Rovibrational Analysis of the ν_3 Band of Diazomethane, H_2CNN

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The ν_3 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 K_a-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 K_a-structure, in two of the fundamental bands. In this paper we report the rovibrational analysis of the ν_3 fundamental band which essentially corresponds to the symmetric methylene deformation (see Table 1). In a following paper we shall report the analysis of the ν_2 band [20].

II. Experimental Procedure

The chemical preparation has been described elsewhere [19]. In handling the H_2CNN 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

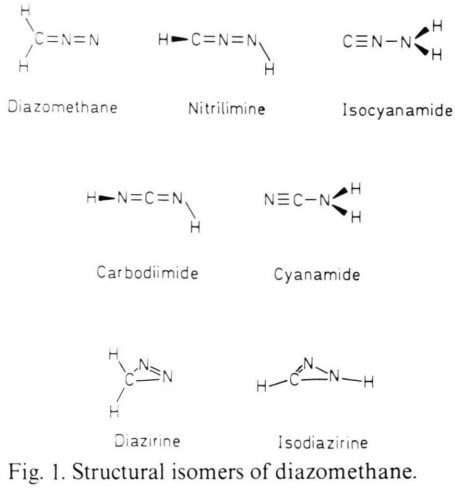

Fig. 1. Structural isomers of diazomethane.

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

Mode	Approximate description	Symmetry species	$\tilde{\nu}_0/\mathrm{cm}^{-1}$	Reference
ν_1	symmetric CH_2 stretch	A_1	3077.1	[13]
ν_2	NN stretch	A_1	2101.577	[20]
ν_3	symmetric CH_2 deformation	A_1	1413.330	this work
ν_4	CN stretch	A_1	1170	[17]
ν_5	CNN bending out of plane	B_1	564.0	[17]
ν_6	CH_2 deformation out of plane	B_1	406.0	[17]
ν_7	antisymmetric CH_2 stretch	B_2	3184.5	[17]
ν_8	asymmetric CH_2 deformation	B_2	1109.0	[17]
ν_9	CNN bending in plane	B_2	421.2	[17]

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 ν_3, which is an A-type band, is shown in Figure 2. Diazomethane is a near prolate asymmetric top ($\varkappa = -0.996$). 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

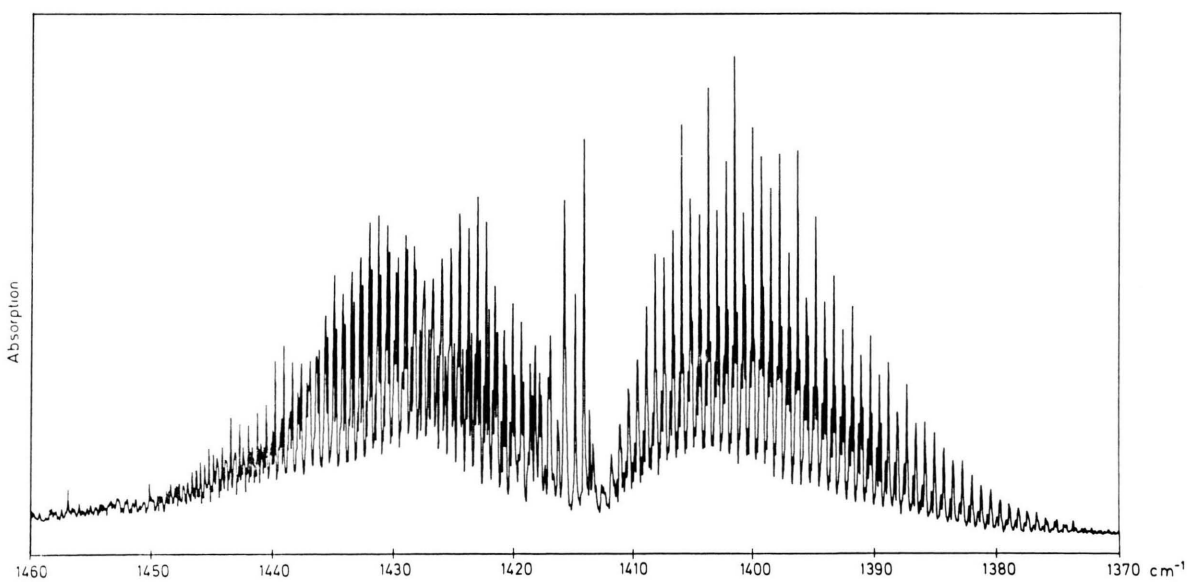

Fig. 2. Survey spectrum of the rovibrational A-type ν_3 band in diazomethane.

