Rovibrational Analysis of the v3 Band of Diazomethane, H2CNN

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The v3 fundamental of diazomethane, which essentially corresponds to a symmetric methylene deformation has been reinvestigated at a resolution of 0.07 cm⁻¹. The J- and K₃-structures of this A-type band have been resolved and analysed for the first time. The rovibrational assignment is given and, using Watson’s S-reduced Hamiltonian, the rotational and quartic centrifugal distortion constants could be determined for the first excited vibrational state of the symmetric methylene deformation.

I. Introduction

Diazomethane is one of a group of isomers of which the structures are given in Figure 1. The most stable isomer of this group is cyanamide, which has been detected in interstellar space [1, 2] and which is regarded as a precursor in prebiotic chemistry [3]. For this reason it is desirable to obtain high resolution spectroscopic data of as many of these isomers as possible in order to investigate their possible role in cosmochemistry. In recent work carried out in our laboratory we have studied the millimeter wave spectra of isocyanamide [4, 5] and diazirine [6]. Moreover we have investigated the infrared spectra of diazirine [7, 8]. For isocyanamide [9] and diazirine [10] millimeter wave spectroscopic studies of isotopically enriched samples are also in progress.

Although diazomethane is widely used in preparative and analytical chemistry, little is known about the spectroscopical properties of this extremely explosive compound. There are numerous infrared investigations at low or medium resolution, which were made about twenty years ago [11–17]. The first high resolution spectrum [18] was observed in the microwave region. The rotational spectrum has been investigated further in the millimeter wave region in our laboratory [19]. In this context we have started again the infrared spectroscopical study of this compound. For the first time we have been able to resolve and analyse the rotational structure, including both the J and the K₃-structure, in two of the fundamental bands. In this paper we report the rovibrational analysis of the v3 fundamental band which essentially corresponds to the symmetric methylene deformation (see Table 1). In a following paper we shall report the analysis of the v2 band [20].

II. Experimental Procedure

The chemical preparation has been described elsewhere [19]. In handling the H₂CNN sample we avoided the transition from the liquid to the solid phase, with the result that no explosions took place. In order to condition the 10 cm glass cell it was filled several times with a few mbar of diazomethane. The resulting polyethylene film on the glass walls and the KBr-windows prevented rapid
decomposition of diazomethane. The mid infrared spectrum of diazomethane at 13 mbar was recorded with a Digilab Fourier transform spectrometer FTS 20B, which was purged with dry nitrogen. A MCT detector, cooled with liquid nitrogen, was used to detect the interferograms. In order to obtain a good signal to noise ratio at 0.07 cm\(^{-1}\) resolution 400 interferograms were coadded and Fourier transformed. The resulting spectrum has been calibrated with DBr lines recorded under the same conditions [21].

III. Analysis

A survey spectrum of \(v_3\), which is an A-type band, is shown in Figure 2. Diazomethane is a near prolate asymmetric top (\(\kappa = -0.996\)). On the right hand side of Fig. 2 the P-branch shows a characteristic pattern, whereas the R-branch on the left hand side is more compressed and does not exhibit such regular structure. The starting point for the analysis was the assignment of the Q-branches, which are well separated due to a large change in the rotational constant \(A\). Figure 3 shows the band center region with the Q-branches and the beginnings of the P- and R-branches. Due to the \(C_{2v}\) symmetry of the molecule the Q-branches show intensity alternation. We were finally able to assign rovibrational transitions in the P- and R-branches up to \(J = 45\) and \(K_a = 7\). For this slightly asymmetric top only the asymmetry splitting of the \(K_a = 1\) lines could be

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**Table 1. Fundamental vibrations of diazomethane (notation slightly modified according to the recommendation given in [23]).**

