The Infrared Spectrum of Diazirine, $\text{H}_2\text{C}^{15}\text{N}_2$ Rovibrational Analysis of the ν_3 Fundamental

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Z. Naturforsch. **41a**, 1159–1165 (1986); received June 16, 1986

The mid-infrared spectrum of ^{15}N -labeled diazirine has been recorded using a Fourier transform spectrometer at a resolution of 0.08 cm^{-1} . The ν_3 fundamental at 1452.49 cm^{-1} which essentially corresponds to a symmetric methylene deformation has been analyzed in detail. The rovibrational assignment is given and, using Watson's A-reduced Hamiltonian, the rotational and centrifugal distortion constants for the $\nu_3 = 1$ level could be determined.

Introduction

In recent years diazirine, the only experimentally known cyclic isomer of diazomethane, has been of great interest. With the intention of providing a complete set of molecular constants for the ground and the first excited vibrational states of diazirine, an investigation of this molecule, which presents an unusual molecular structure, has been carried out by means of microwave, millimeter wave [1–4], and Fourier transform infrared spectroscopy [5–8]. The infrared spectra of diazirine and its isotopomers $\text{H}_2^{13}\text{CN}_2$, $\text{H}_2\text{C}^{15}\text{N}_2$, and D_2CN_2 have been recorded in isotopically enriched samples with a Fourier transform spectrometer at a resolution of 0.08 cm^{-1} . For the parent species the rovibrational assignment of the ν_3 fundamental (A-type band, A_1 species, CH_2 deformation), the ν_7 fundamental (B-type band, B_1 species, CN asymmetric stretching) and of the ν_9 fundamental (C-type band, B_2 species, CH_2 rocking) have been carried out [5, 6, 8] developing methods for the rotational assignment and for the analysis of the band structure of this very asymmetric rotor. The ν_3 band of $\text{H}_2^{13}\text{CN}_2$ has also been analyzed [7].

In order to continue the thorough study of this molecule, the infrared spectrum and the rovibrational analysis of the ν_3 fundamental of $\text{H}_2\text{C}^{15}\text{N}_2$,

resulting in the determination of the molecular constants for the vibrational state $\nu_3 = 1$, has been carried out and will be reported here.

Experimental Procedures

Isotopically enriched ^{15}N -diazirine was prepared by means of a modification of the method of Ohme and Schmitz, which is described elsewhere [1, 9]. In this case ^{15}N -enriched formamide (Merck, Sharp and Dohme, Canada; 96.2 atomic% ^{15}N) was used as a precursor.

The infrared spectrum of $\text{H}_2\text{C}^{15}\text{N}_2$ was recorded using a Digilab Fourier transform spectrometer FTS-20B in the range $450\text{--}3800\text{ cm}^{-1}$ 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. In order to obtain a reasonable signal-to-noise ratio at a resolution better than 0.08 cm^{-1} , 600 interferograms were coadded and Fourier transformed. The sample cell was 10 cm long and equipped with KBr windows. The sample pressure was about 2000 Pa.

Calibration was made with HBr lines [10] recorded under the same conditions.

Results and Discussion

The $^{15}\text{N}_2$ -diazirine molecule belongs to the symmetry point group C_{2v} . The nine fundamental vibra-

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C_{2v}	E	C_{2a}	σ_{ab}	σ_{ac}	
A_1	1	1	1	1	T_a
A_2	1	1	-1	-1	R_a
B_1	1	-1	1	-1	T_b, R_c
B_2	1	-1	-1	1	T_c, R_b
Γ_{3N}^{tot}	15	-1	3	3	
$\Gamma_{\text{spin}}^{\text{tot}}$	16	4	8	8	

$$\Gamma_{\text{vib}} = 4A_1 \oplus A_2 \oplus 2B_1 \oplus 2B_2$$

$\uparrow \qquad \qquad \qquad \uparrow \qquad \qquad \uparrow$
 Band contour $\rightarrow$ A-type B-type C-type

$I(^{15}\text{N}) = 1/2$; $I(^1\text{H}) = 1/2$; $I(^{12}\text{C}) = 0$; $I_{\text{tot}} = 16$

$$\Gamma_{\text{spin}} = 9A_1 \oplus A_2 \oplus 3B_1 \oplus 3B_2$$

$K_a K_c$	Γ_{rot}	Weight
ee	A_1	6
eo	A_2	6
oe	B_1	10
oo	B_2	10

Fig. 1. Symmetry information for $^{15}\text{N}_2$ -diazirine.

Table 1. Fundamental vibrations of $^{15}\text{N}_2$ -diazirine.

