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# HARMONIC FORCE FIELDS AND MEAN AMPLITUDES OF VIBRATION FOR SOME MOLECULES CONTAINING NITROGEN: METHANAL AZINE

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## ABSTRACT

A harmonic force field was developed for methanal azine. The force constants were used to calculate mean amplitudes of vibration, perpendicular amplitude correction coefficients and Coriolis coupling coefficients.

## INTRODUCTION

Methanal azine, $H_2CN_2CH_2$, is the simplest acyclic azine. Spectroscopic studies[1] of the vapour and solid gave conclusive evidence for the s-transoid centrosymmetric planar structure, which belongs to the symmetry point group $C_{2h}$. The cited work[1] deals with infrared spectra in the vapour and solid states and Raman shifts in the solid. A complete assignment of the vibrational wavenumbers for $(CH_2)_2N_2$ was proposed. Spectra of several deuterated compounds were also recorded.

In the present work a harmonic force field is developed on the basis of the $C_{2h}$ structure for methanal azine. The proposed assignment[1] is tested in relation to reasonable force constants. The final set of force constants is used to calculate various molecular properties: Coriolis coupling coefficients[2], mean amplitudes of vibration[3], and perpendicular amplitude correction coefficients[3].

## MOLECULAR MODEL

Figure 1 shows the s-transoid centrosymmetric planar structure of symmetry $C_{2h}$ adopted for the methanal azine molecule. The applied structural parameters

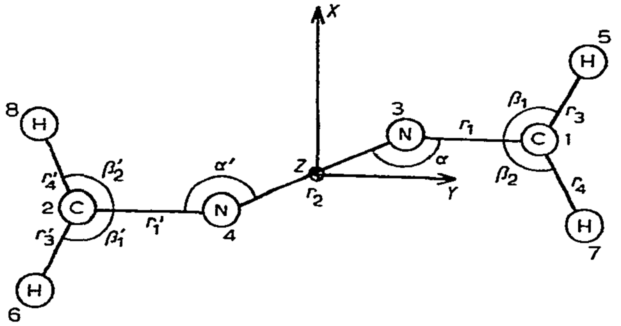

Fig. 1. Molecular model for methanal azine; symmetry $C_{2h}$. The in-plane valence coordinates are indicated. The applied out-of-plane valence coordinates are: (i) $CH_2$ out-of-plane bendings $\gamma$ and $\gamma'$ for the atoms 7-5-1-3 and 8-6-2-4, respectively, (ii) CN torsions $\tau_1$ and $\tau_1'$ involving the atoms 5-1-3-4 and 6-2-4-3, respectively, and (iii) the NN torsion $\tau_2$ for 1-3-4-2. The capital letters $R_1$, $R_2$, $R_3$ and $R_4$ are used to designate the appropriate equilibrium distances of C=N, N–N, C–H (1–5 or 2–6) and C–H (1–7 or 2–8), respectively.

are $R_1(C{=}N) = 127$ pm, $R_2(N{-}N) = 141$ pm, $R_3 = R_4(C{-}H) = 109.2$ pm, $\angle CNN = 109°$, $\angle HCH = 132°$.

## SYMMETRY COORDINATES

Figure 1 along with its legend defines a suitable set of valence coordinates or the molecular vibrations of the model considered. The normal modes of vibration are distributed among the different symmetry species of the $C_{2h}$ point group according to

$$\Gamma = 7A_g + 3A_u + 2B_g + 6B_u$$

A complete set of independent symmetry coordinates was constructed from the valence coordinates as given below:

*Species $A_g$*

$$S_1 = 2^{-\frac{1}{2}}(r_1 + r_1'),\quad S_2 = r_2,\quad S_3 = 2^{-\frac{1}{2}}(r_3 + r_3'),\quad S_4 = 2^{-\frac{1}{2}}(r_4 + r_4'),$$
$$S_5 = (R_1R_2/2)^{\frac{1}{2}}(\alpha + \alpha'),\ S_6 = (R_1R_3/2)^{\frac{1}{2}}(\beta_1 + \beta_1'),\ S_7 = (R_1R_4/2)^{\frac{1}{2}}(\beta_2 + \beta_2').$$

