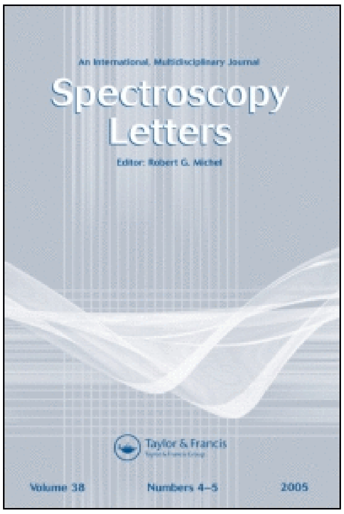

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# Harmonic Frequencies and Potential Energy Distributions of Partially Deuterated Methyl Cyanide

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# HARMONIC FREQUENCIES AND POTENTIAL ENERGY DISTRIBUTIONS OF PARTIALLY DEUTERATED METHYL CYANIDE

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## INTRODUCTION

Although the vibrational spectra and force constants of $CH_3CN$ and $CD_3CN$ have been thoroughly studied, partially deuterated methyl cyanide has received much less attention. The infrared spectrum of $CD_2HCN$ has only recently been reported[1] and that of $CH_2DCN$ has not yet appeared. Normal coordinate analysis for neither partially deuterated species has appeared. We report here harmonic frequencies and potential energy distributions for both partially deuterated methyl cyanide species, $CH_2DCN$ and $CD_2HCN$, based on force fields and structural parameters from $CH_3CN$ and $CD_3CN$. The calculated frequencies for $CD_2HCN$ are compared with the observed infrared frequencies. The vibrational interaction of the relatively high CN stretching frequency and the CD stretching frequencies is also discussed.

Force constants of methyl cyanide have been reported by a number of investigators. Pillai and Cleveland[2] determined a valence force field based on observed frequencies of $CH_3CN$. Nakagawa and Shimanouchi[3] reported a Urey-Bradley force field for methyl cyanide based on vibrational frequency and Coriolis zeta data. Duncan[4] calculated a constrained Hybrid-Orbital Force Field and normal coordinates for $CH_3CN$ and $CD_3CN$ based on more complete isotopic frequency, Coriolis zeta and centrifugal stretching data. More recently, Yamadera and Krimm[5] in a study of a number of nitriles, obtained a valence force field for methyl cyanide which gave quite good agreement with the observed frequencies of $CH_3CN$ and $CD_3CN$ although no normal coordinates or potential energy distributions based on this force field were reported.

## CALCULATIONS

$CH_3CN$ and $CD_3CN$ have $C_{3v}$ symmetry (4 $A_1$ and 4 E vibrational modes). Upon partial deuteration the symmetry is reduced to $C_s$ (8 a' and 4 a'' modes). The inverse kinetic energy (G) matrices were calculated from standard formulae[6,7] in terms of thirteen bond and bond angle internal coordinates in Figure 1. Molecular parameters used are as follows:

| | |
|---|---|
| $r_{CH} = 1.110$ Å | $M_H = 1.008$ amu |
| $r_{CC} = 1.458$ Å | $M_D = 2.014$ amu |
| $r_{CN} = 1.157$ Å | $M_C = 12.00$ amu |
| $\alpha = \beta = 109.47^o$ | $M_N = 14.00$ amu |

Symmetry coordinates for $CH_3CN$ and $CD_3CN$ ($C_{3v}$) are listed below:[8]

$A_1$ species

$$S_1 = 3^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3)$$

$$S_2 = 6^{-1/2}(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$$

$$S_3 = \Delta r_4 \qquad S_4 = \Delta r_5$$

$$S_{redundant} = 6^{-1/2}(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)$$

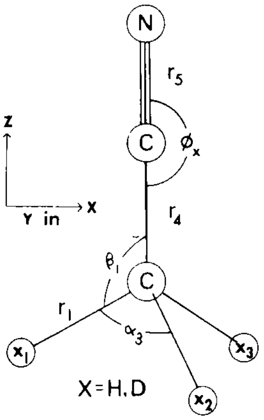

FIGURE 1 - Internal Coordinates of Methyl Cyanide. $\phi_x$ is in the $NCCX_1$ Plane. $\phi_y$ is in a Plane Perpendicular to the $NCCX_1$ Plane.