Symmetry species	Mode	Approximate description	cm^{-1}
A_1	ν_1	sCH stretch	3015.4 ^a
	ν_2	NN stretch	1585.2 ^a
	ν_3	CH_2 deformation	1452.49
	ν_4	sCN stretch	973.5
A_2	ν_5	CH_2 twist	[959] ^b
B_1	ν_6	CH_2 wag	967.2
	ν_7	aCN stretch	786.8
B_2	ν_8	aCH stretch	3131.6
	ν_9	CH_2 rock	1123.7

^a Perturbed by Fermi resonance. ^b Estimated value.

tions and their symmetry species are $4A_1(\nu_1-\nu_4)$, $A_2(\nu_5)$, $2B_1(\nu_6, \nu_7)$, and $2B_2(\nu_8, \nu_9)$. In Fig. 1 the correlation between the symmetry species of the vibrational irreducible representation and the band contour is given. The spin statistics for the rovibra-

tional levels are also shown (cf. similar table for parent species in [5]).

Figure 2 shows a survey spectrum of $^{15}\text{N}_2$ -diazirine recorded at low resolution between 600 and 3400 cm^{-1} . The A- and C-type bands exhibit the typical PQR envelop, while the B-type bands present two peaks on either side of the band center (PQQR envelop).

In Table 1 the fundamental vibrations and their descriptions are reported. For the $\nu_5(A_2)$ mode, which is infrared inactive, there are no experimental data; the value listed is deduced from the vibrational analysis of all the substituted species [11]. Since the lowest fundamental is around 800 cm^{-1} , the spectrum is free at least up to 1600 cm^{-1} from overtone and combination bands. The spectrum in Fig. 2 shows the strong Fermi resonance between ν_2 and $2\nu_7$ at 1600 cm^{-1} , and at 3000 cm^{-1} the interaction due to the Fermi resonance of the ν_1 , $\nu_2 + \nu_3$, and $2\nu_7 + \nu_3$ bands.

The region covered by the rovibrational structure of the ν_3 band is shown in Figure 3. Since a precursor enriched to 96.2% in ^{15}N was used for the preparation, the resulting isotopic distribution is 92.5% $\text{H}_2\text{C}^{15}\text{N}_2$, 7.3% $\text{H}_2\text{C}^{14}\text{N}^{15}\text{N}$ and about 0.1% of $\text{H}_2\text{C}^{14}\text{N}_2$, so that it was impossible to detect the spectrum of the main isotopic species. However the spectrum exhibits a strong unresolved Q-branch at 1456.4 cm^{-1} , which is evidently the Q-branch of the mixed isotopomer $\text{H}_2\text{C}^{14}\text{N}^{15}\text{N}$.

For the numerical analysis of the rovibrational transitions both the ground and the excited state levels were fitted to Watson's A-reduced rotational Hamiltonian [12] in the I^r representation:

$$\begin{aligned} H_{\text{rot}} = & 1/2(B+C)\mathbf{P}^2 + [A - 1/2(B+C)]\mathbf{P}_a^2 \\ & - \Delta_J \mathbf{P}^4 - \Delta_{JK} \mathbf{P}^2 \mathbf{P}_a^2 - \Delta_K \mathbf{P}_a^4 + H_{JK} \mathbf{P}^4 \mathbf{P}_a^2 \\ & + H_{KJ} \mathbf{P}^2 \mathbf{P}_a^4 + [1/2(B-C) - 2\delta_J \mathbf{P}^2](\mathbf{P}_b^2 - \mathbf{P}_c^2) \\ & + [(-\delta_K \mathbf{P}_a^2), (\mathbf{P}_b^2 - \mathbf{P}_c^2)]_+, \end{aligned}$$

where $\mathbf{P}$, $\mathbf{P}_a$, $\mathbf{P}_b$, and $\mathbf{P}_c$ are the operators for the total angular momentum and its components, respectively; A , B , and C are the reduced rotational constants for the given vibrational state. Δ_J , Δ_{JK} , Δ_K , δ_J , and δ_K are the quartic and H_{JK} , H_{KJ} , are sextic centrifugal distortion constants.

The assignment of the rovibrational transitions was done with extensive use of modern computed-assisted methods of calculations, simulations, and graphic representation [5, 7]. For this A-type band

Fig. 2. A survey spectrum (resolution 1.0 cm^{-1}) of $\text{H}_2\text{C}^{15}\text{N}_2$.

Fig. 3. The ν_3 band of diazirine, $\text{H}_2\text{C}^{15}\text{N}_2$. The asterisk indicates the Q-branch of the ν_3 fundamental of the isotopomer $\text{H}_2\text{C}^{14}\text{N}^{15}\text{N}$.

Table 2. Molecular constants in Watson's A-reduced Hamiltonian for the ν_3 fundamental of $\text{H}_2\text{C}^{15}\text{N}_2$.