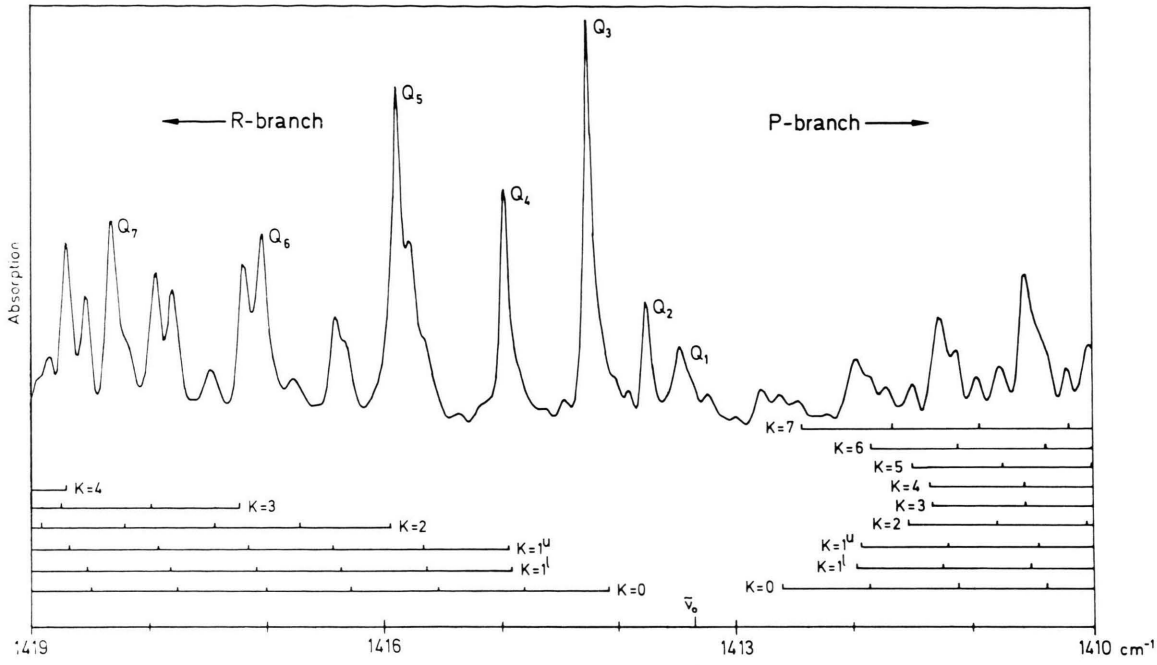

Fig. 3. Band center region of the ν_3 fundamental of diazomethane with the assignment of the K_a subbands ($K = K_a$).

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

$$\nu_3 = 0: \quad \hat{H}_{\text{eff}} = \hat{H}_{\text{rot}}(\nu_3 = 0)\,,$$

$$\nu_3 = 1: \quad \hat{H}_{\text{eff}} = E_{\text{vib}} + \hat{H}_{\text{rot}}(\nu_3 = 1)\,,$$

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:

$$\begin{aligned}\hat{H}_{\text{rot}} = {} & \tfrac{1}{2}(B+C)\,\hat{P}^2 + (A - \tfrac{1}{2}(B+C))\,\hat{P}_z^2 \\ & - D_J \hat{P}^4 - D_{JK} \hat{P}^2 \hat{P}_z^2 - D_K \hat{P}_z^4 \\ & + (\tfrac{1}{4}(B-C) + d_1 \hat{P}^2)(\hat{P}_+^2 + \hat{P}_-^2) \\ & + d_2(\hat{P}_+^4 + \hat{P}_-^4) + H_{JK} \hat{P}^4 \hat{P}_z^2 + H_{KJ} \hat{P}^2 \hat{P}_z^4 \\ & - L_{KJ} \hat{P}^2 \hat{P}_z^6 + S_{JK} \hat{P}^4 \hat{P}_z^6 + S_{KJ} \hat{P}^2 \hat{P}_z^8 \\ & - T_{KJ} \hat{P}^2 \hat{P}_z^{10} + U_{KJ} \hat{P}^2 \hat{P}_z^{12}\,,\end{aligned}$$

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 $\hat{P}_\pm = \hat{P}_x \pm i\hat{P}_y$. 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 σ 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 ν_3 fundamental of diazomethane.

