



ANALYSIS OF THE THREE LOWEST FREQUENCY VIBRATION-ROTATION BANDS OF DIAZOMETHANE

L. NEMES¹, J. VOGT² and M. WINNEWISSER³

¹Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, Budaörsi út 45, Pf. 132, H-1502 Budapest, Hungary

²Abteilung für Strukturdocumentation, Universität Ulm, Pf. 4066, D-7900 Ulm, Federal Republic of Germany

³Physikalisch-Chemisches Institut, Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-6300 Gießen, Federal Republic of Germany

ABSTRACT

The infrared Fourier-transform spectrum of gaseous H_2CNN (diazomethane) has been analysed between 800 and 250 wavenumber, at a spectral resolution 0.07 wavenumber. A preliminary analysis of the coarse and fine rotational structure of the three vibrational-rotational bands: ν_5 , ν_6 and ν_9 is reported. Using r_e structure rotational constant values, the vibration-rotation constants for the vibrational ground state are obtained as $\alpha(A)=+4018$ MHz, $\alpha(B)=-34.78$ MHz and $\alpha(C)=-15.23$ MHz. A preliminary estimate for the Coriolis zeta coefficient (a-type) is $|\zeta(5,9)|=0.91$ and $|\zeta(6,9)|=0.13$.

EXPERIMENTAL

Gaseous diazomethane was prepared by Pechmann's method (ref. 1) using N-nitroso-methyl-urea as precursor. Samples of the gas were studied at pressures 3-10 Torr (0.4-1.3 kPa) in an infrared gas cell of length 10 cm. FTIR spectra were taken on a Digilab FTS 20 B interferometer at the Justus-Liebig-University of Gießen, West Germany. Calibration of the far-infrared spectra (below 550 cm^{-1}) was achieved by water vapour line wavenumbers.

INTRODUCTION

Diazomethane belongs to the slightly asymmetric planar top category. Its point group symmetry C_{2v} leads to five non-totally symmetric vibrational fundamentals: ν_5 , ν_6 (b_1 modes), and ν_7 , ν_8 and ν_9 (b_2 modes)[§]. Its molecular geometry was quite early derived from microwave studies (ref. 2). Several works have been published about the analysis of the infrared spectrum (refs. 3-6), and the harmonic

[§]The numbering of vibrational modes applied here differs from that used in older references, and follows Mulliken's recommendations (ref. 10).

force-field has also been calculated (refs. 7-9). Because of the lack of modern high-resolution studies of the low-lying infrared bands, the problem of vibration-rotation interactions in this molecule is still wanting a final solution.

The present work is the direct continuation of Moore and Pimentel's early analysis, the only advance achieved here is due to the higher resolution and better quality of the Fourier-transform spectra, and to the availability of high-precision ground state rotational constants for the normal isotopomer (ref. 1). Some qualitative aspects of the predominant Coriolis interactions in this molecule shall also be mentioned.

ANALYSIS OF THE ROTATIONAL STRUCTURE

Tables 1, 2 and 3 contain the present assignments for the sub-band Q-heads of the modes ν_5 , ν_6 and ν_9 . In the tables uncertain assignments are indicated by question marks, whereas values obtained by ground state combination differences are denoted by "gscd".

TABLE 1

Q-heads for the ν_5 band (in cm^{-1})

| K''_a | R-branch | P-branch |
|---------|-------------|-------------|
| 0 | band centre | - |
| 1 | asym.broad. | band centre |
| 2 | 623.07 | ? |
| 3 | 650.44 | 527.95? |
| 4 | 679.19 | 518.41 gscd |
| 5 | 708.85 | 511.06 gscd |
| 6 | 739.17 | 505.30 |
| 7 | 769.78 | |

TABLE 2

Q-heads for the ν_6 band (in cm^{-1})

| K''_a | R-branch | P-branch |
|---------|-------------|-------------|
| 0 | band centre | - |
| 1 | asym.broad. | band centre |
| 2 | 439.6 gscd | 382.18 |
| 3 | 447.71? | 358.72 |
| 4 | 454? | 334.94 |
| 5 | - | 310.58? |

TABLE 3
Q-heads for the ν_9 band (in cm^{-1})

| K''_a | R-branch | P-branch |
|---------|-------------|-------------|
| 0 | band centre | - |
| 1 | asym.broad. | band centre |
| 2 | 455.53 | ? |
| 3 | 470.01 | 371.38 |
| 4 | 444.51 | 350.92 |
| 5 | 498.63 | 330.76 |
| 6 | - | 310.58 |
| 7 | - | 290.25 |
| 8 | - | 269.66 |
| 9 | - | 248.80? |