*Species $A_u$*

$$S_1 = [R_1(R_3R_4)^{\frac{1}{2}}/2]^{\frac{1}{2}}(\gamma + \gamma'),\quad S_2 = (R_2R_3)^{\frac{1}{2}}(\tau_1 + \tau_1'),\quad S_3 = R_1\tau_2.$$

*Species $B_g$*

$$S_1 = [R_1(R_3R_4)^{\frac{1}{2}}/2]^{\frac{1}{2}}(\gamma - \gamma'),\quad S_2 = (R_2R_3)^{\frac{1}{2}}(\tau_1 - \tau_1').$$

*Species $B_u$*

$$S_1 = 2^{-\frac{1}{2}}(r_1 - r_1'),\quad S_2 = 2^{-\frac{1}{2}}(r_3 - r_3'),\quad S_3 = 2^{-\frac{1}{2}}(r_4 - r_4'),$$
$$S_4 = (R_1R_2/2)^{\frac{1}{2}}(\alpha - \alpha'),\quad S_5 = (R_1R_3/2)^{\frac{1}{2}}(\beta_1 - \beta_1'),$$
$$S_6 = (R_1R_4/2)^{\frac{1}{2}}(\beta_2 - \beta_2').$$

TABLE 1

SYMMETRY FORCE CONSTANTS ($hNm^{-1}$) FOR METHANAL AZINE

Species $A_g$

| | | | | | | |
|---|---|---|---|---|---|---|
| 8.570 | | | | | | |
| 0.836 | 3.573 | | | | | |
| −0.041 | 0.023 | 4.976 | | | | |
| −0.032 | −0.007 | 0.040 | 4.976 | | | |
| 0.378 | 0.214 | −0.002 | 0.007 | 1.222 | | |
| 0.053 | 0.017 | −0.008 | 0.014 | −0.003 | 0.716 | |
| 0.254 | 0.051 | 0.013 | −0.003 | 0.007 | 0.286 | 0.744 |

Species $A_u$

| | | |
|---|---|---|
| 0.119 | | |
| −0.014 | 0.122 | |
| 0.001 | −0.001 | 0.0285 |

Species $B_g$

| | |
|---|---|
| 0.110 | |
| 0.004 | 0.0853 |

Species $B_u$

| | | | | | |
|---|---|---|---|---|---|
| 9.623 | | | | | |
| −0.036 | 4.932 | | | | |
| −0.036 | 0.029 | 4.932 | | | |
| 0.000 | −0.003 | 0.003 | 0.734 | | |
| 0.226 | 0.001 | 0.006 | 0.000 | 0.763 | |
| 0.226 | 0.006 | 0.001 | 0.000 | 0.264 | 0.763 |

TABLE 2

POTENTIAL ENERGY DISTRIBUTION TERMS* FOR $C_2H_4N_2$ (wavenumbers in $cm^{-1}$)

Species $A_g$

| | |
|---|---|
| 3092 | $50r_4+50r_3$ |
| 2958 | $49r_3+49r_4$ |
| 1615 | $55r_1+24\beta_1$ |
| 1413 | $45\beta_2+22\alpha+20r_1$ |
| 1198 | $55\beta_1+29r_2+24r_1+21\beta_2$ |
| 851 | $44r_2+40\beta_2+36\beta_1$ |
| 605 | $48\alpha+29r_2$ |

Species $A_u$

| | |
|---|---|
| 1019.5 | $88\gamma+23\tau_1$ |
| 380 | $78\tau_1$ |
| 115 | $99\tau_2$ |

Species $B_g$

| | |
|---|---|
| 1016 | $81\gamma$ |
| 366 | $84\tau_1$ |

Species $B_u$

| | |
|---|---|
| 3078 | $50r_3+50r_4$ |
| 2943 | $49r_3+49r_4$ |
| 1637 | $68r_1$ |
| 1397.3 | $32r_1+22\beta_1+22\beta_2$ |
| 1166.1 | $73\beta_1+73\beta_2$ |
| 380 | $95\alpha$ |

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* Terms below 20 are omitted.