E species

$S_5 = 6^{-1/2}(2\Delta r_1 - \Delta r_2 - \Delta r_3)$ $\qquad S'_5 = 2^{-1/2}(\Delta r_2 - \Delta r_3)$

$S_6 = 6^{-1/2}(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$ $\qquad S'_6 = 2^{-1/2}(\Delta\alpha_2 - \Delta\alpha_3)$

$S_7 = 6^{-1/2}(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$ $\qquad S'_7 = 2^{-1/2}(\Delta\beta_2 - \Delta\beta_3)$

$S_8 = \Delta\phi_x$ $\qquad S'_8 = \Delta\phi_y$

For partially deuterated methyl cyanide ($C_s$), the reduced symmetry leads to a reclassification of the above coordinates. The correlation from $C_{3v}$ to $C_s$ symmetry is

$$\begin{tikzcd} A_1 \arrow[r] & a' \\ E \arrow[r] \arrow[ur] & a'' \end{tikzcd}$$

For $C_s$ symmetry $S_1$ through $S_8$ are a' and $S'_5$ through $S'_8$ are a''. The $r_1$, $\alpha_1$ and $\beta_1$ coordinates are associated with the isotopically unique hydrogen atom. To better approximate the expected normal coordinates of partially deuterated methyl cyanide, $S_1$ and $S_5$ (both a') were changed as follows: $S_1 = \Delta r_1$ , $S_5 = 2^{-1/2}(\Delta r_2 + \Delta r_3)$.

$S_1$ represents the change in the isotopically unique CH(D) bond, $r_1$; $S_5$ represents the corresponding symmetric change in the remaining symmetrically equivalent pair, $r_2$ and $r_3$. The other coordinates for the partially deuterated species are as given for $CH_3CN$ and $CD_3CN$ ($C_{3v}$).

The force field of Yamadera and Krimm[5] used in this work was reported in terms of the thirteen bond and bond angle internal (not symmetry) coordinates of Figure 1. This force field was transformed into the symmetry force field ($F_{sym} = UF\tilde{U}$) using the $C_s$ set of symmetry coordinates. The G matrices were transformed in an analogous way. The vibrational secular equation was formed from the G and F matrices for all isotopic species and solved for harmonic frequencies and potential energy distributions. The results are in Table 1. The normal coordinates (L and $L^{-1}$ matrices normalized to $L\tilde{L} = G$)were also obtained and although not reported here are available from the authors on request. The harmonic frequencies of $CH_3CN$ and $CD_3CN$ were also calculated using this same force field. The results were in each case within one wavenumber of those calculated by Yamadera and Krimm.[5]

## DISCUSSION

Although no observed frequencies have as yet been reported for $CH_2DCN$, Duncan, McKean and Michie[1] have reported observed infrared frequencies of $CD_2HCN$. These observed frequencies are included in Table 1 with those calculated in this work. For the symmetric (a') frequencies the average deviation between observed and calculated values is less than 0.5%; quite satisfactory considering that these observed frequencies were not part of the data originally used to fit the force field. The largest deviation is for the predominantly $CD_2$

TABLE 1

Calculated Harmonic Frequencies and Potential Energy Distributions for $CD_2HCN$ and $CH_2DCN$.

