THE FOURIER TRANSFORM AND DIODE LASER SPECTRUM OF THE ν_2 BAND OF DIAZOMETHANE

Jürgen VOGT¹, Manfred WINNEWISSER

Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-6300 Giessen, West Germany

and

Koichi YAMADA and Gisbert WINNEWISSER

I. Physikalisches Institut, Universität zu Köln, Universitätsstrasse 14, D-5000 Cologne 41, West Germany

Received 5 August 1983

The infrared spectrum of the ν_2 band (NN stretching) of gaseous diazomethane at 2100 cm^{-1} has been measured by means of an interferometer and a tunable diode laser spectrometer. For the first time the rotational J and K_a structure of this A-type parallel band has been resolved. Since the spectrum was found to be perturbed it was not possible to fit the upper state levels to an overall hamiltonian. Nine subbands have been analysed with the support of millimeter wave data for the ground vibrational state. Term values for the $\nu_2 = 1$ vibrational state with K_a up to 5 have been obtained and subband origins, effective rotational constants B and centrifugal distortion constants D and H were determined for each K_a substate.

1. Introduction

Diazomethane is an extremely explosive compound which is widely used in preparative and analytical chemistry. Despite these applications little is known about its spectroscopic properties. Rather early the question arose whether this challenging compound has an extended or cyclic structure. Pechmann [1], who prepared this substance in 1894 for the first time, assumed a cyclic configuration. Not until 40 years later could the interpretation of various physical measurements resolve the question of the configuration unambiguously. The ultraviolet spectrum [2] and measurements of the dipole moments of aliphatic diazo compounds [3] were interpreted under the assumption of a cyclic structure, whereas the electron diffraction data [4] and additional ultraviolet studies [5] came to the opposite result. These discrepancies in the interpretations were removed by the first infrared

spectrum [6], which could only be interpreted with a structure analogous to that of ketene.

Since that time it has been accepted that diazomethane is an acyclic, planar molecule with C_{2v} symmetry. After this first infrared spectrum several other infrared spectroscopic studies followed [7–12] at low or medium resolution. In 1954 the J -rotational structure of the fundamental ν_2 was resolved in a gas-phase spectrum [8], from which effective rotational constants were determined on the basis of a rigid rotor model. However, the first high-resolution spectra of the main isotopic species and its deuterated isotopomers were recorded in the microwave region some years later [13]; no absorption frequencies were reported. As an extension of that early work the microwave spectra of further isotopomers and an r_s structure were reported [14]. Again, no absorption frequencies were given.

From the recent millimeter wave measurement in this laboratory of the main isotopic species of diazomethane, rotational and centrifugal distortion constants have been determined for the ground

¹ Part of the author's dissertation, Justus-Liebig-Universität Giessen (D26).

vibrational state [15]. We have also investigated the rovibrational spectrum in the mid infrared region. For the first time we have been able to resolve and analyse both the J and K_a structure of two bands of this slightly asymmetric top molecule ($\kappa = -0.996$). Recently we have described the rovibrational analysis of the ν_3 fundamental band [16], whereas in the present paper we report the analysis of the ν_2 fundamental band.

2. Experimental procedures

The chemical preparation has been described in ref. [15]; in avoiding the transition from the liquid to the solid phase we experienced no explosions. The absorption cells were conditioned by filling them several times with a few mbar diazomethane before the actual measurements. The resulting polyethylene layer on the glass walls prevented very effectively the otherwise rapid decomposition of diazomethane. Fig. 1 shows a survey spectrum of diazomethane at 13 mbar. It was recorded in Giessen with a Fourier transform infrared spectrometer (Digilab FTS 20B) at low resolution. In the assignment given in fig. 1 and in table 1, which was derived by Moore and Pimentel in 1964 [12], the numbering of the fundamentals is slightly

modified in accordance with the present international recommendation [17]. The fundamental ν_2 is one of the strongest bands and essentially corresponds to the NN-stretching mode.

Due to the strong absorption the high-resolution data could be recorded at lower pressure. The Fourier transform spectrum was measured in a 10 cm glass cell with KBr windows at a pressure of 4 mbar. The instrument was purged with dry nitrogen in order to avoid absorptions due to atmospheric water and carbon dioxide. A HgCdTe (MCT) detector, cooled with liquid nitrogen, was used to detect the interferograms. In order to obtain a reasonable signal-to-noise ratio at 0.07 cm^{-1} resolution, 400 interferograms were co-added ($\approx 8\text{ h}$) and Fourier transformed without apodization. The ν_2 band observed under these conditions is displayed in fig. 2. The wavenumber scale was calibrated with the rovibrational spectrum of DBr [18] which was recorded under the same conditions.

Some regions of the band were measured with a tunable diode laser spectrometer (Laser Analytics, model LS3) at the University of Cologne. With this spectrometer we could obtain Doppler-limited resolution. This spectrometer was operated in two modes separately or simultaneously: (1) source modulation and (2) Stark modulation. Details of

Fig. 1. Survey spectrum of diazomethane at a pressure of 13 mbar in a 10 cm cell with the vibrational assignment of the bands according to ref. [12].

Table 1

Fundamental vibrations of diazomethane. (Numbering of the fundamentals slightly modified according to the recommendation given in ref. [17])

Mode	Approximate description	Symmetry species	$\tilde{\nu}_0$ (cm ⁻¹)	Ref.
ν_1	symmetric CH ₂ stretching	A ₁	3077.1	[8]
ν_2	NN stretching	A ₁	2101.577	this work
ν_3	symmetric CH ₂ deformation	A ₁	1413.330	[16]
ν_4	CN stretching	A ₁	1170	[12]
ν_5	CNN bending out of plane	B ₁	564.0	[12]
ν_6	CH ₂ deformation out of plane	B ₁	406.0	[12]
ν_7	antisymmetric CH ₂ stretching	B ₂	3184.5	[12]
ν_8	asymmetric CH ₂ deformation	B ₂	1109.0	[12]
ν_9	CNN bending in plane	B ₂	421.2	[12]

the source modulation mode, in which the spectrometer normally runs for good sensitivity, have been described elsewhere [19,20]. The use of Stark modulation with a diode laser spectrometer is described in ref. [21]. For the investigation of this band ≈ 1 mbar diazomethane was filled into a 1 m glass cell with BaF₂ windows. The observed line positions were calibrated by the rotational fine structure of the ν_1 band of OCS, the vacuum transition wavenumbers of which have been precisely determined by Fourier transform [22] and diode laser spectroscopy [23].