	Ground state ^a	$\nu_3 = 1$
A/cm^{-1}	1.28772055	1.290252 (98) ^b
B/cm^{-1}	0.773897232	0.771636 (28)
C/cm^{-1}	0.536891243	0.5375082 (53)
$\Delta_J \times 10^6/\text{cm}^{-1}$	1.00406	1.056 (53)
$\Delta_{JK} \times 10^6/\text{cm}^{-1}$	3.3437	3.30 (58)
$\Delta_K \times 10^6/\text{cm}^{-1}$	-0.8701	-0.8701 ^c
$\delta_J \times 10^6/\text{cm}^{-1}$	0.309814	0.333 (27)
$\delta_K \times 10^6/\text{cm}^{-1}$	2.45845	2.56 (17)
$H_{JK} \times 10^{10}/\text{cm}^{-1}$	-0.2648	-0.2648 ^c
$H_{KJ} \times 10^{10}/\text{cm}^{-1}$	0.749	0.749 ^c
$\tilde{\nu}_0/\text{cm}^{-1}$	—	1452.4879 (16)
σ/cm^{-1} (number of lines: 532)	—	0.014
κ	-0.3687	-0.3779

^a Ground state constants from [1] held fixed during the fit.^b Figures in parentheses are standard deviations in units of the least significant figures.^c Constrained to the ground state value during the fitting procedure.

the following selection rules were taken into account: $\Delta J = 0, \pm 1$, $\Delta K_a = 0$, $\Delta K_c = \pm 1$. The P, Q, and R branches are then each composed of subbranches designated by the notation $^{e,o}\Delta J (\Delta K_a, \Delta K_c)$, where e or o means that the sum of the three quantum numbers for the ground state is even or odd respectively, $^{e,o}\text{P}(0,1)$, $^{e,o}\text{Q}(0,1)$, $^{e,o}\text{Q}(0,-1)$, $^{e,o}\text{R}(0,1)$.

A first calculation of the rovibrational transition wavenumbers, together with the relative intensity of each line, was made using the ground state constants [1], for both states. Then, for each K_a , a correlation diagram was made of the deviation of the computed wavenumbers from the experimental positions of the peaks of the spectrum for increasing J' [13]. In each diagram it was possible to find a series of pairs of points for the P and R branch transitions going to the same excited rovibrational level. Since the differences observed between the P and R branch points depend only on the ground state constants which are very accurately determined from the

Fig. 4. Portion of the P-branch of the ν_3 fundamental in ^{15}N -labeled diazirine, compared with the spectrum computed with the adjusted constants reported in Table 2.

Table 3. Observed rovibrational transitions (wavenumbers/cm⁻¹) and assignment for the ν_3 fundamental of $^{15}\text{N}_2$ -diazirine.