| a' species | ν(obs.)[a] | ν(calc.) | P.E.D. |
|---|---|---|---|
| $CD_2HCN$ | 2985 | 2992 | $S_1(99)$ |
| | 2273 | 2274 | $S_3(12)$, $S_4(84)$, $S_5(4)$ |
| | 2184 | 2160 | $S_2(1)$, $S_4(5)$, $S_5(94)$ |
| | 1282 | 1283 | $S_2(58)$, $S_3(2)$, $S_6(17)$, $S_7(22)$ |
| | 1076 | 1068 | $S_2(23)$, $S_3(14)$, $S_4(2)$, $S_6(53)$, $S_7(8)$ |
| | 936 | 941 | $S_3(27)$, $S_4(4)$, $S_6(28)$, $S_7(39)$, $S_8(2)$ |
| | 837 | 831 | $S_2(19)$, $S_3(44)$, $S_4(6)$, $S_6(1)$, $S_7(27)$, $S_8(2)$ |
| | 345 | 346 | $S_7(3)$, $S_8(96)$ |
| $CH_2DCN$ | —— | 2974 | $S_5(99)$ |
| | —— | 2273 | $S_1(6)$, $S_3(12)$, $S_4(83)$ |
| | —— | 2202 | $S_1(92)$, $S_4(6)$, $S_7(1)$ |
| | —— | 1433 | $S_2(21)$, $S_6(74)$, $S_7(5)$ |
| | —— | 1283 | $S_1(1)$, $S_2(69)$, $S_3(2)$, $S_6(24)$, $S_7(4)$ |
| | —— | 944 | $S_3(59)$, $S_4(8)$, $S_7(32)$ |
| | —— | 833 | $S_2(11)$, $S_3(27)$, $S_4(4)$, $S_7(55)$, $S_8(3)$ |
| | —— | 344 | $S_7(4)$, $S_8(96)$ |
| a'' species | | | |
| $CD_2HCN$ | 2263 | 2246 | $S'_5(98)$, $S'_6(1)$, $S'_7(1)$ |
| | ~1282 | 1277 | $S'_5(1)$, $S'_6(98)$, $S'_7(1)$ |
| | ~ 900[b] | 831 | $S'_5(1)$, $S'_6(1)$, $S'_7(93)$, $S'_8(5)$ |
| | ~ 345 | 338 | $S'_7(5)$, $S'_8(94)$ |
| $CH_2DCN$ | —— | 3009 | $S'_5(100)$ |
| | —— | 1279 | $S'_6(73)$, $S'_7(27)$ |
| | —— | 1006 | $S'_6(27)$, $S'_7(70)$, $S'_8(3)$ |
| | —— | 354 | $S'_6(1)$, $S'_7(2)$, $S'_8(97)$ |

[a] Reference 1

[b] Not observed; estimated from Q branch perturbations in 936 (a') mode.

stretching mode; the observed mode 24 cm$^{-1}$ higher than that calculated in this work. As has been discussed in detail by McKean[9] CH(D) stretching modes are often complicated by Fermi resonance with the first overtone of methyl deformation modes, and this may be responsible for the deviation in this case.

The observed antisymmetric (a'') frequencies were not as precisely determined as the symmetric (a') frequencies. Three of the (a'') frequencies were reported as approximate; one of these estimated from Q branch perturbations present in the 936 cm$^{-1}$ (a') mode. This uncertainty in the observed (a'') frequencies may be responsible for the deviations between observed and calculated values.

As has been previously noted[10] the predominantly CN stretching frequency in $CH_3CN$ is slightly increased upon complete deuteration, contrary to what might be expected upon substitution of more massive deuterium atoms. This is due to vibrational mixing and normal coordinate changes between the predominantly CN and CD stretching modes. This small frequency increase was also noted in this work upon partial deuteration; most of the increase occuring at the initial deuterium substitution. For the series $CH_3CN$, $CH_2DCN$, $CD_2HCN$ and $CD_3CN$ the predominantly CN stretching frequency is calculated at 2269, 2273, 2274 and 2274 cm$^{-1}$ respectively. To discern the vibrational mode changes occuring upon stepwise deuteration, calculations were also made on the hypothetical molecules, $CH_2XCN$, CHDXCN and $CD_2XCN$ for $M_x$ = 1.0 to 2.0 amu at intervals of 0.2 amu. The calculated frequencies of the four highest modes ($\nu_1$, $\nu_2$, $\nu_3$, $\nu_4$), irrespective of symmetry, are in Table 2. These four modes are the predominantly CH(D) and CN stretching frequencies. In Figure 2 these four frequencies are plotted vs $M_x$. In Figure 3 the

TABLE 2

Calculated Harmonic Frequencies $\nu_1$, $\nu_2$, $\nu_3$, $\nu_4$ (Four Highest Irrespective of Symmetry) for $CH_2XCN$, CHDXCN and $CD_2XCN$.