The Stark modulation mode was used only for assignment. A block diagram of the experimental

arrangement is given in fig. 3. In this mode of operation the laser beam, which is frequency modulated with 5 kHz, traverses the mode selector and the Stark cell, which consists of two parallel-plate electrodes 2 mm apart. Since the Stark modulator generates a square-wave-modulated electric field with a modulation frequency of 1 kHz, the absorption signal is additionally modulated. This modulated infrared signal is received by a liquid nitrogen cooled MCT detector and fed into two independent phase-sensitive detectors (PSD). In the first one the signal is demodulated at 10 kHz and the resulting (second derivative) source modulated spectrum is displayed on one channel of the

Fig. 2. Fourier transform spectrum of the fundamental ν_2 of diazomethane recorded with a resolution of 0.07 cm⁻¹ and a pressure of 4 mbar in a 10 cm absorption cell.

Fig. 3. Block diagram of the tunable diode laser spectrometer employing Stark modulation mode.

dual channel recorder, whereas in the second amplifier the signal is demodulated at 1 kHz in order to obtain the Stark spectrum on the second channel of the recorder. These two spectra can then be compared.

3. Analysis

Fig. 2 shows a survey spectrum of the A-type parallel band ν_2 between 2050 and 2140 cm^{-1} . The

fine structure in the R branch is considerably compressed, as expected for a stretching vibration. Because the rovibrational transitions overlap very much in the R branch and because the laser diode available in the present study covered the wave-number region of the P branch, only the P and Q branches have been analysed in detail. In fig. 4 the band center region with the Q and P branches as observed with the Fourier transform spectrometer is displayed. The rovibrational assignment shown was obtained with the help of the following criteria: (1) Loomis-Wood diagrams, (2) asymmetry splittings, (3) Stark effects, (4) spin statistics using the information from both spectrometers, and (5) band contour simulation for the Fourier transform spectra.

Our initial attempt to assign the ν_2 band was to try to calculate asymmetric rotor transitions and simulate the band contour of the Fourier transform spectrum, at least for low J and K_a values. This approach led to a swift assignment of ν_3 [16], but was totally unsuccessful with ν_2 . Since the band turned out to be strongly perturbed we were forced to look at each subband separately and to rely heavily on the diode laser spectrum to reach and to confirm the assignment.

Fig. 4. Band center region in the Fourier transform spectrum of diazomethane with the assignment of the K_a subbands ($K = K_a$).

As the K_a subbands can be treated as bands of linear molecules, where $(B + C)/2$ corresponds to an effective rotational constant B , the identification of lines belonging to each of these subbands was the starting point of the rovibrational analysis. This was done by means of Loomis–Wood diagrams [24–26]. The subbands in the P branch could be initially assigned and fitted by using a polynomial of the type

$$\nu = \nu_{\text{sub}} + (B' + B'')m + (B' - B'' - D' + D'')m^2 - 2(D' + D'')m^3 - (D' - D'')m^4, \quad (1)$$

where m is defined as $m = -J''$ for the P branch. The constants B'' and D'' are the effective rotational and centrifugal distortion constants for the ground state, and B' and D' are those for the excited state. By comparison of the effective ground state constants with those determined from the millimeter wave spectrum [15], it was then possible to assign some of these subbands to the correct K_a value. However, the final fits were carried out using eqs. (4) and (5).

An additional proof for the assignment was the asymmetry splitting of the transitions and its dependence on J for $K_a = 0$. For this slightly asym-

metric top only the asymmetry splitting of the $K_a = 1$ lines could be resolved with the Fourier transform spectrometer. However, this splitting can be observed even at higher K_a with the higher resolution of the diode laser data. In fig. 5 two sections of the P branch are compared for the Fourier transform and diode laser spectra. It was found that the $K_a = 2$ lines already split at $J'' = 11$, whereas the splitting of the $K_a = 3$ lines starts to be resolvable at $J'' = 32$ (see table 2 and fig. 5). However, it was not possible to resolve the asymmetry splitting for $K_a = 4$ and 5.

The Stark effect is conveniently used in microwave spectroscopy to improve sensitivity and to confirm assignments. This method can also be applied in diode laser spectroscopy in the infrared region [21]. Normally the Stark pattern cannot be resolved in the infrared region due to the limited field strength of 4 kV/cm. Therefore, it was impossible to obtain a value for the electric dipole moment. However, we can easily distinguish lines having first-order Stark effect from those having second-order Stark effect at low J values. Transitions exhibiting first-order Stark effect are strongly modulated so that strong signals in the Stark-modulated spectrum result, whereas transitions with a

Fig. 5. Comparison of the Fourier transform spectrum of diazomethane with the diode laser spectrum for two sections of the P branch of the ν_2 fundamental band.

Table 2

Observed rovibrational transitions (wavenumbers in cm^{-1}) and assignment for the ν_2 fundamental of diazomethane.