J'(K_a',K_c')-J"(K_a'',K_c'')	OBS.	OBS-CALC
P-branch: K_a=1[1]		
2(1, 2)- 3(1, 3)	1411.2450	0.0056
5(1, 5)- 6(1, 6)	1409.0500	0.0148
8(1, 8)- 9(1, 9)	1406.8280	0.0049
9(1, 9)-10(1,10)	1406.0980	0.0140
10(1,10)-11(1,11)	1405.3650	0.0209
11(1,11)-12(1,12)	1404.6020	-0.0013
12(1,12)-13(1,13)	1403.8670	0.0053
13(1,13)-14(1,14)	1403.1330	0.0137
14(1,14)-15(1,15)	1402.3680	-0.0081
15(1,15)-16(1,16)	1401.6370	0.0050
16(1,16)-17(1,17)	1400.8970	0.0099
17(1,17)-18(1,18)	1400.1340	-0.0074
18(1,18)-19(1,19)	1399.4030	0.0081
19(1,19)-20(1,20)	1398.6330	-0.0146
20(1,20)-21(1,21)	1397.8990	-0.0004
21(1,21)-22(1,22)	1397.1340	-0.0165
22(1,22)-23(1,23)	1396.3950	-0.0058
23(1,23)-24(1,24)	1395.6530	0.0027
24(1,24)-25(1,25)	1394.8910	-0.0081
25(1,25)-26(1,26)	1394.1540	0.0070
26(1,26)-27(1,27)	1393.3850	-0.0092
27(1,27)-28(1,28)	1392.6470	0.0064
28(1,28)-29(1,29)	1391.8780	-0.0083
29(1,29)-30(1,30)	1391.1400	0.0088
30(1,30)-31(1,31)	1390.3710	-0.0043
31(1,31)-32(1,32)	1389.6300	0.0113
32(1,32)-33(1,33)	1388.8550	-0.0063
33(1,33)-34(1,34)	1388.1060	0.0027
34(1,34)-35(1,35)	1387.3490	0.0046
35(1,35)-36(1,36)	1386.5790	-0.0059
36(1,36)-37(1,37)	1385.8360	0.0113
37(1,37)-38(1,38)	1385.0640	0.0003
38(1,38)-39(1,39)	1384.3020	-0.0001
39(1,39)-40(1,40)	1383.5440	0.0042
40(1,40)-41(1,41)	1382.7870	0.0102
41(1,41)-42(1,42)	1382.0090	-0.0042
43(1,43)-44(1,44)	1380.5010	0.0171
44(1,44)-45(1,45)	1379.7240	0.0056
P-branch: K_a=1[U]		
1(1, 0)- 2(1, 1)	1411.9410	-0.0015
8(1, 7)- 9(1, 8)	1406.7080	-0.0054
9(1, 8)-10(1, 9)	1405.9770	0.0109
10(1, 9)-11(1,10)	1405.2050	-0.0137
11(1,10)-12(1,11)	1404.4720	0.0008
12(1,11)-13(1,12)	1403.7100	-0.0136
13(1,12)-14(1,13)	1402.9690	-0.0070
14(1,13)-15(1,14)	1402.2410	0.0128
15(1,14)-16(1,15)	1401.4690	-0.0114
16(1,15)-17(1,16)	1400.7380	0.0055
17(1,16)-18(1,17)	1400.0030	0.0185
18(1,17)-19(1,18)	1399.2330	-0.0034
19(1,18)-20(1,19)	1398.5050	0.0168
20(1,19)-21(1,20)	1397.7330	-0.0069
21(1,20)-22(1,21)	1397.0000	0.0085
22(1,21)-23(1,22)	1396.2340	-0.0089
23(1,22)-24(1,23)	1395.4930	-0.0012
24(1,23)-25(1,24)	1394.7550	0.0097
25(1,24)-26(1,25)	1393.9900	-0.0063
26(1,25)-27(1,26)	1393.2600	0.0129
27(1,26)-28(1,27)	1392.4850	-0.0127
28(1,27)-29(1,28)	1391.7550	0.0069
29(1,28)-30(1,29)	1390.9810	-0.0173
30(1,29)-31(1,30)	1390.2480	-0.0003
P-branch: K_a=3		
8(3, 5)- 9(3, 6)	1407.5920	-0.0157
10(3, 7)-11(3, 8)	1406.0980	-0.0226
11(3, 8)-12(3, 9)	1405.3650	-0.0113
13(3,10)-14(3,11)	1403.8670	-0.0192
14(3,11)-15(3,12)	1403.1330	-0.0074
16(3,13)-17(3,14)	1401.6370	-0.0102
17(3,14)-18(3,15)	1400.8970	-0.0029
18(3,15)-19(3,16)	1400.1340	-0.0181
19(3,16)-20(3,17)	1399.4030	-0.0008
20(3,17)-21(3,18)	1398.6330	-0.0220