## HARMONIC FORCE FIELD

A harmonic force field for methanal azine was produced from an initial approximate valence force field through several steps of iteration. It seems not to be of interest to report any details of these calculations here. The final force field in terms of the symmetry force constants is given in Table 1. The force constants were adjusted so as to reproduce exactly the vibrational wavenumbers for $C_2H_4N_2$ shown in Table 2. These values are observed vapour wavenumbers[1] along with experimental data for the solid state corrected with estimated gas–solid frequency shifts. The present calculations confirm the vibrational assignment proposed in the cited work[1] except for a detail in species $A_u$. The proposed assignment[1] contains the solid-phase wavenumber $\nu_9 = 679\ \mathrm{cm}^{-1}$, which is estimated to correspond to about 665 $\mathrm{cm}^{-1}$ in the vapour phase. All our attempts failed to get a value with this order of magnitude within reasonable ranges of force constants. It should be born in mind that the previous assignment[1] is rather tentative, and it was explicitly pointed out that the assignment of the wavenumbers $\nu_7$, $\nu_9$, $\nu_{10}$, $\nu_{11}$ and $\nu_{12}$ was particularly difficult. The value for $\nu_9$ is among the most uncertain ones. Hence the discrepancy described with our calculations should not be surprising. In the final set of vibrational wavenumbers we have taken $\nu_9 = 380\ \mathrm{cm}^{-1}$. This value is used twice (as $\nu_9$ and $\nu_{18}$).

Perhaps the most interesting features of the force field for the molecule in question are the N–N and C=N stretching force constants. From our final force field one obtains $f(\mathrm{N{-}N}) = 3.573\ \mathrm{hNm}^{-1}$ and $f(\mathrm{C{=}N}) = 9.096\ \mathrm{hNm}^{-1}$.

Table 2 shows the potential energy distribution[4,5] defined in terms of usual symbols by

$$X_{ik} = 100\ F_{ii}L_{ik}^{2}/\lambda_k.$$

## ISOTOPIC WAVENUMBERS

Table 3 shows the calculated vibrational wavenumbers for $C_2D_4N_2$ along with the experimental data[1]. The solid-phase wavenumbers were tentatively corrected for vapour-solid wavenumber shifts as in the case of $C_2H_4N_2$. It is found to be a generally satisfactory agreement between the calculated and experimental values considering the tentative nature of the assignment proposed previously[1]. In particular it is noticed that the questionable value of $\nu_6 = 814\ \mathrm{cm}^{-1}$ is not confirmed by the present calculations. We must also question the assignment of 640 $\mathrm{cm}^{-1}$ (649 $\mathrm{cm}^{-1}$ in the solid phase) to $\nu_9$ on the same grounds as it was done for the $C_2H_4N_2$ compound.

The vibrational wavenumbers were also calculated for the three isotopic molecules $C_2H_2D_2N_2$. The results are collected in Table 4. In view of the uncertainties in the assignments discussed above one cannot expect these values to reproduce quantitatively the vibrational wavenumbers of the partially deuterated

TABLE 3

VIBRATIONAL WAVENUMBERS (cm$^{-1}$) FOR PERDEUTEROMETHANAL AZINE, $C_2D_4N_2$

| *Species* | *No.* | *Calc.* | *Expt.*[a] | *Species* | *No.* | *Calc.* | *Expt.*[a] |
|---|---|---|---|---|---|---|---|
| $A_g$ | 1 | 2338 | 2309 | $B_g$ | 11 | 793 | 795 |
| | 2 | 2151 | 2189 | | 12 | 297 | — |
| | 3 | 1522 | 1560 | | | | |
| | 4 | 1178 | 1205 | $B_u$ | 13 | 2322 | 2310 |
| | 5 | 1029 | 1052 | | 14 | 2147 | 2182 |
| | 6 | 687 | (814?) | | 15 | 1552 | 1580 |
| | 7 | 556 | — | | 16 | 1047 | 1036 |
| $A_u$ | 8 | 800 | 816 | | 17 | 930 | 962 |
| | 9 | 274 | (640?) | | 18 | 327 | — |
| | 10 | 105 | — | | | | |