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	OBS.	OBS-CALC	$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	OBS.	OBS-CALC	$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	OBS.	OBS-CALC
P-branch: $K_a=0$			27(1,26)-28(1,27)	2079.6110	-0.0196 F	47(2,45)-48(2,46)	2061.8430	-0.0053 F
2(0,2)-3(0,3)	2099.3444	0.0018 D	28(1,27)-29(1,28)	2078.7270	-0.0216 F	48(2,46)-49(2,47)	2060.8860	-0.0010 F
3(0,3)-4(0,4)	2098.5856	-0.0004 D	29(1,28)-30(1,29)	2077.8740	0.0121 F	Q-branch: $K_a=3^1$		
5(0,5)-6(0,6)	2097.0544	-0.0016 D	30(1,29)-31(1,30)	2076.9680	-0.0027 F	3(3,0)-3(3,1)	2101.6625	0.0005 D
6(0,6)-7(0,7)	2096.2823	-0.0006 D	31(1,30)-32(1,31)	2076.0748	0.0000 D	4(3,1)-4(3,2)	2101.6438	0.0003 D
7(0,7)-8(0,8)	2095.5041	-0.0006 D	32(1,31)-33(1,32)	2075.1742	-0.0003 D	5(3,2)-5(3,3)	2101.6202	-0.0001 D
9(0,9)-10(0,10)	2093.9354	0.0017 D	33(1,32)-34(1,33)	2074.2700	0.0004 D	6(3,3)-6(3,4)	2101.5932	0.0006 D
10(0,10)-11(0,11)	2093.1415	0.0003 D	38(1,37)-39(1,38)	2069.6776	0.0000 D	P-branch: $K_a=3^1$		
13(0,13)-14(0,14)	2090.7357	0.0000 D	43(1,42)-44(1,43)	2064.9650	-0.0109 F	3(3,1)-4(3,2)	2098.7068	-0.0006 D
14(0,14)-15(0,15)	2089.9234	-0.0006 D	44(1,43)-45(1,44)	2064.0225	-0.0001 D	4(3,2)-5(3,3)	2097.9493	-0.0010 D
18(0,18)-19(0,19)	2086.6137	0.0000 D	45(1,44)-46(1,45)	2063.0658	0.0006 D	5(3,3)-6(3,4)	2097.1884	-0.0002 D
P-branch: $K_a=1^1$			46(1,45)-47(1,46)	2062.1080	0.0045 F	6(3,4)-7(3,5)	2096.4225	0.0003 D
1(1,1)-2(1,2)	2100.8930	-0.0239 F	47(1,46)-48(1,47)	2061.1330	-0.0047 F	7(3,5)-8(3,6)	2095.6523	0.0011 D
2(1,2)-3(1,3)	2100.1580	-0.0183 F	48(1,47)-49(1,48)	2060.1672	-0.0005 D	8(3,6)-9(3,7)	2094.8640	-0.0115 F
3(1,3)-4(1,4)	2099.4313	0.0004 D	49(1,48)-50(1,49)	2059.1939	0.0002 D	9(3,7)-10(3,8)	2094.0960	0.0007 D
4(1,4)-5(1,5)	2098.6806	-0.0003 D	P-branch: $K_a=2^1$			10(3,8)-11(3,9)	2093.3102	-0.0001 D
5(1,5)-6(1,6)	2097.9255	-0.0006 D	2(2,1)-3(2,2)	2100.4540	0.0118 F	11(3,9)-12(3,10)	2092.5130	-0.0076 F
6(1,6)-7(1,7)	2097.1663	-0.0004 D	3(2,2)-4(2,3)	2099.6918	0.0024 F	12(3,10)-13(3,11)	2091.7290	0.0026 F
7(1,7)-8(1,8)	2096.4030	0.0004 D	4(2,3)-5(2,4)	2098.9322	0.0002 D	13(3,11)-14(3,12)	2090.9296	0.0022 F
8(1,8)-9(1,9)	2095.6341	0.0003 D	5(2,4)-6(2,5)	2098.1692	-0.0007 D	14(3,12)-15(3,13)	2090.1220	-0.0017 D
9(1,9)-10(1,10)	2094.8640	0.0036 F	6(2,5)-7(2,6)	2097.4011	-0.0021 F	15(3,13)-16(3,14)	2089.3230	0.0076 F
10(1,10)-11(1,11)	2094.0835	0.0012 D	7(2,6)-8(2,7)	2096.6317	-0.0003 D	16(3,14)-17(3,15)	2088.5270	0.0094 F
11(1,11)-12(1,12)	2093.2994	-0.0001 D	8(2,7)-9(2,8)	2095.8573	0.0012 D	17(3,15)-18(3,16)	2087.6940	0.0094 F
12(1,12)-13(1,13)	2092.5130	0.0008 F	9(2,8)-10(2,9)	2095.0739	-0.0018 F	18(3,16)-19(3,17)	2086.8622	0.0000 D
13(1,13)-14(1,14)	2091.7290	0.0089 F	10(2,9)-11(2,10)	2094.2905	-0.0002 D	19(3,17)-20(3,18)	2086.0348	-0.0001 D