21(3,18)-22(3,19)	1397.8990	-0.0067
22(3,19)-23(3,20)	1397.1340	-0.0219
23(3,20)-24(3,21)	1396.3950	-0.0106
24(3,21)-25(3,22)	1395.6530	-0.0019
25(3,22)-26(3,23)	1394.8910	-0.0126
26(3,23)-27(3,24)	1394.1540	0.0021
27(3,24)-28(3,25)	1393.3850	-0.0147
28(3,25)-29(3,26)	1392.6470	-0.0001
29(3,26)-30(3,27)	1391.8780	-0.0159
30(3,27)-31(3,28)	1391.1400	-0.0003
31(3,28)-32(3,29)	1390.3710	-0.0152
32(3,29)-33(3,30)	1389.6300	-0.0017
33(3,30)-34(3,31)	1388.8550	-0.0217
34(3,31)-35(3,32)	1388.1060	-0.0152
35(3,32)-36(3,33)	1387.3490	-0.0163
37(3,34)-38(3,35)	1385.8360	-0.0160
43(3,40)-44(3,41)	1381.2820	-0.0196
P-branch: K_a=5		
5(5, 0)- 6(5, 1)	1411.4750	-0.0105
6(5, 1)- 7(5, 2)	1410.7400	-0.0043
7(5, 2)- 8(5, 3)	1410.0070	0.0045
8(5, 3)- 9(5, 4)	1409.2660	0.0057
9(5, 4)-10(5, 5)	1408.5120	-0.0056
10(5, 5)-11(5, 6)	1407.7820	0.0076
11(5, 6)-12(5, 7)	1407.0370	0.0063
12(5, 7)-13(5, 8)	1406.2850	-0.0016
13(5, 8)-14(5, 9)	1405.5460	0.0041
14(5, 9)-15(5,10)	1404.7880	-0.0087
15(5,10)-16(5,11)	1404.0500	-0.0011
16(5,11)-17(5,12)	1403.3060	0.0010
17(5,12)-18(5,13)	1402.5590	0.0006
18(5,13)-19(5,14)	1401.8200	0.0087
19(5,14)-20(5,15)	1401.0660	0.0023
20(5,15)-21(5,16)	1400.3100	-0.0057
21(5,16)-22(5,17)	1399.5660	-0.0011
22(5,17)-23(5,18)	1398.8080	-0.0101
23(5,18)-24(5,19)	1398.0640	-0.0046
24(5,19)-25(5,20)	1397.3080	-0.0107
25(5,20)-26(5,21)	1396.5650	-0.0032
26(5,21)-27(5,22)	1395.8080	-0.0093
27(5,22)-28(5,23)	1395.0690	0.0031
28(5,23)-29(5,24)	1394.3300	0.0160
29(5,24)-30(5,25)	1393.5710	0.0094
30(5,25)-31(5,26)	1392.8290	0.0202
31(5,26)-32(5,27)	1392.0700	0.0146
33(5,28)-34(5,29)	1390.5650	0.0177
37(5,32)-38(5,33)	1387.5450	0.0197
P-branch: K_a=7		
9(7, 2)-10(7, 3)	1410.9330	0.0048
10(7, 3)-11(7, 4)	1410.1910	0.0047
11(7, 4)-12(7, 5)	1409.4560	0.0120
12(7, 5)-13(7, 6)	1408.6910	-0.0102
13(7, 6)-14(7, 7)	1407.9560	-0.0020
14(7, 7)-15(7, 8)	1407.2290	0.0146
15(7, 8)-16(7, 9)	1406.4540	-0.0163
16(7, 9)-17(7,10)	1405.7320	0.0062
17(7,10)-18(7,11)	1405.0020	0.0212
18(7,11)-19(7,12)	1404.2780	-0.0075
19(7,12)-20(7,13)	1403.5060	0.0163
21(7,14)-22(7,15)	1401.9890	-0.0078
22(7,15)-23(7,16)	1401.2560	0.0063
23(7,16)-24(7,17)	1400.4930	-0.0091
24(7,17)-25(7,18)	1399.7640	0.0099
26(7,19)-27(7,20)	1398.2490	-0.0078
28(7,21)-29(7,22)	1396.7410	-0.0168
R-branch: K_a=0		
5(0, 5)- 4(0, 4)	1417.0110	-0.0052
8(0, 8)- 7(0, 7)	1419.2430	0.0230
9(0, 9)- 8(0, 8)	1419.9600	0.0069
10(0,10)- 9(0, 9)	1420.6870	0.0016
11(0,11)-10(0,10)	1421.4340	0.0171
12(0,12)-11(0,11)	1422.1320	-0.0154
13(0,13)-12(0,12)	1422.8590	-0.0180
25(0,25)-24(0,24)	1431.5300	-0.0101
26(0,26)-25(0,25)	1432.2480	-0.0049
27(0,27)-26(0,26)	1432.9660	0.0019
28(0,28)-27(0,27)	1433.6780	0.0044