[a] Wavenumbers from vapour spectra and those from the solid corrected with estimated vapour–solid frequency shifts.

TABLE 4

CALCULATED VIBRATIONAL WAVENUMBERS (cm$^{-1}$) FOR PARTIALLY DEUTERATED METHANAL AZINE, $C_2H_2D_2N_2$

| | $H_2CN_2CD_2$ ($C_s$) | $HDCN_2CHD$ ($C_s$) | $HDCN_2CDH$ ($C_{2h}$) |
|---|---|---|---|
| in-plane | 3085 | 3026 | 3033 ($A_g$) |
| | 2951 | 3024 | 3018 ($B_u$) |
| | 2330 | 2235 | 2235 ($A_g$) |
| | 2149 | 2231 | 2228 ($B_u$) |
| | 1627 | 1588 | 1588 ($B_u$) |
| | 1538 | 1560 | 1556 ($A_g$) |
| | 1402 | 1346 | 1367 ($A_g$) |
| | 1209 | 1282 | 1311 ($B_u$) |
| | 1065 | 1127 | 1079 ($A_g$) |
| | 1026 | 972 | 970 ($B_u$) |
| | 745 | 742 | 742 ($A_g$) |
| | 583 | 581 | 593 ($A_g$) |
| | 351 | 350 | 351 ($B_u$) |
| out-of-plane | 1018 | 951 | 887 ($A_u$) |
| | 797 | 884 | 880 ($B_g$) |
| | 372 | 325 | 327 ($B_g$) |
| | 287 | 317 | 319 ($A_u$) |
| | 110 | 110 | 113 ($A_u$) |

molecules in question. They do not give a sufficiently firm basis for definite assignments of the observed wavenumbers[1] to the different isotopic species. Nevertheless, the present calculations are believed to give a fairly good qualitative picture of the isotopic shifts.

In particular the present calculations reproduce correctly the trends of isotopic shifts for $C_2H_4N_2$, $C_2H_2D_2N_2$ and $C_2D_4N_2$ for the three bands discussed in the experimental work[1]. (i) The bands of wavenumbers from 3235 through 3170 to 3140 $cm^{-1}$ are assigned to $\nu_3+\nu_{15}$ in $C_2H_4N_2$, $C_2H_2D_2N_2$ and $C_2D_4N_2$, respectively[1], and not to CH stretching modes as previously[6]. This revised assignment is confirmed by the present calculations, from which the corresponding values are 3252, (3165, 3148, 3144) and 3074 $cm^{-1}$, where the figures in parentheses pertain to $H_2CN_2CD_2$ ($C_s$), HDCN$_2$CHD ($C_s$) and HDCN$_2$CDH ($C_{2h}$), respectively; cf. Table 4. (ii) For the C=N stretching $B_g$ mode ($\nu_{15}$) the experimental values from 1637 through 1608 to 1581 $cm^{-1}$ are reported[1]. The present calculations give 1637, (1627, 1588, 1588) and 1552 $cm^{-1}$. (iii) Finally the $\nu_8+\nu_{11}$ combination band is reported to be 2033, 1853 and 1615 $cm^{-1}$ for the three isotopic species in question[1]. From the present calculations one obtains 2035.5, (1815, 1835, 1767) and 1593 $cm^{-1}$, respectively. In none of the three cases (i)–(iii) is the agreement quantitative enough to allow decisive conclusions about assignments to the three different $C_2H_2D_2N_2$ molecules.

