

Mean Amplitudes of Vibration and Related Quantities for Methyl Isocyanide

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Mean amplitudes of vibration for CH_3NC and CD_3NC have been calculated from spectroscopic data and a normal coordinate analysis. The linear shrinkage effects and perpendicular amplitude correction coefficients are also reported.

In a previous paper¹ we have calculated the mean amplitudes of vibrations for the molecule methyl cyanide (CH_3CN and CD_3CN), as we felt the values given by Venkateswarlu and Purushothaman² unreliable. In this paper we have extended such studies to methyl isocyanide (CH_3NC and CD_3NC) by carrying out a new normal

coordinate analysis. Once again we find that our values differ from those given by Venkateswarlu *et al.*^{2,3}

Force field. In Duncan's work⁴ a harmonic force field for methyl isocyanide is developed using centrifugal distortion constants and Coriolis coupling coefficients as additional experimental data along with the observed frequencies. In the present work we used Duncan's symmetry coordinates and force constants. The vibrational assignments used in the calculations for CH_3NC and CD_3NC were the ones reported by Williams⁵ and by Mattern and Fletcher,⁶ respectively. Calculated frequencies from Duncan's force field were in good agreement with the observed frequencies. In the present work this force field was adjusted to fit exactly the CH_3NC frequencies. Since the new force field does not deviate much from the one of Duncan,⁴ the refined force constants are not given here. This last refinement increased the deviations from observed frequencies in CD_3NC , as might be expected. In the subsequent calculations we therefore used the unrefined

Table 1. Mean amplitudes of vibration (u) and linear shrinkage effect (δ) for CH_3NC and CD_3NC , and calculated interatomic distances (R) in Å.

u or δ	R	CH_3NC		CD_3NC	
		$T=0$	298 K	$T=0$	298 K
$u(\text{C}-\text{H})$	1.094	0.0779	0.0779	0.0666	0.0666
$u(\text{C}-\text{N})$	1.427	0.0465	0.0469	0.0464	0.0468
$u(\text{N}=\text{C})$	1.167	0.0351	0.0351	0.0351	0.0351
$u(\text{C}\cdots\text{C})$	2.594	0.0508	0.0513	0.0507	0.0512
$u(\text{N}\cdots\text{H})$	2.064	0.1012	0.1015	0.0872	0.0881
$u(\text{H}\cdots\text{H})$	1.790	0.1251	0.1252	0.1054	0.1058
$u(\text{C}\cdots\text{H})$	3.129	0.1165	0.1239	0.1014	0.1108
$\delta(\text{C}\cdots\text{C})$	2.594	0.0102	0.0179	0.0098	0.0174

Table 2. Perpendicular amplitude correction coefficients (K) for CH_3NC and CD_3NC .

K	CH_3NC		CD_3NC	
	$T=0$	298 K	$T=0$	298 K
$K(\text{C}-\text{H})$	0.0116	0.0127	0.0083	0.0094
$K(\text{C}-\text{N})$	0.0036	0.0061	0.0033	0.0053
$K(\text{N}=\text{C})$	0.0069	0.0122	0.0072	0.0130
$K(\text{C}\cdots\text{C})$	0.0003	0.0004	0.0006	0.0009
$K(\text{N}\cdots\text{H})$	0.0076	0.0107	0.0054	0.0082
$K(\text{H}\cdots\text{H})$	0.0109	0.0124	0.0075	0.0090
$K(\text{C}\cdots\text{H})$	0.0023	0.0023	0.0014	0.0015

force field. Among the calculated frequencies is $\nu_1 = 2099 \text{ cm}^{-1}$ for CD_3NC . In the present calculations the structural parameters were adopted from Duncan,⁴ viz. $\text{C-H} = 1.094 \text{ \AA}$, $\text{C-N} = 1.427 \text{ \AA}$, $\text{N=C} = 1.167 \text{ \AA}$ and $\angle\text{HCH} = 109^\circ 45'$.

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*-values⁷ 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 coefficients³ 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 spectrum⁶ ($400-80 \text{ cm}^{-1}$) 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 ($250-40 \text{ cm}^{-1}$) was recorded at room temperature, using a RIIC model 520 Fourier-spectrometer and a light pipe gas cell (path length $\sim 6 \text{ m}$) described elsewhere.⁶ The spectrum of the saturated vapor ($p \sim 0.1 \text{ mmHg}$) 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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