29(0,29)-28(0,28)	1434.3950	0.0136
33(0,33)-32(0,32)	1437.1850	-0.0102
34(0,34)-33(0,33)	1437.9090	0.0149
37(0,37)-36(0,36)	1439.9660	-0.0141
38(0,38)-37(0,37)	1440.6810	0.0092
39(0,39)-38(0,38)	1441.3790	0.0173
42(0,42)-41(0,41)	1443.4060	-0.0149
43(0,43)-42(0,42)	1444.1190	0.0152
R-branch: K_a=1[1]		
7(1, 7)- 6(1, 6)	1418.5140	-0.0136
8(1, 8)- 7(1, 7)	1419.2430	-0.0082
9(1, 9)- 8(1, 8)	1419.9600	-0.0138
10(1,10)- 9(1, 9)	1420.6870	-0.0084
11(1,11)-10(1,10)	1421.4340	0.0180
12(1,12)-11(1,11)	1422.1320	-0.0036
13(1,13)-12(1,12)	1422.8590	0.0049
14(1,14)-13(1,13)	1423.5800	0.0084
15(1,15)-14(1,14)	1424.3000	0.0120
16(1,16)-15(1,15)	1425.0180	0.0146
17(1,17)-16(1,16)	1425.7360	0.0183
18(1,18)-17(1,17)	1426.4270	-0.0040
19(1,19)-18(1,18)	1427.1360	-0.0071
20(1,20)-19(1,19)	1427.8600	0.0059
21(1,21)-20(1,20)	1428.5800	0.0159
22(1,22)-21(1,21)	1429.2900	0.0171
24(1,24)-23(1,23)	1430.6650	-0.0221
28(1,28)-27(1,27)	1433.4810	-0.0209
29(1,29)-28(1,28)	1434.2030	0.0003
30(1,30)-29(1,29)	1434.9180	0.0157
36(1,36)-35(1,35)	1439.0650	-0.0102
37(1,37)-36(1,36)	1439.7830	0.0164
39(1,39)-38(1,38)	1441.1270	-0.0188
40(1,40)-39(1,39)	1441.8320	-0.0017
46(1,46)-45(1,45)	1445.9230	-0.0136
R-branch: K_a=1[U]		
5(1, 4)- 4(1, 3)	1417.1660	-0.0002
6(1, 5)- 5(1, 4)	1417.9100	-0.0018
7(1, 6)- 6(1, 5)	1418.6790	0.0218
8(1, 7)- 7(1, 6)	1419.4150	0.0125
9(1, 8)- 8(1, 7)	1420.1420	-0.0055
10(1, 9)- 9(1, 8)	1420.8760	-0.0162
11(1,10)-10(1, 9)	1421.6350	-0.0017
12(1,11)-11(1,10)	1422.3660	-0.0149
20(1,19)-19(1,18)	1428.3380	0.0159
21(1,20)-20(1,19)	1429.0680	0.0052
22(1,21)-21(1,20)	1429.8160	0.0130
23(1,22)-22(1,21)	1430.5630	0.0204
24(1,23)-23(1,22)	1431.2930	0.0113
25(1,24)-24(1,23)	1432.0250	0.0049
26(1,25)-25(1,24)	1432.7600	0.0022
27(1,26)-26(1,25)	1433.4810	-0.0139
32(1,31)-31(1,30)	1437.1850	0.0164
33(1,32)-32(1,31)	1437.9090	0.0082
34(1,33)-33(1,32)	1438.6240	-0.0080
35(1,34)-34(1,33)	1439.3610	-0.0011
36(1,35)-35(1,34)	1440.0960	0.0047
37(1,36)-36(1,35)	1440.8240	0.0047
38(1,37)-37(1,36)	1441.5510	0.0048
R-branch: K_a=2		
5(2, 4)- 4(2, 3)	1417.4420	0.0050
8(2, 7)- 7(2, 6)	1419.6400	-0.0018
9(2, 8)- 8(2, 7)	1420.3600	-0.0156
10(2, 9)- 9(2, 8)	1421.0870	-0.0218
11(2,10)-10(2, 9)	1421.8210	-0.0204
17(2,16)-16(2,15)	1426.2020	-0.0212
23(2,22)-22(2,21)	1430.5630	-0.0167
24(2,23)-23(2,22)	1431.2930	-0.0101
25(2,24)-24(2,23)	1432.0250	-0.0006
26(2,25)-25(2,24)	1432.7600	0.0126
27(2,26)-26(2,25)	1433.4810	0.0127
28(2,27)-27(2,26)	1434.2030	0.0147
29(2,28)-28(2,27)	1434.9180	0.0105
30(2,29)-29(2,28)	1435.6470	0.0213
32(2,31)-31(2,30)	1437.0510	-0.0085
44(2,43)-43(2,42)	1445.5610	-0.0163
45(2,44)-44(2,43)	1446.2650	-0.0150