14(1,14)-15(1,15)	2090.9238	0.0004 D	11(2,10)-12(2,11)	2093.5007	-0.0004 D	20(3,18)-21(3,19)	2085.2048	0.0007 D
15(1,15)-16(1,16)	2090.1251	0.0029 F	12(2,11)-13(2,12)	2092.6900	-0.0170 F	21(3,19)-22(3,20)	2084.3670	0.0000 D
16(1,16)-17(1,17)	2089.3230	0.0067 F	13(2,12)-14(2,13)	2091.9060	-0.0023 F	22(3,20)-23(3,21)	2083.5248	0.0000 D
17(1,17)-18(1,18)	2088.5270	0.0212 F	14(2,13)-15(2,14)	2091.1210	0.0160 F	23(3,21)-24(3,22)	2082.6920	0.0135 F
18(1,18)-19(1,19)	2087.6940	0.0032 F	15(2,14)-16(2,15)	2090.2972	0.0003 D	24(3,22)-25(3,23)	2081.8262	-0.0013 D
19(1,19)-20(1,20)	2086.8705	-0.0006 D	16(2,15)-17(2,16)	2089.4860	0.0018 F	25(3,23)-26(3,24)	2080.9714	-0.0003 D
20(1,20)-21(1,21)	2086.0462	-0.0007 D	17(2,16)-18(2,17)	2088.6550	-0.0116 F	26(3,24)-27(3,25)	2080.1099	-0.0011 D
21(1,21)-22(1,22)	2085.2270	0.0087 F	18(2,17)-19(2,18)	2087.8380	-0.0060 F	27(3,25)-28(3,26)	2079.2590	0.0134 F
22(1,22)-23(1,23)	2084.3819	-0.0030 F	19(2,18)-20(2,19)	2087.0230	0.0066 F	28(3,26)-29(3,27)	2078.3840	0.0087 F
23(1,23)-24(1,24)	2083.5470	-0.0002 D	20(2,19)-21(2,20)	2086.2030	-0.0071 F	29(3,27)-30(3,28)	2077.5120	0.0118 F
24(1,24)-25(1,25)	2082.6920	-0.0128 F	21(2,20)-22(2,21)	2085.3830	-0.0071 F	30(3,28)-31(3,29)	2076.6360	0.0157 F
25(1,25)-26(1,26)	2081.8577	-0.0004 D	22(2,21)-23(2,22)	2084.5630	-0.0071 F	31(3,29)-32(3,30)	2075.7370	0.0015 D
26(1,26)-27(1,27)	2081.0080	0.0012 F	23(2,22)-24(2,23)	2083.7430	-0.0071 F	32(3,30)-33(3,31)	2074.8462	0.0004 D
27(1,27)-28(1,28)	2080.1510	-0.0001 D	24(2,23)-25(2,24)	2082.9230	0.0048 F	33(3,31)-34(3,32)	2073.9520	0.0006 D
32(1,32)-33(1,33)	2075.8075	0.0011 D	P-branch: $K_a=2^u$			34(3,32)-35(3,33)	2073.0460	-0.0006 F
34(1,34)-35(1,35)	2074.0383	0.0002 D	2(2,0)-3(2,1)	2100.4540	0.0099 F	35(3,33)-36(3,34)	2072.1400	-0.0077 F
36(1,36)-37(1,37)	2072.2720	0.0191 F	3(2,1)-4(2,2)	2099.6918	0.0008 D	36(3,34)-37(3,35)	2071.2380	-0.0006 F
39(1,39)-40(1,40)	2069.5430	-0.0008 D	4(2,2)-5(2,3)	2098.9322	-0.0009 D	37(3,35)-38(3,36)	2070.3244	-0.0003 D
43(1,43)-44(1,44)	2065.8800	0.0044 F	5(2,3)-6(2,4)	2098.1692	-0.0013 D	38(3,36)-39(3,37)	2069.4058	-0.0001 D
44(1,44)-45(1,45)	2064.9650	0.0161 F	6(2,4)-7(2,5)	2097.4011	-0.0020 F	39(3,37)-40(3,38)	2068.4660	-0.0163 F
45(1,45)-46(1,46)	2064.0133	-0.0051 F	7(2,5)-8(2,6)	2096.6317	0.0008 D	40(3,38)-41(3,39)	2067.5280	-0.0224 F
46(1,46)-47(1,47)	2063.0798	-0.0044 F	8(2,6)-9(2,7)	2095.8573	0.0035 F	41(3,39)-42(3,40)	2066.5980	-0.0224 F
49(1,49)-50(1,50)	2060.2604	-0.0001 D	9(2,7)-10(2,8)	2095.0739	0.0020 F	42(3,40)-43(3,41)	2065.6710	-0.0182 F
50(1,50)-51(1,51)	2059.3224	0.0100 F	10(2,8)-11(2,9)	2094.2849	-0.0003 D	43(3,41)-44(3,42)	2064.7210	-0.0182 F
P-branch: $K_a=1^u$			11(2,9)-12(2,10)	2093.4937	0.0000 D	44(3,42)-45(3,43)	2063.7912	-0.0002 D
1(1,0)-2(1,1)	2100.8930	0.0056 F	12(2,10)-13(2,11)	2092.6900	-0.0072 F	45(3,43)-46(3,44)	2062.8388	0.0000 D