$J^1(K_a^1, K_c^1) - J^0(K_a^0, K_c^0)$	OBS	O-C	$J^1(K_a^1, K_c^1) - J^0(K_a^0, K_c^0)$	OBS	O-C	$J^1(K_a^1, K_c^1) - J^0(K_a^0, K_c^0)$	OBS	O-C
P-Branch								
33(6,27)-34(6,28)	1410.344	0.0006	23(1,23)-24(1,24)	1426.608	-0.0000	11(2, 4)-12(2, 5)	1436.218	-0.0003
32(7,25)-33(7,26)	1410.344	-0.0027	23(0,23)-24(0,24)	1426.608	-0.0000	12(2,10)-13(2,11)	1436.380	0.016
34(4,30)-35(4,31)	1411.273	-0.0007	22(2,21)-23(2,22)	1426.739	0.018	12(3,10)-13(3,11)	1436.380	-0.003
31(7,24)-32(7,25)	1411.419	-0.001	22(1,21)-23(1,22)	1426.739	0.018	10(5, 5)-11(5, 6)	1436.925	0.002
33(4,29)-34(4,30)	1412.343	0.018	18(5,13)-19(5,14)	1427.000	0.019	13(0,13)-14(0,14)	1437.118	-0.004
31(6,25)-32(6,26)	1412.450	0.012	22(1,22)-23(1,23)	1427.658	0.004	13(1,13)-14(1,14)	1437.118	-0.004
30(7,23)-31(7,24)	1412.450	-0.018	22(0,22)-23(0,23)	1427.658	0.004	12(1,11)-13(1,12)	1437.286	0.002
31(5,26)-32(5,27)	1413.447	0.013	21(2,20)-22(2,21)	1427.756	-0.014	10(3, 7)-11(3, 8)	1437.286	0.010
34(1,33)-35(1,34)	1414.205	-0.023	21(1,20)-22(1,21)	1427.756	-0.014	12(2,11)-13(2,12)	1437.286	0.001
29(2,33)-35(2,34)	1414.205	-0.023	16(6,10)-17(6,11)	1427.756	0.000	10(4, 4)-11(4, 5)	1437.430	-0.017
34(6,23)-35(6,24)	1414.554	0.013	20(2,18)-21(2,19)	1427.892	-0.002	11(2, 9)-12(2,10)	1437.430	0.018
28(7,21)-29(7,22)	1414.554	-0.004	20(3,18)-21(3,19)	1427.892	-0.002	11(3, 9)-12(3,10)	1437.430	-0.028
34(0,34)-35(0,35)	1415.238	0.029	19(3,16)-20(3,17)	1428.003	-0.012	10(4, 7)-11(4, 8)	1437.826	-0.01
34(1,34)-35(1,35)	1415.238	0.029	19(4,16)-20(4,17)	1428.003	-0.013	10(8, 3)-11(8, 4)	1437.826	0.00
33(1,32)-34(1,33)	1415.238	-0.023	18(4,14)-19(4,15)	1428.111	0.007	10(8, 2)-11(8, 3)	1437.826	0.001
33(2,32)-34(2,33)	1415.238	-0.023	18(5,14)-19(5,15)	1428.111	-0.015	9(4, 5)-10(4, 6)	1438.082	0.004
32(3,30)-33(3,31)	1415.347	0.023	17(6,12)-18(6,13)	1428.317	0.004	12(1,12)-13(1,13)	1438.186	0.004
32(3,30)-33(3,31)	1415.347	0.023	20(2,19)-21(2,20)	1428.838	0.015	12(0,12)-13(0,13)	1438.186	0.004
30(4,26)-31(4,27)	1415.468	0.003	20(1,19)-21(1,20)	1428.838	0.015	11(1,10)-12(1,11)	1438.369	0.022
28(6,22)-29(6,23)	1415.595	0.003	16(5,11)-17(5,12)	1428.838	-0.002	11(2,10)-12(2,11)	1438.369	0.020
27(7,20)-28(7,21)	1415.595	-0.001	16(6,11)-17(6,12)	1429.467	-0.005	9(3, 6)-10(3, 7)	1438.369	0.006
33(0,33)-34(0,34)	1416.219	-0.018	20(0,20)-21(0,21)	1429.762	0.013	10(3, 8)-11(3, 9)	1438.543	-0.001
33(1,33)-34(1,34)	1416.219	-0.018	15(7, 8)-16(7, 9)	1429.762	0.024	9(6, 4)-10(6, 5)	1438.968	-0.014
27(6,21)-28(6,22)	1416.648	0.005	20(1,20)-21(1,21)	1429.762	0.013	9(6, 3)-10(6, 4)	1438.968	0.018
26(7,19)-27(7,20)	1416.648	0.024	19(2,18)-20(2,19)	1429.864	-0.011	9(6, 4)-10(6, 4)	1439.087	0.016
32(0,32)-33(0,33)	1417.283	0.014	19(1,18)-20(1,19)	1429.864	-0.011	11(1,11)-12(1,12)	1439.228	-0.013
32(1,32)-33(1,33)	1417.283	0.014	18(2,16)-19(2,17)	1429.993	-0.014	11(0,11)-12(0,12)	1439.228	-0.013
26(6,20)-27(6,21)	1417.677	-0.015	18(3,16)-19(3,17)	1429.993	-0.015	9(8, 2)-10(8, 3)	1439.228	-0.001