## MEAN AMPLITUDES OF VIBRATION AND PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS

The force field developed was used to calculate the mean amplitudes of vibration ($u$ values)[3] and perpendicular amplitude correction coefficients ($K$ values)[3]. These quantities are of great interest in modern gas electron diffraction[7]. The results for all the types of bonded and nonbonded interatomic distances at the temperatures absolute zero and 298 K are given in Table 5 ($C_2H_4N_2$) and Table 6 ($C_2D_4N_2$). In Table 5 the calculated interatomic separations (in pm) are included in parentheses and are supposed to be helpful for identifications of the different distance types.

## CORIOLIS COUPLING COEFFICIENTS

The methanal azine molecule possesses several kinds of Coriolis coupling. Table 7 shows the calculated $\zeta$ values of the $A_g \times B_g$ and $A_u \times B_u$ types, respectively. In both cases there are nonvanishing Coriolis coefficients with respect to the two in-plane Cartesian axes. The X and Y axes of Fig. 1 were rotated into $b$ and $a$ so as to coincide with the principal axes with respect to the moments of inertia. We have chosen as usual $I_b > I_a$.

TABLE 5

MEAN AMPLITUDES OF VIBRATION (*u*) AND PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS (*K*) FOR METHANAL AZINE; pm UNITS

| *Distance* | *(Equil.)* | *u(0K)* | *u(298)* | *K(0)* | *K(298)* |
|---|---|---|---|---|---|
| $C_1{-}H_5$ | (109.2) | 7.76 | 7.76 | 1.91 | 2.21 |
| $C_1{-}H_7$ | (109.2) | 7.76 | 7.76 | 2.30 | 3.31 |
| $C{=}N$ | (127.0) | 4.11 | 4.12 | 0.54 | 1.53 |
| $N{-}N$ | (141.0) | 5.04 | 5.14 | 0.14 | 0.17 |
| $C\cdots N$ | (218.3) | 5.85 | 6.28 | 0.28 | 0.84 |
| $C\cdots C$ | (328.2) | 5.73 | 5.97 | 0.02 | 0.02 |
| $N_3\cdots H_5$ | (198.3) | 9.97 | 10.00 | 1.39 | 2.33 |
| $N_3\cdots H_7$ | (198.3) | 9.86 | 9.89 | 1.56 | 3.54 |
| $N_4\cdots H_5$ | (318.7) | 9.63 | 9.81 | 0.75 | 1.28 |
| $N_4\cdots H_7$ | (219.9) | 13.25 | 13.83 | 1.45 | 3.28 |
| $C_2\cdots H_5$ | (415.8) | 10.56 | 10.82 | 0.43 | 0.51 |
| $C_2\cdots H_7$ | (346.0) | 13.11 | 13.61 | 0.53 | 0.83 |
| $H_5\cdots H_7$ | (199.5) | 11.67 | 11.68 | 2.78 | 3.85 |
| $H_5\cdots H_8$ | (411.0) | 17.19 | 18.09 | 0.89 | 1.22 |
| $H_5\cdots H_6$ | (511.8) | 13.02 | 13.14 | 0.64 | 0.75 |
| $H_7\cdots H_8$ | (394.3) | 16.10 | 16.34 | 0.76 | 0.95 |

TABLE 6

MEAN AMPLITUDES OF VIBRATION (*u*) AND PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS (*K*) FOR PERDEUTEROMETHANAL AZINE; pm UNITS