Table 2 (continued)

$J'(K_a',K_c')$-$J''(K_a'',K_c'')$	OBS.	OBS-CALC
46(2,45)-45(2,44)	1446.9770	-0.0045
R-branch: K_a=3		
6(3, 4)- 5(3, 3)	1418.6790	-0.0158
7(3, 5)- 6(3, 4)	1419.4150	-0.0148
8(3, 6)- 7(3, 5)	1420.1420	-0.0222
9(3, 7)- 8(3, 6)	1420.8760	-0.0221
10(3, 8)- 9(3, 7)	1421.6350	0.0035
11(3, 9)-10(3, 8)	1422.3660	0.0016
12(3,10)-11(3, 9)	1423.0940	-0.0027
13(3,11)-12(3,10)	1423.8260	-0.0025
14(3,12)-13(3,11)	1424.5780	0.0182
15(3,13)-14(3,12)	1425.3020	0.0115
19(3,17)-18(3,16)	1428.2220	0.0138
20(3,18)-19(3,17)	1428.9400	0.0037
21(3,19)-20(3,18)	1429.6620	-0.0019
22(3,20)-21(3,19)	1430.3870	-0.0039
23(3,21)-22(3,20)	1431.1120	-0.0053
24(3,22)-23(3,21)	1431.8340	-0.0092
25(3,23)-24(3,22)	1432.5580	-0.0106
26(3,24)-25(3,23)	1433.2810	-0.0124
27(3,25)-26(3,24)	1434.0050	-0.0126
28(3,26)-27(3,25)	1434.7280	-0.0133
29(3,27)-28(3,26)	1435.4510	-0.0134
30(3,28)-29(3,27)	1436.1760	-0.0109
31(3,29)-30(3,28)	1436.9050	-0.0038
32(3,30)-31(3,29)	1437.6380	0.0078
33(3,31)-32(3,30)	1438.3500	-0.0009
34(3,32)-33(3,31)	1439.0650	-0.0060
35(3,33)-34(3,32)	1439.7830	-0.0075
36(3,34)-35(3,33)	1440.4940	-0.0153
37(3,35)-36(3,34)	1441.2270	-0.0005
38(3,36)-37(3,35)	1441.9600	0.0150
39(3,37)-38(3,36)	1442.6810	0.0191
R-branch: K_a=4		
5(4, 1)- 4(4, 0)	1418.6790	-0.0051
6(4, 2)- 5(4, 1)	1419.4150	-0.0044
7(4, 3)- 6(4, 2)	1420.1420	-0.0121
8(4, 4)- 7(4, 3)	1420.8760	-0.0124
9(4, 5)- 8(4, 4)	1421.6350	0.0130
10(4, 6)- 9(4, 5)	1422.3660	0.0108
11(4, 7)-10(4, 6)	1423.0940	0.0062
12(4, 8)-11(4, 7)	1423.8260	0.0062
14(4,10)-13(4, 9)	1425.3020	0.0197
18(4,14)-17(4,13)	1428.2220	0.0214
19(4,15)-18(4,14)	1428.9400	0.0112
20(4,16)-19(4,15)	1429.6620	0.0056
21(4,17)-20(4,16)	1430.3870	0.0035
22(4,18)-21(4,17)	1431.1120	0.0020
23(4,19)-22(4,18)	1431.8340	-0.0019
24(4,20)-23(4,19)	1432.5580	-0.0032
25(4,21)-24(4,20)	1433.2810	-0.0050
26(4,22)-25(4,21)	1434.0050	-0.0052
27(4,23)-26(4,22)	1434.7280	-0.0058
28(4,24)-27(4,23)	1435.4510	-0.0058
29(4,25)-28(4,24)	1436.1760	-0.0033
30(4,26)-29(4,25)	1436.9050	0.0039
31(4,27)-30(4,26)	1437.6380	0.0156
32(4,28)-31(4,27)	1438.3500	0.0070
33(4,29)-32(4,28)	1439.0650	0.0019
34(4,30)-33(4,29)	1439.7830	0.0005
35(4,31)-34(4,30)	1440.4940	-0.0073
36(4,32)-35(4,31)	1441.2270	0.0074
R-branch: K_a=5		
6(5, 2)- 5(5, 1)	1420.3600	0.0196
7(5, 3)- 6(5, 2)	1421.0870	0.0120
8(5, 4)- 7(5, 3)	1421.8210	0.0120
9(5, 5)- 8(5, 4)	1422.5470	0.0046
10(5, 6)- 9(5, 5)	1423.2790	0.0036
11(5, 7)-10(5, 6)	1423.9990	-0.0088
14(5,10)-13(5, 9)	1426.2020	0.0004
15(5,11)-14(5,10)	1426.9250	-0.0068
20(5,16)-19(5,15)	1430.5630	-0.0113
21(5,17)-20(5,16)	1431.2930	-0.0080
22(5,18)-21(5,17)	1432.0250	-0.0022
23(5,19)-22(5,18)	1432.7600	0.0072
24(5,20)-23(5,19)	1433.4810	0.0032
25(5,21)-24(5,20)	1434.2030	0.0008
26(5,22)-25(5,21)	1434.9180	-0.0080
27(5,23)-26(5,22)	1435.6470	-0.0021
28(5,24)-27(5,23)	1436.3790	0.0073
30(5,26)-29(5,25)	1437.8030	-0.0120
31(5,27)-30(5,26)	1438.5320	-0.0037
32(5,28)-31(5,27)	1439.2500	-0.0057
33(5,29)-32(5,28)	1439.9660	-0.0091
34(5,30)-33(5,29)	1440.6810	-0.0129
36(5,32)-35(5,31)	1442.1200	-0.0095
37(5,33)-36(5,32)	1442.8460	-0.0002
38(5,34)-37(5,33)	1443.5690	0.0067
39(5,35)-38(5,34)	1444.2990	0.0212
40(5,36)-39(5,35)	1445.0100	0.0175
41(5,37)-40(5,36)	1445.7100	0.0035
42(5,38)-41(5,37)	1446.4180	-0.0019
43(5,39)-42(5,38)	1447.1440	0.0115
R-branch: K_a=7		
12(7, 5)-11(7, 4)	1427.1360	-0.0003
13(7, 6)-12(7, 5)	1427.8600	-0.0075
14(7, 7)-13(7, 6)	1428.5800	-0.0183
17(7,10)-16(7, 9)	1430.8010	0.0135
18(7,11)-17(7,10)	1431.5300	0.0139
19(7,12)-18(7,11)	1432.2490	0.0037
20(7,13)-19(7,12)	1432.9660	-0.0059
21(7,14)-20(7,13)	1433.6780	-0.0209
31(7,24)-30(7,23)	1440.9230	-0.0145
32(7,25)-31(7,24)	1441.6480	-0.0100
33(7,26)-32(7,25)	1442.3660	-0.0119
36(7,29)-35(7,28)	1444.5340	0.0004

