force field. Among the calculated frequencies is $\nu_1 = 2099$ cm^{-1} for CD_3NC. In the present calculations the structural parameters were adopted from Duncan,[4] *viz.* C–H = 1.094 Å, C–N = 1.427 Å, N=C = 1.167 Å and ∠HCH = 109°45′.

Mean amplitudes and the linear shrinkage. The force fields were used to calculate the mean amplitudes of vibration and linear shrinkage effect for CH_3NC and CD_3NC. The results are given in Table 1. Perpendicular amplitude correction coefficients or K-values [7] are useful in modern electron diffraction studies in addition to the mean amplitudes of vibration. Table 2 shows the values of K for CH_3NC and CD_3NC from the present calculations.

Discussion. Duncan's statement to the effect that Mattern and Fletcher have misassigned ν_1 of CD_3NC is confirmed by our calculations. It was found that the values given by Venkateswarlu *et al.* for the mean amplitudes,[2] the linear shrinkage [2,3] and perpendicular amplitude correction coefficients [3] differ considerably from our values.

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On the Vibrational Spectra of Maleic Anhydride

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The Raman spectrum of maleic anhydride was first studied by Kahovec *et al.*[1] Later, the fundamental vibrations were assigned by Mirone *et al.*,[2] based on infrared and Raman data. This assignment was slightly revised by di Lauro *et al.*[3] However, no infrared spectra were recorded below 400 cm^{-1}. In continuation of our work on the vibrational spectra of some mono- and dihalo maleic anhydrides [4,5] the far infrared spectrum of maleic anhydride has been recorded. Also, the Raman spectrum has been reinvestigated. These experiments resulted in reassignment of the infrared active non-planar fundamental, ν_{21}.

Experimental. The far infrared spectrum (400–80 cm^{-1}) of maleic anhydride was recorded for benzene solution and for the solid state, using a Perkin-Elmer FIS-3 spectrometer. The solid was studied as a Nujol mull between polyethylene plates, at room temperature as well as at liquid nitrogen temperature. The observed frequencies are given in Table 1. The vapor spectrum (250–40 cm^{-1}) was recorded at room temperature, using a RIIC model 520 Fourier-spectrometer and a light pipe gas cell (path length ~6 m) described elsewhere.[6] The spectrum of the saturated vapor (p ~0.1 mmHg) showed only one, weak but sharp, absorption band, at 161 cm^{-1}. The Raman spectrum was investigated using a CODERG PH1 spectrometer and a Spectra-Physics model 125 He–Ne laser.

The following notation of the symmetry species and normal vibrations is the same as used in Refs. 2 and 3, contrary to that used in Refs. 4 and 5. The B_2-species thus represents the infrared and Raman active 'out-of-plane' vibrations.

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Table 1. Far infrared absorption spectra (400–80 cm^{-1}) of maleic anhydride.[a]

C_6H_6-Sol'n	Solid state 25°C	Solid state −196°C	Assignment
360[b] vw	375[b] vw	388[b] vw	$2\nu_{21}$
271 vw	276 m	276 m	ν_{18} (A_2)
173 m	191 m	198 m	ν_{21} (B_2)
	183 m	186 m	
	110[c] s	120[c] vs	lattice modes
		100[c] w	

[a] Frequency in cm^{-1}. [b] Shoulder. [c] Broad. vw = very weak; w = weak; m = medium; s = strong; vs = very strong.

As given in Table 1, an infrared absorption band of medium intensity is present near 180 cm^{-1} in the solid state as well as in the benzene solution. The crystal spectra also show a broad, strong band near 110 cm^{-1}, supposedly due to lattice vibrations. This band shifts to higher frequencies at low temperatures, as expected.[7]

The band near 180 cm^{-1}, however, must be due to a molecular vibration, because it appears in the solid as well as in the solution spectrum. Furthermore, it is not unreasonable to assign the weak, sharp vapor phase band at 161 cm^{-1} to the same molecular vibration, because vapor/liquid frequency shifts of this order of magnitude are well known.[8] The splitting of this band in the crystalline state is not unexpected, since a factor group analysis shows that each vibration in the isolated molecule should give three infrared active components.[3]

This band cannot be assigned as difference band, because it appears with equal intensity at room temperature and at liquid nitrogen temperature. Consequently, a reassignment of the fundamental vibrations of maleic anhydride must be considered. By studying the Raman spectra of melted, dissolved, and crystalline maleic anhydride we were able to find all Raman bands reported by Mirone *et al.*,[2] except that at 340 cm^{-1}; all attempts to verify this band failed. Also, this band was not observed in the earlier work of Kahovec *et al.*[1] The band was previously assigned [2] as the lowest B_2-fundamental, ν_{21}, which should be active in both the infrared and the Raman spectra. However, there is no absorption to be found in the infrared spectrum at this frequency.

The most obvious solution is to assign ν_{21} to the infrared absorption band observed at 173 cm^{-1} in benzene solution and at ~190 cm^{-1} in the solid. The sharp vapor phase band at 161 cm^{-1} is interpreted as the Q-branch of ν_{21}, which should show C-type band contours. A shoulder observed near 360 cm^{-1} in the infrared solution spectrum may be interpreted as $2\nu_{21}$. We have not been able to find the Raman counterpart of ν_{21}, which must therefore be extremely weak.

The lowest A_2-fundamental, ν_{18}, previously has only been observed in the Raman spectrum at 270 cm^{-1}. This fundamental should, however, have three infrared active components in the crystalline state.[3] An infrared absorption band of medium intensity is in fact found at 276 cm^{-1} in the crystal spectrum, at room temperature as well as at liquid nitrogen temperature. The infrared solution spectrum shows only an extremely weak absorption at this frequency. This evidence strongly supports the assignment of this band as belonging to the infrared inactive A_2-species.

Work on the vibrational spectra of deuterated maleic anhydride is in progress.

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