31(1,31)-32(1,32)	1418.313	0.012	17(3,14)-18(3,15)	1430.128	-0.004	9(8, 1)-10(8, 2)	1439.228	-0.001
31(0,31)-32(0,32)	1418.313	0.012	17(4,14)-18(4,15)	1430.128	-0.008	9(2, 7)-10(2, 8)	1439.437	-0.017
24(7,17)-25(7,18)	1418.584	-0.022	15(7, 9)-16(7,10)	1430.417	-0.018	10(2, 9)-11(2,10)	1439.437	0.022
25(6,19)-26(6,20)	1418.738	-0.001	15(8, 7)-16(8, 8)	1430.417	-0.003	10(1, 9)-11(1,10)	1439.437	0.028
29(1,28)-30(1,29)	1419.428	0.019	14(6, 8)-15(6, 9)	1430.773	0.017	9(3, 7)-10(3, 8)	1439.647	-0.005
29(2,28)-30(2,29)	1419.428	0.019	19(0,19)-20(0,20)	1430.773	-0.024	8(5, 3)-9(5, 4)	1440.195	0.023
27(3,24)-28(3,25)	1419.560	-0.019	19(1,19)-20(1,20)	1430.773	-0.024	10(0,10)-11(0,11)	1440.311	0.008
27(4,24)-28(4,25)	1419.560	-0.019	18(2,17)-19(2,18)	1430.939	0.008	10(1,10)-11(1,11)	1440.311	0.008
23(7,16)-24(7,17)	1419.560	0.025	18(1,17)-19(1,18)	1430.939	0.008	8(5, 4)-9(5, 5)	1440.311	0.008
25(5,20)-26(5,21)	1419.758	0.009	17(3,15)-18(3,16)	1431.093	0.026	8(2, 6)-9(2, 7)	1440.470	0.014
24(6,18)-25(6,19)	1419.758	-0.022	17(2,15)-18(2,16)	1431.093	0.026	9(2, 8)-10(2, 9)	1440.470	-0.014
28(1,27)-29(1,28)	1420.422	-0.026	16(3,13)-17(3,14)	1431.192	0.002	9(1, 8)-10(1, 9)	1440.470	0.001
28(2,27)-29(2,28)	1420.422	-0.026	16(4,13)-17(4,14)	1431.192	-0.006	8(3, 6)-9(3, 7)	1440.783	-0.010
22(7,15)-23(7,16)	1420.422	0.009	15(5,11)-16(5,12)	1431.375	0.006	7(3, 4)-8(3, 5)	1440.964	-0.015
26(3,23)-27(3,24)	1420.638	0.008	14(7, 7)-15(7, 8)	1431.496	0.006	9(0, 9)-10(0,10)	1441.372	0.006
26(4,23)-27(4,24)	1420.638	0.008	18(0,18)-19(0,19)	1431.863	0.014	9(1, 9)-10(1,10)	1441.372	0.006
24(5,19)-25(5,20)	1420.821	0.019	18(1,18)-19(1,19)	1431.863	0.014	8(2, 7)-9(2, 8)	1441.535	-0.025
23(6,17)-24(6,18)	1420.821	0.010	14(7, 8)-15(7, 9)	1431.863	-0.003	8(1, 7)-9(1, 8)	1441.535	0.012
21(7,14)-22(7,15)	1421.251	-0.025	17(2,16)-18(2,17)	1431.984	-0.001	7(5, 2)-8(5, 3)	1441.689	0.017
28(1,28)-29(1,29)	1421.387	-0.018	14(6, 9)-15(6,10)	1431.984	0.022	7(4, 4)-8(4, 5)	1441.689	-0.002
27(1,26)-28(1,27)	1421.501	0.010	17(1,16)-18(1,17)	1431.984	-0.001	7(6, 2)-8(6, 3)	1441.802	-0.017
27(2,26)-28(2,27)	1421.501	0.010	14(8, 6)-15(8, 7)	1431.984	0.001	7(6, 1)-8(6, 2)	1441.802	-0.015
25(3,22)-26(3,23)	1421.676	-0.005	14(4,10)-15(4,11)	1432.116	0.011	7(3, 5)-8(3, 6)	1441.964	-0.013
25(4,22)-26(4,23)	1421.676	-0.005	16(3,14)-17(3,15)	1432.116	-0.010	8(0, 8)-9(0, 9)	1442.428	-0.001
23(5,18)-24(5,19)	1421.843	-0.011	16(2,14)-17(2,15)	1432.116	-0.010	8(1, 8)-9(1, 9)	1442.428	-0.002
22(6,16)-23(6,17)	1421.843	0.021	14(5,10)-15(5,11)	1432.490	-0.005	6(2, 4)-7(2, 5)	1442.646	-0.002
20(7,13)-21(7,14)	1422.220	0.000	13(6, 7)-14(6, 8)	1432.490	0.023	7(2, 6)-8(2, 7)	1442.646	-0.002
26(1,25)-27(1,26)	1422.513	-0.020	17(1,17)-18(1,18)	1432.893	-0.007	6(4, 2)-7(4, 3)	1442.891	0.000
26(2,25)-27(2,26)	1422.513	-0.020	17(0,17)-18(0,18)	1432.893	-0.007	6(4, 3)-7(4, 4)	1443.067	0.007
25(2,23)-26(2,24)	1422.646	0.014	13(4, 9)-14(4,10)	1433.062	0.005	6(6, 1)-7(6, 2)	1443.192	-0.019