The analysis of these Q-branch heads leads to the following constants (in cm^{-1} units):

$$\nu_5: \quad \nu_0 = 568.19(1.93); \quad (A' - \bar{B}') = 10.352(125); \\ (A' - A'') - (\bar{B}' - \bar{B}'') = 1.234(76); \quad D'_K = 8.76(2.32) \times 10^{-3}$$

$$\nu_6: \quad \nu_0 = 408.87(88); \quad (A' - \bar{B}') = 7.119(142); \\ (A' - A'') - (\bar{B}' - \bar{B}'') = -1.359(79); \quad D'_K = -0.0105(6)$$

$$\nu_9: \quad \nu_0 = 415.79(47); \quad (A' - \bar{B}') = 8.133(25); \\ (A' - A'') - (\bar{B}' - \bar{B}'') = -0.373(25); \quad D'_K = -5.35(1.93) \times 10^{-3}$$

In addition some well-resolved series of J-lines have been used to obtain estimates of K-sub-band origins and excited state $\bar{B} = (1/2)(B+C)$ constants. For ν_5 four sub-bands were followed: rR_3 , rR_4 , rR_5 and rR_7 . For ν_6 only one sub-band was analysed: pP_3 , while for ν_9 three sub-bands: rR_3 , rR_5 and pP_5 . The results are contained in Table 4.

The constants in Table 4 were determined by fitting the J-line positions to a rigid symmetric rotor polynomial in running number m:

$$\nu^{P,r} = \nu_0^K + (\bar{B}' + \bar{B}'')m + (\bar{B}' - \bar{B}'')m^2 \quad (1)$$

where ν_0^K stands for the K-th sub-band origin, and $m=J+1$ for the R-branch, while $-J$ for the P-branch. The \bar{B}'' value is 0.3694 cm^{-1} from (ref. 1).

New estimates for the vibration-rotation interaction constant α^B may be derived from the data in Table 4 and from a recent 'ab initio' equilibrium geometry calculation (ref. 11). The r_e geometrical data, computed from a CEPA-1 basis set of 110 contract-

ed GTO's are: $r_e(\text{C-N}) = 130.15$ pm, $r_e(\text{N-N}) = 114.12$ pm, $r_e(\text{C-H}) = 107.34$ pm and $\alpha_e(\text{HCH}) = 124.84^\circ$. Equilibrium rotational constants as calculated from the above geometry are: $A_e = 276977.44$ MHz, $B_e = 11270.65$ MHz and $C_e = 10829.99$ MHz. Upon combining these with the ground state (zero-point average) rotational constants, one has $\alpha^A = -4018$ MHz, $\alpha^B = -34.78$ MHz and $\alpha^C = -15.23$ MHz, thus $\alpha(\text{B+C}) = -50.01$ MHz and $\alpha(\text{B-C}) = -19.55$ MHz.

TABLE 4

Sub-band constants for ν_5 , ν_6 and ν_9 (in cm^{-1})

| Vibrational state/sub-band | | | | |
|----------------------------|--------------|--------------|--------------|--------------|
| $\nu_5 = 1$ | | | | |
| Const. | r_{R_3} | r_{R_4} | r_{R_5} | r_{R_7} |
| $\nu_{\bar{0}K}$ | 650.381(3) | 679.121(3) | 708.796(3) | 769.723(3) |
| \bar{B}' | 0.369575(12) | 0.369575(21) | 0.369507(33) | 0.369485(33) |
| $\nu_6 = 1$ | | | | |
| Const. | P_{P_3} | | | |
| $\nu_{\bar{0}K}$ | 358.701(6) | | | |
| \bar{B}' | 0.369458(51) | | | |
| $\nu_9 = 1$ | | | | |
| Const. | r_{R_3} | r_{R_5} | P_{P_5} | |
| $\nu_{\bar{0}K}$ | 470.102(3) | 498.756(3) | 330.705(2) | |
| \bar{B}' | 0.369288(2) | 0.369080(32) | 0.369620(18) | |

From Tables 2-4 the \bar{B}' value averaged over the different sub-bands is listed below for the three vibrationally excited states: ν_5 : 0.36954(5) cm^{-1} , ν_6 : 0.369458(51) cm^{-1} and ν_9 : 0.36933(27) cm^{-1} . These are all very close to the ground state \bar{B} value, so the corresponding α 's are very small indeed, a few MHz only. The early spectroscopic data of Sheridan show a somewhat different picture (see: Table 1 in (ref. 2)), there $\alpha(\text{B+C})$ is 56.99(50) MHz, 22.28(50) MHz and -25.32(50) MHz for the lowest three vibrational states. This is in contrast to the present data. A higher resolution infrared study shall probably resolve this contradiction

CORIOLIS INTERACTIONS IN DIAZOMETHANE

Moore and Pimentel have dealt with in several papers (refs. 3, 4 and 7) the subject of vibration-rotation interactions in the infrared spectrum of this molecule. Some estimates of the a-axis Coriolis zeta coefficients are reported in those papers. However the resolution of these early studies was very low to allow higher accuracy and even qualitative certainty in the reported values. The resolution of the spectra involved in the present work is also less than sufficient to reveal such details in the J-structure that would be needed for a more dependable determination of the interaction constants. Some qualitative conclusions are still possible.