3(1,2)-4(1,3)	2099.3692	-0.0002 D	13(2,11)-14(2,12)	2091.9060	0.0099 F	48(3,46)-49(3,47)	2059.9529	0.0003 D
4(1,3)-5(1,4)	2098.6019	-0.0011 D	14(2,12)-15(2,13)	2091.0960	0.0099 F	Q-branch: $K_a=3^u$		
5(1,4)-6(1,5)	2097.8200	-0.0116 F	15(2,13)-16(2,14)	2090.2802	0.0011 D	3(3,1)-3(3,0)	2101.6625	0.0005 D
6(1,5)-7(1,6)	2097.0544	-0.0008 D	16(2,14)-17(2,15)	2089.4860	0.0226 F	4(3,2)-4(3,1)	2101.6438	0.0003 D
7(1,6)-8(1,7)	2096.2823	0.0000 D	17(2,15)-18(2,16)	2088.6550	0.0122 F	5(3,3)-5(3,2)	2101.6202	-0.0002 D
8(1,7)-9(1,8)	2095.4876	-0.0002 D	18(2,16)-19(2,17)	2087.8380	0.0206 F	6(3,4)-6(3,3)	2101.5932	0.0005 D
10(1,9)-11(1,10)	2093.9018	0.0011 D	22(2,20)-23(2,21)	2084.4673	-0.0004 D	P-branch: $K_a=3^u$		
11(1,10)-12(1,11)	2093.1015	0.0017 D	23(2,21)-24(2,22)	2083.6181	-0.0002 D	3(3,0)-4(3,1)	2098.7068	-0.0006 D
12(1,11)-13(1,12)	2092.2930	-0.0010 F	25(2,23)-26(2,24)	2081.9047	-0.0004 D	4(3,1)-5(3,2)	2097.9493	-0.0011 D
13(1,12)-14(1,13)	2091.4890	0.0056 F	26(2,24)-27(2,25)	2081.0413	-0.0001 D	5(3,2)-6(3,3)	2097.1884	-0.0003 D
14(1,13)-15(1,14)	2090.6684	0.0005 D	27(2,25)-28(2,26)	2080.1724	-0.0005 D	6(3,3)-7(3,4)	2096.4225	0.0002 D
15(1,14)-16(1,15)	2089.8481	0.0006 D	31(2,29)-32(2,30)	2076.6360	-0.0162 F	7(3,4)-8(3,5)	2095.6523	0.0009 D
16(1,15)-17(1,16)	2089.0250	0.0026 F	32(2,30)-33(2,31)	2075.7609	0.0005 D	8(3,5)-9(3,6)	2094.8640	-0.0118 F
17(1,16)-18(1,17)	2088.1840	-0.0083 F	33(2,31)-34(2,32)	2074.8641	0.0002 D	9(3,6)-10(3,7)	2094.0960	0.0010 D
18(1,17)-19(1,18)	2087.3550	-0.0026 F	34(2,32)-35(2,33)	2073.9634	0.0005 D	10(3,7)-11(3,8)	2093.3102	-0.0005 D
19(1,18)-20(1,19)	2086.5168	-0.0012 D	35(2,33)-36(2,34)	2073.0460	-0.0113 F	11(3,8)-12(3,9)	2092.5130	-0.0081 F
20(1,19)-21(1,20)	2085.6890	0.0154 F	36(2,34)-37(2,35)	2072.1400	-0.0072 F	12(3,9)-13(3,10)	2091.7290	0.0021 F
21(1,20)-22(1,21)	2084.8242	-0.0003 D	37(2,35)-38(2,36)	2071.2380	0.0053 F	13(3,10)-14(3,11)	2090.9296	0.0016 F
22(1,21)-23(1,22)	2083.9706	0.0000 D	38(2,36)-39(2,37)	2070.3133	-0.0003 D	14(3,11)-15(3,12)	2090.1220	-0.0024 F
23(1,22)-24(1,23)	2083.1120	0.0000 F	39(2,37)-40(2,38)	2069.3958	0.0056 F	15(3,12)-16(3,13)	2089.3230	0.0069 F
24(1,23)-25(1,24)	2082.2482	-0.0004 D	40(2,38)-41(2,39)	2068.4660	0.0036 F	16(3,13)-17(3,14)	2088.5270	0.0086 F
25(1,24)-26(1,25)	2081.3804	-0.0002 D	41(2,39)-42(2,40)	2067.5160	-0.0142 F	17(3,14)-18(3,15)	2087.6940	0.0086 F
26(1,25)-27(1,26)	2080.5087	0.0007 D	42(2,40)-43(2,41)	2066.5980	0.0043 F	18(3,15)-19(3,16)	2086.8622	-0.0006 D
			43(2,41)-44(2,42)	2065.6550	0.0020 F	19(3,16)-20(3,17)	2086.0348	-0.0007 D
			44(2,42)-45(2,43)	2064.7210	0.0130 F	20(3,17)-21(3,18)	2085.2048	0.0004 D
			45(2,43)-46(2,44)	2063.7570	-0.0019 F	21(3,18)-22(3,19)	2084.3670	0.0004 D
			46(2,44)-47(2,45)	2062.8070	0.0014 F	22(3,19)-23(3,20)	2083.5248	-0.0001 D