25(3,23)-26(3,24)	1422.646	0.014	16(1,15)-17(1,16)	1433.062	0.018	6(3, 4)-7(3, 5)	1443.192	-0.019
21(6,15)-22(6,16)	1422.801	0.001	16(2,15)-17(2,16)	1433.062	0.018	6(6, 0)-7(6, 1)	1443.192	-0.019
26(1,26)-27(1,27)	1423.480	-0.002	15(2,13)-16(2,14)	1433.189	0.002	7(0, 7)-8(0, 8)	1443.496	0.002
26(0,26)-27(0,27)	1423.480	-0.002	15(3,13)-16(3,14)	1433.189	0.000	7(1, 7)-8(1, 8)	1443.496	-0.000
23(3,20)-24(3,21)	1423.763	-0.025	14(3,11)-15(3,12)	1433.308	0.023	6(1, 5)-7(1, 6)	1443.606	0.014
23(4,20)-24(4,21)	1423.763	-0.025	13(6, 8)-14(6, 9)	1433.308	0.010	6(2, 5)-7(2, 6)	1443.742	-0.014
21(5,16)-22(5,17)	1423.952	0.002	13(7, 7)-14(7, 8)	1433.308	-0.015	5(2, 3)-6(2, 4)	1443.926	-0.008
25(1,25)-26(1,26)	1424.519	-0.004	13(8, 6)-14(8, 7)	1433.488	-0.018	5(3, 2)-6(3, 3)	1444.070	0.022
25(0,25)-26(0,26)	1424.519	-0.004	13(8, 5)-14(8, 6)	1433.488	-0.000	6(0, 6)-7(0, 7)	1444.567	0.009
24(1,23)-25(1,24)	1424.632	0.007	13(5, 9)-14(5,10)	1433.662	-0.004	6(1, 6)-7(1, 7)	1444.567	0.001
24(2,23)-25(2,24)	1424.632	0.007	16(1,16)-17(1,17)	1433.967	0.013	5(2, 4)-6(2, 5)	1444.895	-0.001
19(6,13)-20(6,14)	1424.632	0.004	16(0,16)-17(0,17)	1433.967	0.013	4(2, 2)-5(2, 3)	1445.364	0.027
23(2,21)-24(2,22)	1424.756	0.023	15(2,14)-16(2,15)	1434.095	-0.006	5(0, 5)-6(0, 6)	1445.618	0.000
23(3,21)-24(3,22)	1424.756	0.023	12(4, 8)-13(4, 9)	1434.095	0.016	5(1, 5)-6(1, 6)	1445.618	-0.022
19(8,12)-20(8,13)	1424.756	-0.017	15(1,14)-16(1,15)	1434.095	-0.006	4(3, 1)-5(3, 2)	1445.618	0.009
21(4,17)-22(4,18)	1424.945	-0.000	14(2,12)-15(2,13)	1434.237	-0.010	4(3, 2)-5(3, 3)	1445.817	0.001
19(7,13)-20(7,14)	1425.233	-0.024	14(3,12)-15(3,13)	1434.237	-0.013	4(4, 0)-5(4, 1)	1445.817	0.002
18(8,10)-19(8,11)	1425.233	0.024	13(4,10)-14(4,11)	1434.399	-0.019	4(4, 1)-5(4, 2)	1445.817	-0.010
18(6,12)-19(6,13)	1425.538	0.002	12(6, 7)-13(6, 8)	1434.698	0.013	4(2, 3)-5(2, 4)	1446.089	0.012
23(2,22)-24(2,23)	1425.648	-0.023	12(7, 5)-13(7, 6)	1434.698	-0.019	4(0, 4)-5(0, 5)	1446.692	0.020
23(1,22)-24(1,23)	1425.648	-0.023	15(0,15)-16(0,16)	1434.991	-0.017	3(2, 1)-4(2, 2)	1446.806	-0.012
22(2,20)-23(2,21)	1425.779	-0.006	15(1,15)-16(1,16)	1434.991	-0.017	3(1, 2)-4(1, 3)	1446.904	-0.021
22(3,20)-23(3,21)	1425.779	-0.006	12(8, 5)-13(8, 6)	1434.991	-0.027	3(2, 2)-4(2, 3)	1447.279	-0.021
21(3,18)-22(3,19)	1425.896	-0.004	13(2,11)-14(2,12)	1435.282	-0.025	3(0, 3)-4(0, 4)	1447.715	-0.003
21(4,18)-22(4,19)	1425.896	-0.004	12(3, 9)-13(3,10)	1435.282	-0.025	3(1, 3)-4(1, 4)	1447.823	-0.001
20(4,16)-21(4,17)	1426.017	0.015	12(4, 9)-13(4,10)	1435.516	-0.005	2(1, 1)-3(1, 2)	1448.261	0.018
19(5,14)-20(5,15)	1426.017	0.018	11(6, 5)-12(6, 6)	1435.876	0.005	2(2, 1)-3(2, 2)	1448.583	0.018
18(6,14)-20(6,15)	1426.136	0.029	14(1,14)-15(1,15)	1436.080	0.015	2(0, 2)-3(0, 3)	1448.796	0.010
19(1,11)-19(1,12)	1426.136	-0.019	14(0,14)-15(0,15)	1436.080	0.015	2(1, 2)-3(1, 3)	1448.978	0.027
			13(2,12)-14(2,13)	1436.218	-0.004	1(1, 0)-2(1, 1)	1449.634	0.004
			13(1,12)-14(1,13)	1436.218	-0.004	0(0, 0)-1(0, 1)	1451.192	0.014