First of all it is obvious that as the separation of ν_6 and ν_9 (interacting through a-axis rotation) is only about 7 cm^{-1} , any non-zero coupling term - such as a K-dependent Coriolis term - in the effective rotation-vibration Hamiltonian should lead to a strong mixing of the vibrational wavefunctions for ν_6 and ν_9 . A vibrational state would then emerge - even for low K rotational quantum numbers - that cannot any more be described as an in-plane or out-of-plane mode. Rotational transitions should appear that would not be allowed in the unperturbed case.

Some approximate eigenvector calculations for the perturbation Hamiltonian matrix support indeed this conclusion. The eigenvector elements represent the extent of mixing of the vibrational basis functions, and their K-dependence shows that even for the smallest K values the states $|\nu_6=1\rangle$ and $|\nu_9=1\rangle$ are heavily mixed. Therefore no clean distinction can be made between B-type and C-type infrared bands. Such an a-axis Coriolis interaction can be easily modelled on a computer. A qualitative computer simulation of the unresolved region of the spectrum where both band centres are found shows that the values $|\tau_{59}^a| = 0.91$ and $|\tau_{69}^a| = 0.13$ yield a rough fit to the observed infrared spectra.

There are also interesting aspects in the relative intensities of the three modes ν_5 , ν_6 and ν_9 , especially when compared to the analogous case of the ketene (H_2CCO) molecule (ref. 12). Whereas ν_5 and ν_6 are both strong and of almost equal intensity in the ketene spectrum, in diazomethane ν_5 is definitely weaker than ν_6 . Also while the B-type (or unperturbed B-type) ν_9 is hardly observable in ketene, in diazomethane it is easily seen.

Work is under way to calculate the harmonic force-field of diazomethane by empirical and quantum-chemical methods. The know-

ledge of the form of the normal coordinates should help in the determination of Coriolis zeta constants and the mixing coefficients for the internal symmetry coordinates. The latter are important in intensity calculations.

ACKNOWLEDGEMENTS

One of the authors (L.N.) would like to express his gratitude to the Alexander von Humboldt-Stiftung, Bonn-Bad Godesberg, West Germany for a three-month Dozentenstipendium in 1982 enabling him to initiate the experimental part of this study. The work was carried out at the Molecular Spectroscopy Laboratory of the Physical Chemistry Institute, Justus-Liebig-University of Gießen. The final FTIR spectra were produced by Drs. Jürgen Vogt and Manfred Birk, who is also responsible for the dangerous chemical preparation of stable gaseous diazomethane.

Professor Manfred Winnewisser's hospitality during this Dozentenstipendium is thankfully acknowledged.

REFERENCES

- 1 E. Schafer and M. Winnewisser, *J. Mol. Spectr.*, 97 (1983) 154-164.
- 2 J. Sheridan, *Advances in Molecular Spectroscopy, Proceedings of the IVth International Meeting on Molecular Spectroscopy*, Vol. 1, Pergamon Press, Oxford, 1962.
- 3 C.B. Moore, *J. Chem. Phys.*, 39 (1963) 1884-1889.
- 4 C.B. Moore and G.C. Pimentel, *J. Chem. Phys.*, 40 (1964) 329-341.
- 5 J. Vogt and M. Winnewisser, *Z. Naturforsch.*, 38A (1983) 1138-1145.
- 6 J. Vogt, M. Winnewisser, K. Yamada and G. Winnewisser, *Chem. Phys.*, 83 (1984) 309-318.
- 7 C.B. Moore and G.C. Pimentel, *J. Chem. Phys.*, 40 (1964) 1529-1534, *ibid* 40 (1964) 342-355.
- 8 W.H. Fletcher and W.T. Thompson, *J. Mol. Spectr.*, 25 (1968) 240-268.
- 9 D.C. McKean and J.L. Duncan, *Spectrochim. Acta* 27A (1971) 1879-1891.
- 10 R.S. Mulliken, *J. Chem. Phys.*, 23 (1955) 1997-2011.
- 11 Professor Peter Botschwina: personal communication of unpublished work.
- 12 L. Nemes, *J. Mol. Spectr.*, 72 (1978) 102-123.