w
770 s	771 m

attractive one due to its simplicity, there are a number of features in our results which are unusual for a randomly oriented sample. These are: (1) the method of preparation of the film is exactly that used to prepare oriented films--this method has been widely used[2-4] and always results in spectra showing significant polarization efffects; (2) the spectra of Form I show a very large amount of crystal splitting--usually crystal components are not well resolved in an unoriented film; (3) the bands in the spectra of Form I are exceedingly narrow, again not typical of random samples; and (4) there are significant differences in the two spectra--these are particularly large in the CH stretching region but are significant in other regions of the spectrum as well. The precision in recording band frequencies on the Perkin-Elmer Model 180 is no worse than $\pm$ 0.5 cm^{-1} so that differences of even one cm^{-1} are significant.

If Form I is a second crystal modification of methyl formate the lack of polarization effects can be explained in terms of a crystal class which is cubic. The cubic crystal class is the normal one for plastic crystals and such crystals do not possess polarized infrared spectra, in general. We therefore conclude that the observed data are consistent with two crystal modifications of methyl formate, although the evidence is not definitive.

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