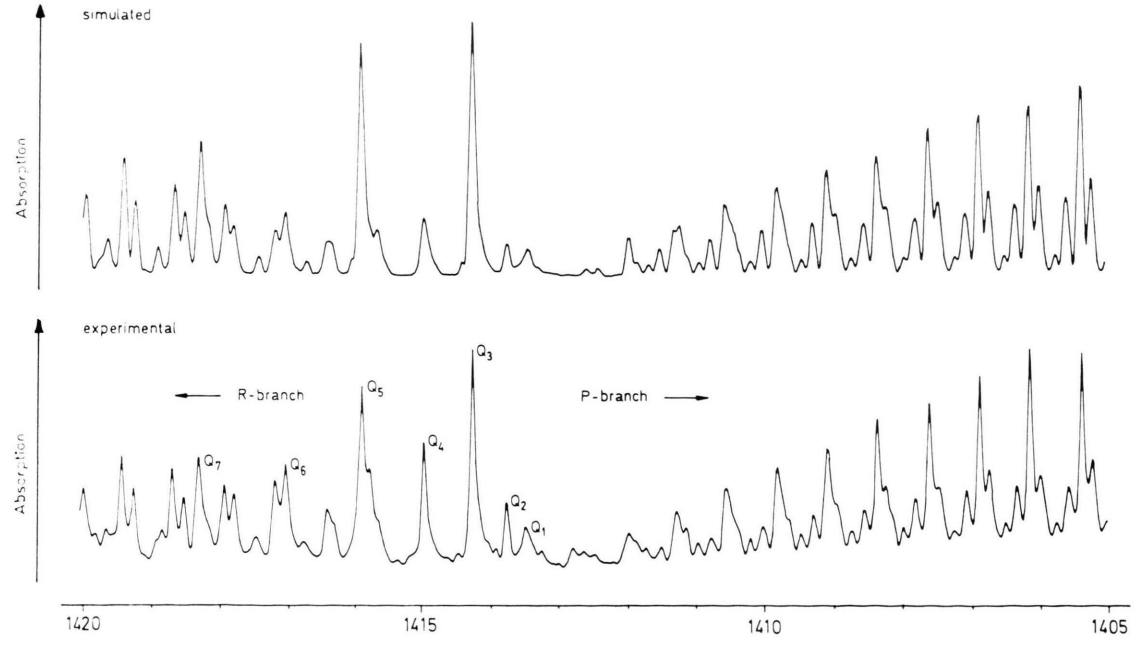

Fig. 4. Comparison of the simulated with the observed spectrum at the band center region of the ν_3 band of diazomethane. The computed spectrum was obtained from the molecular constants given in Table 3.