Table 2 (continued)

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	OBS.	OBS-CALC	$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	OBS.	OBS-CALC	$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	OBS.	OBS-CALC	
23(3, 20) - 24(3, 21)	2082.6920	0.0136 F	7(4, 4) - 8(4, 5)	2095.9841	0.0032 F	P-branch: $K_a=5$			
24(3, 21) - 25(3, 22)	2081.8262	-0.0008 D	8(4, 5) - 9(4, 6)	2095.2050	0.0016 D				
25(3, 22) - 26(3, 23)	2080.9714	0.0006 D	9(4, 6) - 10(4, 7)	2094.4240	0.0031 F				
26(3, 23) - 27(3, 24)	2080.1099	0.0002 D	10(4, 7) - 11(4, 8)	2093.6349	0.0013 D		5(5, 0) - 6(5, 1)	2097.5090	0.0079 F
27(3, 24) - 28(3, 25)	2079.2590	0.0153 F	12(4, 9) - 13(4, 10)	2092.0320	-0.0123 F		6(5, 1) - 7(5, 2)	2096.7336	0.0001 D
28(3, 25) - 29(3, 26)	2078.3840	0.0112 F	13(4, 10) - 14(4, 11)	2091.2440	0.0016 F		7(5, 2) - 8(5, 3)	2095.9633	0.0023 F
29(3, 26) - 30(3, 27)	2077.5120	0.0151 F	14(4, 11) - 15(4, 12)	2090.4379	0.0023 F		8(5, 3) - 9(5, 4)	2095.1856	0.0019 D
30(3, 27) - 31(3, 28)	2076.6360	0.0200 F	15(4, 12) - 16(4, 13)	2089.6200	-0.0039 F		9(5, 4) - 10(5, 5)	2094.4033	0.0019 D
31(3, 28) - 32(3, 29)	2075.7297	-0.0005 D	17(4, 14) - 18(4, 15)	2087.9920	0.0060 F		10(5, 5) - 11(5, 6)	2093.6149	0.0006 D
32(3, 29) - 33(3, 30)	2074.8384	-0.0009 D	18(4, 15) - 19(4, 16)	2087.1540	-0.0057 F		11(5, 6) - 12(5, 7)	2092.8160	-0.0063 F
33(3, 30) - 34(3, 31)	2073.9453	0.0018 D	19(4, 16) - 20(4, 17)	2086.3326	0.0040 F	12(5, 7) - 13(5, 8)	2092.0320	0.0065 F	
34(3, 31) - 35(3, 32)	2073.0460	0.0034 F	20(4, 17) - 21(4, 18)	2085.4740	-0.0187 F	13(5, 8) - 14(5, 9)	2091.2440	0.0203 F	
35(3, 32) - 36(3, 33)	2072.1400	0.0033 F	21(4, 18) - 22(4, 19)	2084.6495	-0.0024 F	14(5, 9) - 15(5, 10)	2090.4181	0.0010 D	
36(3, 33) - 37(3, 34)	2071.2380	0.0123 F	22(4, 19) - 23(4, 20)	2083.8054	-0.0007 D	15(5, 10) - 16(5, 11)	2089.6200	0.0144 F	
37(3, 34) - 38(3, 35)	2070.3089	-0.0007 D	23(4, 20) - 24(4, 21)	2082.9380	-0.0177 F	16(5, 11) - 17(5, 12)	2088.7780	-0.0112 F	
38(3, 35) - 39(3, 36)	2069.3884	0.0000 D	24(4, 21) - 25(4, 22)	2082.1000	-0.0003 D	18(5, 13) - 19(5, 14)	2087.1540	0.0121 F	
39(3, 36) - 40(3, 37)	2068.4660	0.0038 F	25(4, 22) - 26(4, 23)	2081.2398	-0.0004 D	19(5, 14) - 20(5, 15)	2086.3096	-0.0014 D	
40(3, 37) - 41(3, 38)	2067.5160	-0.0148 F	26(4, 23) - 27(4, 24)	2080.3760	0.0008 D	20(5, 15) - 21(5, 16)	2085.4740	-0.0012 F	
41(3, 38) - 42(3, 39)	2066.5980	0.0037 F	27(4, 24) - 28(4, 25)	2079.4990	-0.0063 F	21(5, 16) - 22(5, 17)	2084.6346	0.0000 D	
42(3, 39) - 43(3, 40)	2065.6550	0.0023 F	29(4, 26) - 30(4, 27)	2077.7470	-0.0041 F	22(5, 17) - 23(5, 18)	2083.7888	-0.0002 D	
43(3, 40) - 44(3, 41)	2064.7210	0.0151 F	31(4, 28) - 32(4, 29)	2075.9783	0.0006 D	23(5, 18) - 24(5, 19)	2082.9380	-0.0006 F	
44(3, 41) - 45(3, 42)	2063.7539	-0.0001 D	33(4, 30) - 34(4, 31)	2074.1849	0.0000 D	24(5, 19) - 25(5, 20)	2082.0837	0.0002 D	
45(3, 42) - 46(3, 43)	2062.7967	-0.0003 D	38(4, 35) - 39(4, 36)	2069.6189	-0.0001 D	25(5, 20) - 26(5, 21)	2081.2231	-0.0003 D	
46(3, 43) - 47(3, 44)	2061.8430	0.0082 F	40(4, 37) - 41(4, 38)	2067.7510	-0.0080 F	26(5, 21) - 27(5, 22)	2080.3588	0.0002 D	
47(3, 44) - 48(3, 45)	2060.8860	0.0186 F	41(4, 38) - 42(4, 39)	2066.8250	0.0030 F	27(5, 22) - 28(5, 23)	2079.4990	0.0101 F	
48(3, 45) - 49(3, 46)	2059.8949	0.0000 D	42(4, 39) - 43(4, 40)	2065.8800	0.0000 F	28(5, 23) - 29(5, 24)	2078.6060	-0.0083 F	
Q-branch: $K_a=4$			Q-branch: $K_a=5$			29(5, 24) - 30(5, 25)	2077.7470	0.0120 F	
4(4, 0) - 4(4, 1)	2101.9757	-0.0007 D	5(5, 0) - 5(5, 1)	2101.9294	-0.0006 D	30(5, 25) - 31(5, 26)	2076.8420	-0.0087 F	
5(4, 1) - 5(4, 2)	2101.9517	-0.0003 D	6(5, 1) - 6(5, 2)	2101.8999	-0.0007 D	31(5, 26) - 32(5, 27)	2075.9621	0.0004 D	
6(4, 2) - 6(4, 3)	2101.9214	-0.0012 D	7(5, 2) - 7(5, 3)	2101.8655	-0.0007 D	33(5, 28) - 34(5, 29)	2074.1690	-0.0002 D	
7(4, 3) - 7(4, 4)	2101.8881	-0.0002 D	8(5, 3) - 8(5, 4)	2101.8267	-0.0003 D	37(5, 32) - 38(5, 33)	2070.5060	-0.0204 F	
8(4, 4) - 8(4, 5)	2101.8490	0.0000 D	9(5, 4) - 9(5, 5)	2101.7819	-0.0009 D	38(5, 33) - 39(5, 34)	2069.6038	0.0001 D	
9(4, 5) - 9(4, 6)	2101.8049	0.0000 D	10(5, 5) - 10(5, 6)	2101.7332	-0.0006 D	39(5, 34) - 40(5, 35)	2068.6630	-0.0132 F	
P-branch: $K_a=4$			11(5, 6) - 11(5, 7)	2101.6791	-0.0007 D	40(5, 35) - 41(5, 36)	2067.7510	0.0071 F	
5(4, 2) - 6(4, 3)	2097.5090	-0.0124 F	12(5, 7) - 12(5, 8)	2101.6117	-0.0092 F	41(5, 36) - 42(5, 37)	2066.8250	0.0183 F	
6(4, 3) - 7(4, 4)	2096.7540	0.0004 D			42(5, 37) - 43(5, 38)	2065.8800	0.0152 F		
					44(5, 39) - 45(5, 40)	2063.9663	-0.0003 D		
					45(5, 40) - 46(5, 41)	2063.0108	0.0004 D		
					48(5, 43) - 49(5, 44)	2060.1127	-0.0002 D		