Table 3 (continued)

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	OBS	O-C	$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	OBS	O-C	$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	OBS	O-C
R-Branch			13(1,12)-12(1,11)	1467.742	0.000	22(3,20)-21(3,19)	1478.260	-0.020
			14(0,14)-13(0,13)	1468.050	0.011	19(8,12)-18(8,11)	1478.260	-0.016
			14(1,14)-13(1,13)	1468.050	0.011	20(6,15)-19(6,14)	1478.437	0.008
2(1,2)-1(1,1)	1454.884	0.008	11(4,7)-10(4,6)	1468.050	-0.025	19(6,13)-18(6,12)	1478.631	0.014
2(0,2)-1(0,1)	1455.044	0.002	13(2,11)-12(2,10)	1468.572	0.021	23(1,22)-22(1,21)	1478.631	0.008
2(1,1)-1(1,0)	1455.347	0.006	12(8,5)-11(8,4)	1468.689	-0.003	23(2,22)-22(2,21)	1478.631	0.008
3(2,2)-2(2,1)	1456.434	0.010	12(8,4)-11(8,3)	1468.689	-0.004	21(5,17)-20(5,16)	1478.736	0.011
4(2,3)-3(2,2)	1457.681	0.003	12(6,7)-11(6,6)	1468.784	0.028	25(4,17)-24(4,16)	1478.736	0.009
4(3,2)-3(3,1)	1457.866	0.022	15(1,15)-14(1,14)	1469.125	-0.002	24(1,24)-23(1,23)	1478.991	0.014
4(2,2)-3(2,1)	1458.124	-0.009	15(0,15)-14(0,14)	1469.125	-0.002	24(0,24)-23(0,23)	1478.991	0.014
5(0,5)-4(0,4)	1458.301	-0.011	14(2,12)-13(2,11)	1469.624	0.002	19(8,11)-18(8,10)	1478.991	0.017
5(2,4)-4(2,3)	1458.905	0.012	14(3,12)-13(3,11)	1469.624	0.008	23(2,21)-22(2,20)	1479.354	-0.014
5(1,4)-4(1,3)	1459.218	0.004	13(5,9)-12(5,8)	1469.894	0.024	23(3,21)-22(3,20)	1479.354	-0.014
5(4,2)-4(4,1)	1459.218	-0.001	15(2,14)-14(2,13)	1469.894	-0.014	21(6,16)-20(6,15)	1479.521	0.017
5(4,1)-4(4,0)	1459.218	-0.001	15(1,14)-14(1,13)	1469.894	-0.014	21(5,16)-20(5,15)	1479.521	-0.016
6(1,6)-5(1,5)	1459.362	0.000	13(8,6)-12(8,5)	1470.055	-0.005	24(2,23)-23(2,22)	1479.699	-0.017
6(0,6)-5(0,5)	1459.362	-0.015	13(8,5)-12(8,4)	1470.055	-0.009	24(1,23)-23(1,22)	1479.699	-0.017
5(3,2)-4(3,1)	1459.362	-0.000	13(7,6)-12(7,5)	1470.174	0.010	25(1,25)-24(1,24)	1480.081	0.005
5(2,2)-4(2,1)	1459.580	-0.004	14(3,11)-13(3,10)	1470.493	0.012	25(0,25)-24(0,24)	1480.081	0.005
6(2,5)-5(2,4)	1460.065	-0.000	13(4,9)-12(4,8)	1470.493	-0.009	21(7,15)-20(7,14)	1480.249	0.002
6(1,5)-5(1,4)	1460.316	0.008	13(6,7)-12(6,6)	1470.493	-0.013	22(6,17)-21(6,16)	1480.558	-0.015
7(1,7)-6(1,6)	1460.443	0.000	15(2,13)-14(2,12)	1470.684	-0.010	20(7,13)-19(7,12)	1480.558	0.010
7(0,7)-6(0,6)	1460.443	-0.007	15(3,13)-14(3,12)	1470.684	-0.010	28(8,12)-19(8,11)	1480.558	-0.012
6(3,4)-5(3,3)	1460.443	-0.026	16(2,15)-15(2,14)	1470.995	0.000	25(1,24)-24(1,23)	1480.834	0.022
6(2,4)-5(2,3)	1460.960	0.005	16(1,15)-15(1,14)	1470.995	0.000	25(2,24)-24(2,23)	1480.834	0.022
7(2,6)-6(2,5)	1461.208	0.005	14(6,9)-13(6,8)	1471.414	-0.013	26(1,26)-25(1,25)	1481.173	-0.002
7(1,6)-6(1,5)	1461.344	-0.002	16(3,14)-15(3,13)	1471.770	-0.005	22(7,16)-21(7,15)	1481.335	-0.004
8(1,8)-7(1,7)	1461.523	-0.005	16(2,14)-15(2,13)	1471.770	-0.006	25(3,23)-24(3,22)	1481.549	0.000
8(0,8)-7(0,7)	1461.523	0.009	14(6,8)-13(6,7)	1472.076	-0.019	25(2,23)-24(2,22)	1481.549	0.000