| | $M_x$(amu) | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ |
|---|---|---|---|---|---|
| $CH_2XCN$ | 1.2 | 3009(a'') | 2976(a') | 2759(a') | 2268(a') |
| | 1.4 | 3009 | 2974 | 2578 | 2268 |
| | 1.6 | 3009 | 2974 | 2433 | 2267 |
| | 1.8 | 3009 | 2974 | 2318 | 2263 |
| CHDXCN[a] | 1.2 | 2993(A) | 2763(A) | 2273(A) | 2201(A) |
| | 1.4 | 2992 | 2583 | 2273 | 2199 |
| | 1.6 | 2992 | 2439 | 2273 | 2195 |
| | 1.8 | 2992 | 2327 | 2272 | 2188 |
| $CD_2XCN$ | 1.2 | 2766(a') | 2274(a') | 2246(a'') | 2159(a') |
| | 1.4 | 2584 | 2274 | 2245 | 2156 |
| | 1.6 | 2442 | 2274 | 2245 | 2152 |
| | 1.8 | 2331 | 2273 | 2245 | 2143 |

[a] CHDXCN ($M_x \neq$ H,D) belongs to the $C_1$ point group (no symmetry). Thus all modes are of the same symmetry (A).

contribution of the CN symmetry coordinate ($S_4$) to the potential energy distribution is plotted vs $M_x$. Since significant P.E.D. shifts occur in the neighborhood of $M_x$ = 1.0(H) and 2.0(D), calculations were made at 0.04 amu intervals from $M_x$ = 1.0 to 1.2 and 1.8 to 2.0 amu and these were incorporated in Figures 2 and 3 although not tabulated in Table 2. As can be seen in Figure 3 the predominantly CN stretching frequency undergoes a systematic shift from $\nu_4$ to $\nu_1$ upon the gradual deuteration represented by the abscissa, $M_x$. In Figure 2 for $CH_2XCN$, as an example, as $M_x$ increases in the neighborhood of $M_x$ = 1.9 amu, $\nu_4$ is losing CN stretching and gaining CX stretching character; $\nu_3$ is shifting character