second-order Stark effect are only partially modulated, and thus are much weaker in the Stark spectrum. Although this method was only applied at low J , where sufficiently large Stark splittings are expected, we were able to obtain information concerning K_a . In the case of $K_a = 0$, for which the Q branch is forbidden and there is no asymmetry splitting, the assignments could be clearly confirmed from the Stark spectrum. Due to the second-order Stark effect the $K_a = 0$ lines were not fully modulated and consequently could not be detected, whereas they are prominent in the source modulation spectrum.

The last discrete criterion in the assignment process was spin statistics. According to the C_{2v} symmetry of the molecule, energy levels with odd K_a should have three times the statistical weight of levels with even K_a values. Thus, the spin statistics

must support the assignment of the K_a substates.

Since the P branch region of the fundamental band overlaps with the combination bands $\nu_4 + 2\nu_6$ and $\nu_4 + 3\nu_6 - \nu_6$, not all observed transitions could be assigned to the fundamental band. This can be seen in fig. 5, where numerous lines in the diode laser spectrum remain unassigned.

Using all the information which had been obtained the band was simulated by calculating each subband separately and then superimposing them in the simulated spectrum. Since only low- K_a lines were reliably assigned, and extrapolation in K_a was not possible due to the irregularity of the successive subbands, the simulation is not perfect and is further hindered by the overlapping combination bands. For the same reasons, it was not possible to extend the assignment into the R branch. However, by the five criteria described

Fig. 6. (a) Subband origins of the ν_2 band of diazomethane as a function of K_a . (b) Subband origins of the ν_3 band. This comparison shows dramatically the perturbations exhibited in the ν_2 band system.

above we have been able to assign rovibrational transitions in the P branch up to $K_a = 5$ and $J = 51$, as indicated in table 2. The diode laser data (187 lines), especially the Q-branch lines, fully confirmed the subband assignment and contributed clusters of high-resolution data which compose a significant portion of the lines (total number of lines 315) included in the final least-squares fits, since most of the Fourier transform lines are not fully resolved. All these lines in their turn would have been almost impossible to assign

by themselves, since the R branch was not available to provide combination differences.

As can be seen from figs. 4 and 6, the ν_2 fundamental is seriously perturbed. In general the positions of the 4Q branches should form a regular series with respect to K_a in the absence of resonances. Since the classification of the resonances (Coriolis or Fermi), the identity and even the number of energy levels in resonance with the level $\nu_2 = 1$ have not yet been determined, we cannot derive an exact hamiltonian describing all rovibrational transitions of this band. Consequently each subband is described by a set of effective constants. The energy levels are represented by

$$E(\nu, K, J)/h = G(\nu, K) + F(\nu, K, J), \quad (2)$$

$$F(\nu, K, J) = B_{\nu K} J(J+1) - D_{\nu K} J^2(J+1)^2 + H_{\nu K} J^3(J+1)^3, \quad (3)$$

where ν represents the vibrational quantum number ν_2 and K the rotational quantum number K_a . The rovibrational transitions are given by the differences in these levels,

$$\nu = [E(1, K', J') - E(0, K'', J'')]/h, \quad (4)$$

$$\begin{aligned} \nu = \nu_{\text{sub}} &+ B_{1K'} J'(J'+1) - D_{1K'} J'^2(J'+1)^2 \\ &+ H_{1K'} J'^3(J'+1)^3 - B_{0K''} J''(J''+1) \\ &+ D_{0K''} J''^2(J''+1)^2 - H_{0K''} J''^3(J''+1)^3 \end{aligned} \quad (5)$$

and

$$\nu_{\text{sub}} = G(1, K') - G(0, K''). \quad (6)$$

Using eq. (5) the effective molecular parameters for $\nu_2 = 1$ have been adjusted for each subband by least-squares fits. Since the millimeter wave measurements [15] are much more accurate than the present data, the effective rotational and centrifugal distortion constants of the ground vibrational state have been held fixed at the values obtained from the pure rotational spectrum. In table 2 the list of observed infrared transitions is given in vacuum wavenumbers; the transitions determined from the diode laser spectrum are labeled with D, whereas the transitions measured by the Fourier transform spectrum are indicated by F. Because of the different accuracies the diode laser

Table 3
Effective molecular constants of the ν_2 fundamental band of diazomethane ^{a,b)}

	$K_a = 0$	$K_a = 1^1$	$K_a = 1^u$	$K_a = 2^1$	$K_a = 2^u$
B' (MHz)	10985.2(11)	10888.889(11)	11115.086(7)	11003.48(11)	11002.752(13)
B'' (MHz)	11075.3833(29)	10959.9233(16)	11190.0293(8)	11073.8044(6)	11073.7500(18)
D' (kHz)	-24.0(80)	10.299(13)	10.4014(84)	4.51(61)	-18.073(19)
D'' (kHz)	29.526(15)	10.2643(86)	10.6642(42)	8.2966(13)	-16.925(12)
H' (Hz)	-99(15)	0.524(36)	-0.2973(24)	-9.10(81)	-0.3202(74)
H'' (Hz)	0.450(26)	0.328(14)	-0.315(7)	-	-0.356(23)
$\bar{\nu}_{\text{sub}}$ (cm ⁻¹)	2101.5771(10)	2102.3839(1)	2102.3854(1)	2102.6725(1)	2102.6746(1)
σ (cm ⁻¹)	0.0013	0.0014	0.0011	0.0015	0.0014
	$K_a = 3^1$	$K_a = 3^u$	$K_a = 4$	$K_a = 5$	
B' (MHz)	11002.456(7)	11002.616(8)	10995.448(6)	10991.560(2)	
B'' (MHz)	11071.7633(18)	11071.7644(26)	11068.8930(4)	11065.1155(4)	
D' (kHz)	2.0698(91)	2.2644(92)	2.3786(47)	3.0243(20)	
D'' (kHz)	0.9783(86)	0.985(12)	2.4337(10)	3.0422(10)	
H' (Hz)	-0.1895(28)	0.4951(28)	-	-	
H'' (Hz)	-0.329(13)	0.349(18)	-	-	
$\bar{\nu}_{\text{sub}}$ (cm ⁻¹)	2101.6897(1)	2101.6897(1)	2102.0254(1)	2102.0037(1)	
σ (cm ⁻¹)	0.0012	0.0012	0.0012	0.0014	

^{a)} Ground-state constants as obtained from the millimeter wave spectrum [15] were held fixed in the fit.