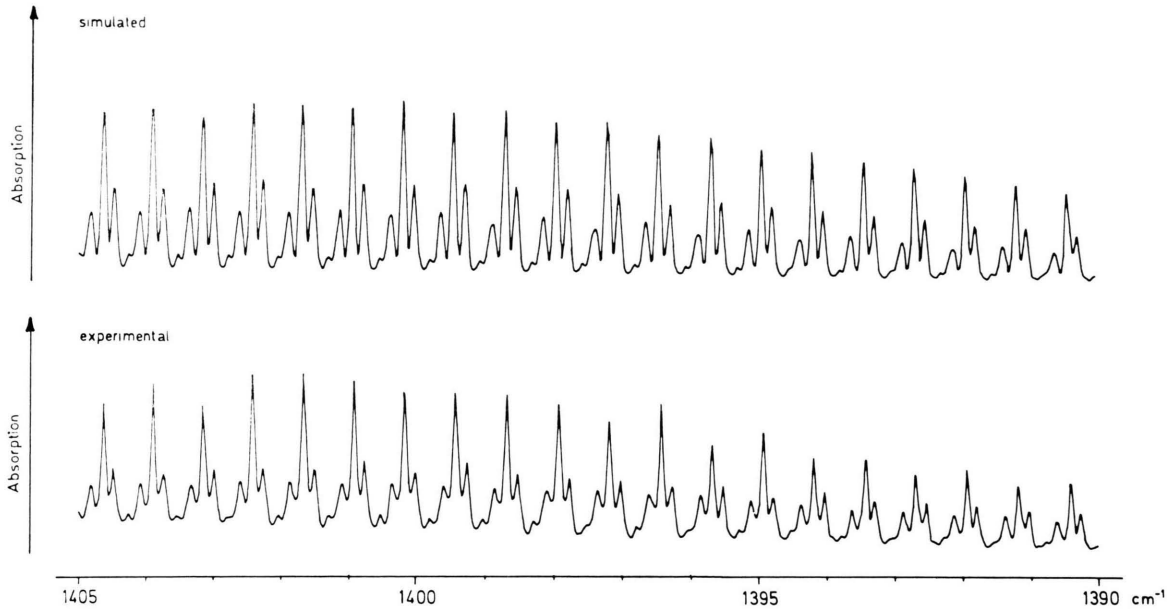

Fig. 5. Simulation of the P-branch region of the ν_3 band of diazomethane. The computed spectrum was obtained from the molecular constants given in Table 3.

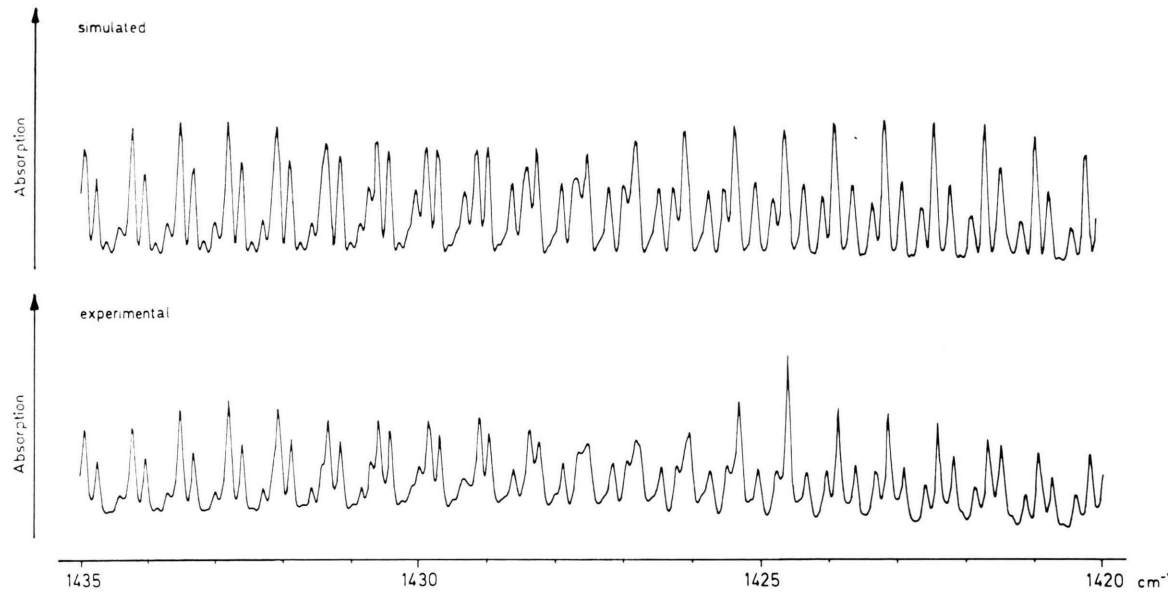

Fig. 6. Simulation of the R-branch region of the ν_3 band of diazomethane. The computed spectrum was obtained from the molecular constants given in Table 3.

Table 3. Rotational and centrifugal distortion constants in Watson's S-reduced Hamiltonian for the fundamental ν_3 in diazomethane[a,b].

	ground state[c]	$\nu_3 = 1$[d]
A/MHz	272 979.1 (81)	276 135.3 (45)
B/MHz	11 305.42697 (45)	11 309.56 (27)
C/MHZ	10 845.22028 (47)	10 825.54 (25)
D_J/kHz	4.14620 (74)	4.290 (69)
D_{JK}/kHz	396.817 (92)	407.3 (30)
D_K/kHz	22 000[e]	24 229.2 (809)
d_1/kHz	−0.19255 (43)[f]	−0.594 (81)
d_2/kHz	−0.05727 (39)	–
H_{JK}/Hz	2.081 (42)	–
H_{KJ}/Hz	−492.4 (83)	–
L_{KJ}/Hz	1.26 (30)	–
S_{JK}/mHz	0.2085 (56)	–
S_{KJ}/mHz	−34.1 (49)	–
T_{KJ}/mHz	−0.257 (38)	–
U_{KJ}/mHz	−0.00162 (11)	–
$\tilde{\nu}_0$/cm^{-1}	–	1413.3302 (17)
σ/cm^{-1}	–	0.011
$\varkappa$	−0.996489	−0.996351

[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.

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 ν_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 ν_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.

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