<table>
<thead>
<tr>
<th>Mode</th>
<th>Approximate description</th>
<th>Symmetry species</th>
<th>(\nu_0/cm^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1)</td>
<td>symmetric CH(_2) stretch</td>
<td>(A_1)</td>
<td>3077.1</td>
<td>[13]</td>
</tr>
<tr>
<td>(v_2)</td>
<td>NN stretch</td>
<td>(A_1)</td>
<td>2101.577</td>
<td>[20]</td>
</tr>
<tr>
<td>(v_3)</td>
<td>symmetric CH(_2) deformation</td>
<td>(A_1)</td>
<td>1413.330</td>
<td>this work</td>
</tr>
<tr>
<td>(v_4)</td>
<td>CN stretch</td>
<td>(A_1)</td>
<td>1170</td>
<td>[17]</td>
</tr>
<tr>
<td>(v_5)</td>
<td>CNN bending out of plane</td>
<td>(B_1)</td>
<td>564.0</td>
<td>[17]</td>
</tr>
<tr>
<td>(v_6)</td>
<td>CH(_2) deformation out of plane</td>
<td>(B_1)</td>
<td>406.0</td>
<td>[17]</td>
</tr>
<tr>
<td>(v_7)</td>
<td>antisymmetric CH(_2) stretch</td>
<td>(B_2)</td>
<td>3184.5</td>
<td>[17]</td>
</tr>
<tr>
<td>(v_8)</td>
<td>asymmetric CH(_2) deformation</td>
<td>(B_2)</td>
<td>1109.0</td>
<td>[17]</td>
</tr>
<tr>
<td>(v_9)</td>
<td>CNN bending in plane</td>
<td>(B_2)</td>
<td>421.2</td>
<td>[17]</td>
</tr>
</tbody>
</table>

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Fig. 2. Survey spectrum of the rovibrational A-type \(v_3\) band in diazomethane.
resolved. In Fig. 3 the assignment is indicated below the spectrum for low $J$ values.

For the numerical analysis of the rovibrational transitions effective Hamiltonians were fitted for the ground and excited states. The effective Hamiltonians are

\[
\begin{align*}
  v_3 = 0: & \quad \hat{H}_{\text{eff}} = \hat{H}_{\text{rot}} (v_3 = 0), \\
  v_3 = 1: & \quad \hat{H}_{\text{eff}} = \hat{H}_{\text{vib}} + \hat{H}_{\text{rot}} (v_3 = 1),
\end{align*}
\]

where $\hat{H}_{\text{rot}}$ is Watson’s S-reduced Hamiltonian. This Hamiltonian [22] normally contains only rotational and quartic and sextic centrifugal distortion constants. In order to fit pure rotational transitions arising from high $K_a$-rotational levels in the ground state, it is necessary to introduce several higher order distortion constants. The rotational Hamiltonians thus have the following form:

\[
\begin{align*}
  \hat{H}_{\text{rot}} = & \left( B + C \right) \hat{P}_z^2 + \left( A - \frac{1}{2} \left( B + C \right) \right) \hat{P}_z^2 \\
  & - D_J \hat{P}_z^4 - D_{JK} \hat{P}_z^2 \hat{P}_z^2 - D_K \hat{P}_z^4 \\
  & + \left( \frac{1}{4} \left( B - C \right) + d_1 \hat{P}_z^2 \right) \left( \hat{P}_z^2 + \hat{P}_z^2 \right) \\
  & + d_2 \left( \hat{P}_z^2 + \hat{P}_z^2 \right) + H_{JK} \hat{P}_z^4 \hat{P}_z^2 + H_{KJ} \hat{P}_z^2 \hat{P}_z^4 \\
  & - L_{KJ} \hat{P}_z^2 \hat{P}_z^2 + S_{JK} \hat{P}_z^4 \hat{P}_z^2 + S_{KJ} \hat{P}_z^2 \hat{P}_z^2 \\
  & - T_{KJ} \hat{P}_z^2 \hat{P}_z^10 + U_{KJ} \hat{P}_z^2 \hat{P}_z^{12},
\end{align*}
\]