^{b)} In parentheses standard deviations in units of the last significant figures.

observations have been weighted more than the Fourier transform lines by a factor of 100 in the least-squares fits. The resulting effective molecular parameters are listed in table 3 for both vibrational states.

4. Discussion and conclusion

In the first "high"-resolution study of this band Mills and Thompson [8] found a doublet structure which they believed to arise from the tautomer nitrilimine, HCNNH. However, in this study that doublet structure can be easily explained by the K_a structure of the ν_2 band of diazomethane. The band center, which was previously determined to be 2102.42 and 2102.2 cm⁻¹ [8,9], respectively, can now be given definitely as 2101.577 cm⁻¹. A serious difficulty was encountered in fitting all the data with an asymmetric-top hamiltonian, because shifts in the line positions due to perturbations were clearly observed in the present high-precision measurements. Therefore, only the effective rotational and centrifugal distortion constants B , D and H have been determined. The dependence of

the subband origins upon K_a for the ν_2 band is shown in fig. 6a, which is in sharp contrast to the behaviour of the subband origins in ν_3 shown in fig. 6b. The origin of this perturbation is not yet known; however, the constants for the $K_a = 0$ subband indicate also the presence of a perturbation.

One source of perturbation is probably the Fermi resonance between the energy states ν_2 and $2\nu_4$ at 2317 cm⁻¹. As can easily be seen in fig. 1 the fundamental ν_4 , which essentially corresponds to a CN-stretching mode, and the first overtone $2\nu_4$ have comparable intensities. The enhanced intensity of the overtone could be explained with intensity borrowing through a Fermi resonance. This would not be K_a dependent; it would shift the whole band and the K_a and J dependent terms would be secondary and systematic. In this case a smooth curve should result. Probably the Fermi resonance does not explain the observed irregularity. On the other hand a resonance is also possible with the combination state $\nu_4 + 2\nu_6$ at 1990 cm⁻¹. Moreover Coriolis resonances cannot be excluded. The erratic K_a dependence of the ν_2 band indicates a-type Coriolis interactions with at least one other level. In order to understand these perturbations

further high-resolution spectroscopic data are mandatory. At present the bending fundamentals ν_5 , ν_6 and ν_9 , which exhibit strong Coriolis resonances, are being reinvestigated [27].

Acknowledgement

The authors would like to express their thanks to Dr. B.P. Winnewisser for many helpful discussions and critically reading and commenting on the manuscript. The experimental work was partly supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. All calculations were carried out at the Hochschulrechenzentrum of the Justus-Liebig-Universität Giessen, a service which is gratefully acknowledged.

References

- [1] H. von Pechmann, *Chem. Ber.* 27 (1894) 1888.
- [2] F.W. Kirkbride and R.G.W. Norrish, *J. Chem. Soc.* (1933) 119.
- [3] N.V. Sidgwick, L.E. Sutton and W. Thomas, *J. Chem. Soc.* (1933) 406.
- [4] H. Boersch, *Monatsh. Chem.* 65 (1935) 311.
- [5] G. Kortüm, *Z. Physik. Chem.* 50b (1941) 361.
- [6] D.A. Ramsay, *J. Chem. Phys.* 17 (1949) 666.
- [7] B.L. Crawford, W.H. Fletcher and D.A. Ramsay, *J. Chem. Phys.* 19 (1951) 406.
- [8] I.M. Mills and H.W. Thompson, *J. Chem. Soc. Faraday Trans.* 50 (1954) 1270.
- [9] W.H. Fletcher and T.P. Garrett, *J. Chem. Phys.* 25 (1956) 50.
- [10] C.B. Moore, *J. Chem. Phys.* 39 (1963) 1884.
- [11] C.B. Moore and G.C. Pimentel, *J. Chem. Phys.* 40 (1964) 342.
- [12] C.B. Moore and G.C. Pimentel, *J. Chem. Phys.* 40 (1964) 329.
- [13] A.P. Cox, L.F. Thomas and J. Sheridan, *Nature* 181 (1958) 1000.
- [14] J. Sheridan, in: *Advances in molecular spectroscopy, Proceedings of the 4th International Meeting on Molecular Spectroscopy*, Vol. 1, ed. A. Mangini (Pergamon, Oxford, 1962).
- [15] E. Schäfer and M. Winnewisser, *J. Mol. Spectry.* 97 (1983) 154.
- [16] J. Vogt and M. Winnewisser, *Z. Naturforsch.* 38a (1983), to be published.
- [17] R.S. Mulliken, *J. Chem. Phys.* 23 (1955) 1997.
- [18] A.R.H. Cole, IUPAC – Table of wavenumbers for the calibration of infrared spectrometers (Pergamon, Oxford, 1977).
- [19] K. Yamada, R. Schieder, G. Winnewisser and A.W. Mantz, *Z. Naturforsch.* 35a (1980) 690.
- [20] K. Yamada and G. Winnewisser, *Z. Naturforsch.* 36a (1981) 23.
- [21] K. Yamada and M. Takami, *J. Mol. Spectry.* 84 (1980) 431.
- [22] G. Guelachvili, *Opt. Commun.* 30 (1979) 361.
- [23] W. Klebsch, K. Yamada and G. Winnewisser, *Z. Naturforsch.* 38a (1983) 157.
- [24] F.W. Loomis and R.W. Wood, *Phys. Rev.* 32 (1928) 223.
- [25] J.F. Scott and K.N. Rao, *J. Mol. Spectry.* 20 (1966) 461.
- [26] T. Nakagawa and J. Overend, *J. Mol. Spectry.* 50 (1974) 333.
- [27] J. Vogt, L. Nemes, M. Birk and M. Winnewisser, private communication.