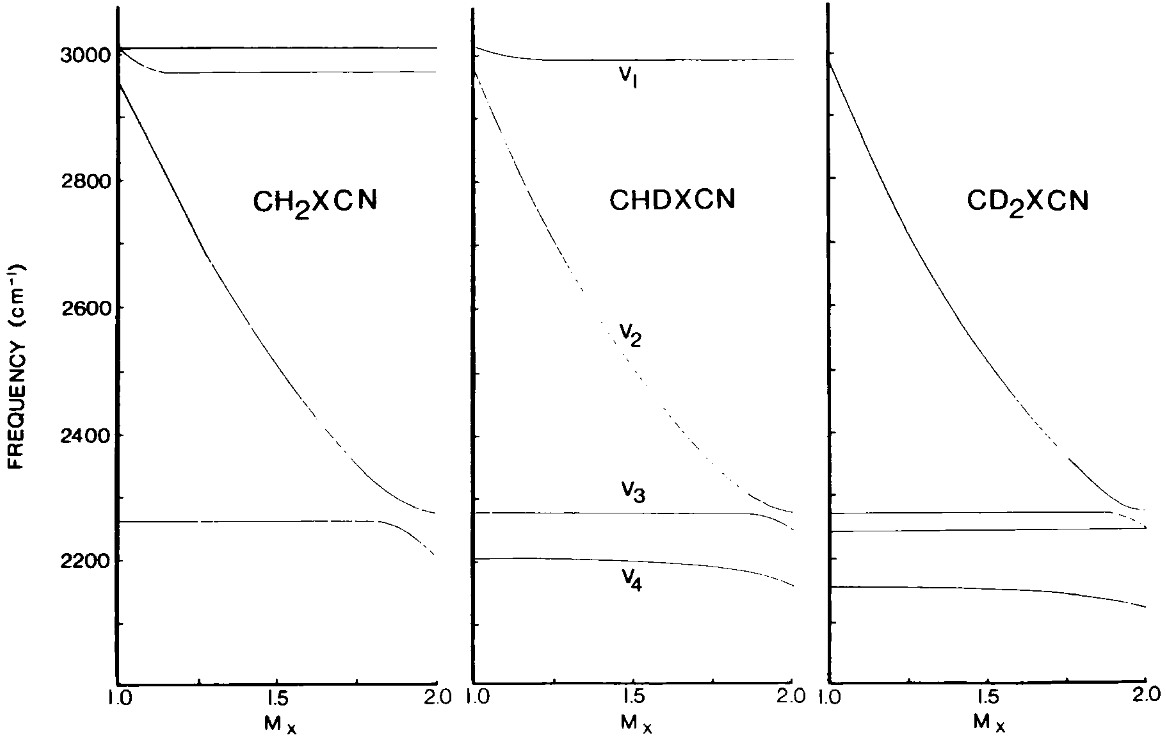

FIGURE 2

The Four Highest Frequencies, Irrespective of Symmetry, of $CH_2XCN$, CHDXCN and $CD_2XCN$ vs the Mass of X ($M_x$) in amu.

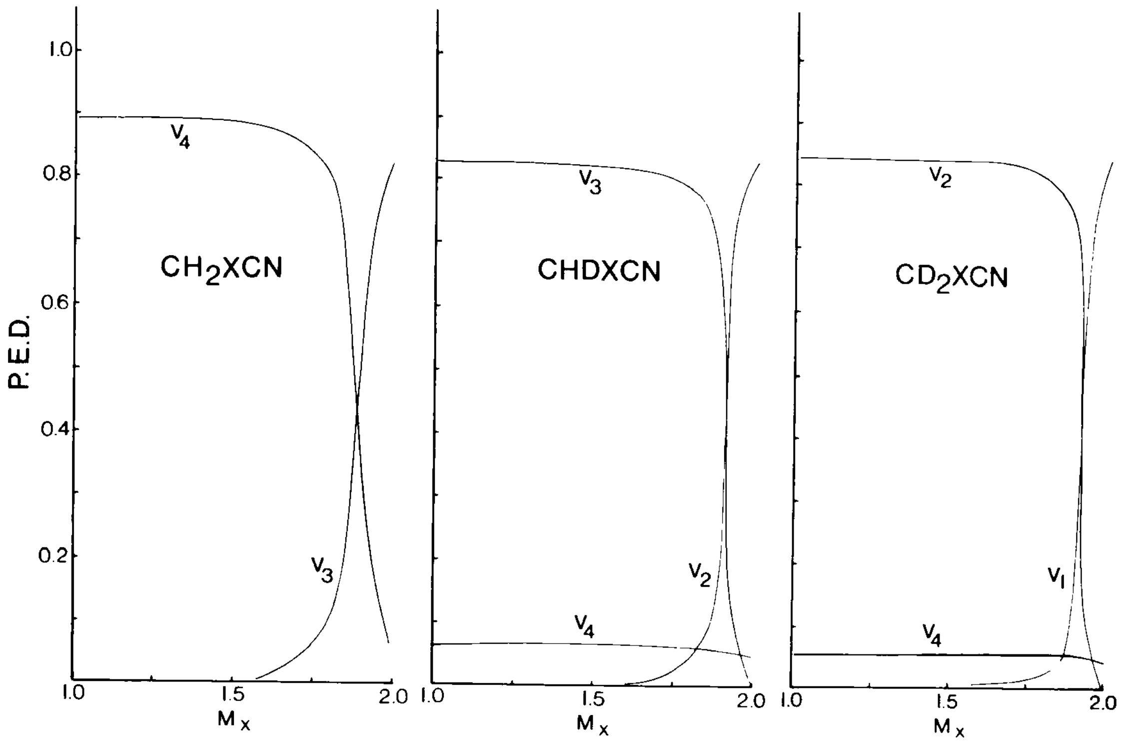

FIGURE 3

The Contribution of the CN Symmetry Coordinate ($S_4$) to the Potential Energy Distribution (P.E.D.) for the Four Highest Frequencies of $CH_2XCN$, CHDXCN and $CD_2XCN$ vs the Mass of X ($M_x$) in amu.

in a reverse fashion. An analogous shift occurs around $M_x$ = 1.9 amu for CHDXCN and $CD_2XCN$.

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