where $\hat{P}$, $\hat{P}_x$, $\hat{P}_y$, and $\hat{P}_z$ are the operators for the total angular momentum and its components, respectively. The ladder operators are given by $\hat{P}_z = \hat{P}_z \pm i \hat{P}_y$. The coefficients $A$, $B$ and $C$ are Watson’s reduced rotational constants in the $I^r$ axis representation. $D_J$, $D_{JK}$, $D_K$, $d_1$ and $d_2$ are quartic distortion constants whereas $H_{JK}$ and $H_{KJ}$ are the only sextic centrifugal distortion constants found necessary. The remaining constants are higher order distortion constants.

Since the millimeter wave measurements [19] are much more precise than the present infrared measurements the rotational and centrifugal distortion constants of the ground vibrational state were taken from the analysis of those measurements and held fixed during the least squares analysis. The rotational and quartic centrifugal distortion constants have been determined for the excited state from the 321 rovibrational transitions which are listed in Table 2. Due to the limited resolution many blended lines could be assigned to several rovibrational transitions. Consequently, these transitions have been weighted in such a way that the total weight of each line position is unity in the fit. The standard deviation $\sigma$ of the fit was 0.011 cm$^{-1}$ which is about one sixth of the resolution at which the
Table 2. Observed rovibrational transitions (wavenumbers/cm\(^{-1}\)) and assignment for the \(v_3\) fundamental of diazomethane.

<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>((0,0))</td>
<td>221</td>
<td>231</td>
<td>241</td>
<td>251</td>
<td>261</td>
<td>271</td>
<td>281</td>
<td>291</td>
</tr>
<tr>
<td>((1,1))</td>
<td>311</td>
<td>321</td>
<td>331</td>
<td>341</td>
<td>351</td>
<td>361</td>
<td>371</td>
<td>381</td>
</tr>
<tr>
<td>((2,2))</td>
<td>401</td>
<td>411</td>
<td>421</td>
<td>431</td>
<td>441</td>
<td>451</td>
<td>461</td>
<td>471</td>
</tr>
<tr>
<td>((3,3))</td>
<td>501</td>
<td>511</td>
<td>521</td>
<td>531</td>
<td>541</td>
<td>551</td>
<td>561</td>
<td>571</td>
</tr>
</tbody>
</table>

**P-branch:** \(K'_{3}=1^p\)

1. 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 |
2. 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
3. 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 |

**P-branch:** \(K'_{3}=1^p\)

1. 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
2. 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 |
3. 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 |

**P-branch:** \(K'_{3}=0\)

1. 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 |
2. 100 | 101 | 102 | 103 | 104 | 105 | 106 | 107 | 108 |
3. 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 |

**P-branch:** \(K'_{3}=3\)

1. 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 |
2. 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
3. 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 |

**R-branch:** \(K'_{3}=1^p\)

1. 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 |
2. 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 |
3. 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 |

**R-branch:** \(K'_{3}=0\)

1. 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 |
2. 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 |
3. 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 |

**R-branch:** \(K'_{3}=3\)

1. 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 |
2. 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 |
3. 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 |

**R-branch:** \(K'_{3}=1^p\)

1. 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 |
2. 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 |
3. 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 |

Fig. 4. Comparison of the simulated with the observed spectrum at the band center region of the $v_3$ band of diazo-
methane. The computed spectrum was obtained from the molecular constants given in Table 3.
Fig. 5. Simulation of the P-branch region of the \( v_3 \) band of diazomethane. The computed spectrum was obtained from the molecular constants given in Table 3.