| *Distance* | *u(0K)* | *u(298)* | *K(0)* | *K(298)* |
|---|---|---|---|---|
| $C_1{-}D_5$ | 6.64 | 6.64 | 1.31 | 1.68 |
| $C_1{-}D_7$ | 6.64 | 6.64 | 1.56 | 2.66 |
| $C{=}N$ | 4.11 | 4.11 | 0.54 | 1.58 |
| $N{-}N$ | 5.03 | 5.13 | 0.21 | 0.29 |
| $C\cdots N$ | 5.79 | 6.26 | 0.28 | 0.87 |
| $C\cdots C$ | 5.68 | 5.95 | 0.04 | 0.04 |
| $N_3\cdots D_5$ | 8.59 | 8.68 | 1.05 | 2.08 |
| $N_3\cdots D_7$ | 8.47 | 8.56 | 1.14 | 3.20 |
| $N_4\cdots D_5$ | 8.48 | 8.71 | 0.53 | 1.09 |
| $N_4\cdots D_7$ | 11.44 | 12.37 | 1.09 | 3.02 |
| $C_2\cdots D_5$ | 9.24 | 9.63 | 0.27 | 0.37 |
| $C_2\cdots D_7$ | 11.32 | 12.14 | 0.34 | 0.66 |
| $D_5\cdots D_7$ | 9.83 | 9.85 | 1.79 | 2.98 |
| $D_5\cdots D_8$ | 14.64 | 16.06 | 0.59 | 1.01 |
| $D_5\cdots D_6$ | 11.11 | 11.33 | 0.36 | 0.45 |
| $D_7\cdots D_8$ | 13.64 | 14.17 | 0.38 | 0.50 |

TABLE 7

CORIOLIS COUPLING COEFFICIENTS OF TYPES $A_g \times B_g$ AND $A_u \times B_u$ FOR METHANAL AZINE

| $A_g \times B_g$ | | | $A_u \times B_u$ | | |
|---|---|---|---|---|---|
| | $\zeta^a(i,j)$ | $\zeta^b(i,j)$ | | $\zeta^a(i,j)$ | $\zeta^b(i,j)$ |
| (1, 11) | 0.781 | −0.491 | (8, 13) | −0.777 | 0.489 |
| (2, 11) | −0.112 | −0.464 | (9, 13) | 0.265 | 0.252 |
| (3, 11) | 0.412 | 0.574 | (10, 13) | 0.153 | −0.019 |
| (4, 11) | −0.185 | −0.453 | (8, 14) | 0.114 | 0.464 |
| (5, 11) | −0.300 | −0.078 | (9, 14) | −0.785 | 0.365 |
| (6, 11) | −0.286 | 0.046 | (10, 14) | −0.140 | 0.044 |
| (7, 11) | 0.035 | 0.033 | (8, 15) | −0.385 | −0.589 |
| (1, 12) | −0.239 | −0.210 | (9, 15) | −0.211 | 0.345 |
| (2, 12) | 0.666 | −0.297 | (10, 15) | −0.333 | −0.480 |
| (3, 12) | 0.048 | −0.378 | (8, 16) | 0.291 | 0.438 |
| (4, 12) | −0.413 | 0.158 | (9, 16) | 0.280 | −0.091 |
| (5, 12) | −0.001 | −0.681 | (10, 16) | −0.345 | −0.720 |
| (6, 12) | −0.563 | −0.351 | (8, 17) | 0.382 | −0.077 |
| (7, 12) | 0.098 | 0.335 | (9, 17) | 0.289 | 0.768 |
| | | | (10, 17) | 0.411 | −0.073 |
| | | | (8, 18) | −0.067 | −0.032 |
| | | | (9, 18) | −0.326 | −0.294 |
| | | | (10, 18) | 0.747 | −0.494 |

One Coriolis coupling coefficient was observed[1] for $C_2H_4N_2$, viz. $|\zeta^a(8,17)| = 0.49 \pm 0.05$. The calculated value of $0.38_2$ falls outside the reported limits of experimental error, but it does have the right order of magnitude. When taking into account the general sensitivity of Coriolis coupling coefficients with changes in force constants we feel that the agreement between the theory and experiment is satisfactory in the present case.

## NOTE

In this paper the modern SI units are applied. (1 pm $= 10^{-2}$ Å, 1 hNm$^{-1}$ = 1 mdyne Å$^{-1}$ = $10^5$ dyne cm$^{-1}$.)

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