Fig. 6. Simulation of the R-branch region of the \( v_3 \) band of diazomethane. The computed spectrum was obtained from the molecular constants given in Table 3.
Table 3. Rotational and centrifugal distortion constants in Watson's S-reduced Hamiltonian for the fundamental ν3 in diazomethane\(^a\).b. | ground state\(^c\) | \(v_3 = 1\)\(^d\) |
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>(A/\text{MHz})</td>
<td>272 979.1 (81)</td>
</tr>
<tr>
<td>(B/\text{MHz})</td>
<td>11 305.42697 (45)</td>
</tr>
<tr>
<td>(C/\text{MHz})</td>
<td>10 845.22028 (47)</td>
</tr>
<tr>
<td>(D_J/\text{kHz})</td>
<td>4.14620 (74)</td>
</tr>
<tr>
<td>(D_K/\text{kHz})</td>
<td>396.817 (92)</td>
</tr>
<tr>
<td>(D_JK/\text{kHz})</td>
<td>22 000(^e)</td>
</tr>
<tr>
<td>(d_1/\text{kHz})</td>
<td>-0.19255 (43)(^f)</td>
</tr>
<tr>
<td>(d_2/\text{kHz})</td>
<td>-0.05727 (39)</td>
</tr>
<tr>
<td>(HJK/\text{Hz})</td>
<td>2.081 (42)</td>
</tr>
<tr>
<td>(LJK/\text{Hz})</td>
<td>-492.4 (83)</td>
</tr>
<tr>
<td>(S_{JK}/\text{mHz})</td>
<td>1.26 (30)</td>
</tr>
<tr>
<td>(S'_{JK}/\text{mHz})</td>
<td>0.2085 (56)</td>
</tr>
<tr>
<td>(T_{JK}/\text{mHz})</td>
<td>-34.1 (49)</td>
</tr>
<tr>
<td>(U_{JK}/\text{mHz})</td>
<td>-0.257 (38)</td>
</tr>
<tr>
<td>(\nu_0/\text{cm}^{-1})</td>
<td>-0.00162 (11)</td>
</tr>
<tr>
<td>(\nu_0/\text{cm}^{-1})</td>
<td>-0.00162 (11)</td>
</tr>
</tbody>
</table>

\(a\) ground state constants held fixed.
\(b\) in parentheses standard deviations in units of the last significant figures.
\(c\) taken from [19],
\(d\) present work.
\(e\) from perpendicular bands.
\(f\) corrected value.

The spectrum was recorded. The resulting rotational and centrifugal distortion constants are listed and compared with the ground state constants in Table 3.

In order to confirm the assignment the adjusted molecular parameters given in Table 3 were used in calculating the transition wavenumbers and relative intensities, thus providing the basis for a simulation of the observed spectrum. Figure 4 shows the band center region with the beginning of the P- and R-branches, the lower trace being the observed spectrum and the upper trace the simulated spectrum. Considering the fact that no hot bands have been assigned the theoretical spectrum simulates the observed one very well. In Fig. 5 the characteristic pattern of the P-branch is well reproduced, whereas in the R-branch (Fig. 6) the main features of the observed spectrum are in reasonably good agreement with the prediction. The rovibrational assignment of this band has thus been demonstrated.

IV. Conclusions

From the rovibrational analysis of the A-type \(\nu_3\) band of diazomethane the rotational and quartic centrifugal distortion constants were determined for the first excited vibrational state of the symmetric methylene deformation. Comparing these molecular parameters with those of the ground vibrational state in Table 3 we see that the rotational constant \(A\) and the distortion constant \(D_K\) are significantly increased upon excitation of this vibration, whereas the rotational constants \(B\) and \(C\) are only slightly modified. Furthermore the distortion constants \(D_J\) and \(D_{JK}\) are increased. In a previous study [14], in which only the \(J\)-structure of this fundamental could be resolved, only the effective rotational constant \((B + C)/2\) and the band center \(\nu_0\) could be obtained. In our work the value for the band center has been refined from 1414.3 cm\(^{-1}\) [14] to 1413.330 cm\(^{-1}\) due to better resolution and a correct rovibrational assignment.

Acknowledgements

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