7(3,5)-6(3,4)	1461.740	0.015	17(2,16)-16(2,15)	1472.076	-0.004	23(6,18)-22(6,17)	1481.624	-0.018
7(4,4)-6(4,3)	1461.931	0.011	17(1,16)-16(1,15)	1472.076	-0.004	23(5,18)-22(5,17)	1481.624	-0.024
7(5,3)-6(5,2)	1461.931	0.001	15(5,11)-14(5,10)	1472.232	0.020	24(5,20)-23(5,19)	1481.941	-0.011
7(5,2)-6(5,1)	1461.931	0.015	18(1,18)-17(1,17)	1472.418	0.016	24(4,20)-23(4,19)	1481.941	-0.011
7(6,2)-6(6,1)	1461.931	0.015	18(0,18)-17(0,17)	1472.418	0.016	27(1,27)-26(1,26)	1482.295	0.017
7(6,1)-6(6,0)	1461.931	-0.012	16(4,13)-15(4,12)	1472.554	-0.025	27(0,27)-26(0,26)	1482.295	0.017
7(4,3)-6(4,2)	1462.054	-0.012	17(3,15)-16(3,14)	1472.554	-0.009	26(3,24)-25(3,23)	1482.617	-0.022
9(0,9)-8(0,8)	1462.605	-0.005	17(2,15)-16(2,14)	1472.834	-0.023	26(2,24)-25(2,23)	1482.617	-0.022
9(1,9)-8(1,8)	1462.605	-0.004	15(7,9)-14(7,8)	1472.834	-0.022	25(5,21)-24(5,20)	1483.028	-0.002
8(3,6)-7(3,5)	1462.955	0.008	15(8,8)-14(8,7)	1472.834	0.013	27(1,26)-26(1,25)	1483.028	0.024
8(4,5)-7(4,4)	1463.269	0.021	18(1,17)-17(1,16)	1473.158	-0.010	27(2,26)-26(2,25)	1483.028	0.024
8(5,4)-7(5,3)	1463.269	-0.017	15(7,8)-14(7,7)	1473.158	0.005	25(4,21)-24(4,20)	1483.028	-0.002
8(6,3)-7(6,2)	1463.269	-0.000	18(2,17)-17(2,16)	1473.158	-0.010	28(1,28)-27(1,27)	1483.398	0.018
8(6,2)-7(6,1)	1463.269	-0.002	16(5,12)-15(5,11)	1473.326	-0.001	28(0,28)-27(0,27)	1483.398	0.018
8(7,1)-7(7,0)	1463.269	-0.005	16(4,12)-15(4,11)	1473.502	0.012	24(6,18)-23(6,17)	1483.517	0.001
8(7,2)-7(7,1)	1463.269	-0.005	19(1,19)-18(1,18)	1473.502	0.007	27(3,25)-26(3,24)	1483.745	0.014
8(2,8)-7(2,7)	1463.385	0.027	15(5,10)-14(5,9)	1473.502	-0.001	27(2,25)-26(2,24)	1483.745	0.014
8(4,4)-7(4,3)	1463.569	-0.017	17(3,14)-16(3,13)	1473.634	-0.013	28(2,27)-27(2,26)	1484.115	0.013
10(0,10)-9(0,9)	1463.685	-0.008	17(4,14)-16(4,13)	1473.634	-0.006	26(5,22)-25(5,21)	1484.115	0.004
10(1,10)-9(1,9)	1463.685	-0.007	15(6,9)-14(6,8)	1473.634	-0.026	26(4,22)-25(4,21)	1484.115	0.004
9(3,7)-8(3,6)	1464.101	-0.016	18(3,16)-17(3,15)	1473.933	-0.006	29(1,29)-28(1,28)	1484.481	-0.001
10(1,9)-9(1,8)	1464.533	0.026	16(6,11)-15(6,10)	1473.933	0.005	29(0,29)-28(0,28)	1484.481	-0.001
9(4,6)-8(4,5)	1464.533	-0.013	18(2,16)-17(2,15)	1473.933	-0.006	25(6,19)-24(6,18)	1484.581	0.017
9(5,5)-8(5,4)	1464.634	-0.019	16(8,9)-15(8,8)	1474.210	0.003	28(2,26)-27(2,25)	1484.840	0.016
9(6,4)-8(6,3)	1464.634	-0.000	16(7,10)-15(7,9)	1474.226	0.025	26(5,21)-25(5,20)	1484.840	-0.016
9(6,3)-8(6,2)	1464.634	-0.008	20(0,20)-19(0,19)	1474.586	-0.002	29(2,28)-28(2,27)	1485.196	-0.003
9(7,3)-8(7,2)	1464.634	0.010	16(5,11)-15(5,10)	1474.586	0.002	27(5,23)-26(5,22)	1485.196	0.004
9(7,2)-8(7,1)	1464.634	0.010	20(1,20)-19(1,19)	1474.586	-0.002	27(4,23)-26(4,22)	1485.196	0.004
9(8,2)-8(8,1)	1464.634	-0.004	18(3,15)-17(3,14)	1474.711	-0.009	29(1,28)-28(1,27)	1485.196	-0.003
9(8,1)-8(8,0)	1464.634	-0.008	18(4,15)-17(4,14)	1474.711	-0.006	26(7,20)-25(7,19)	1485.586	-0.028
11(0,11)-10(0,10)	1464.769	-0.008	19(3,17)-18(3,16)	1475.034	0.010	30(0,30)-29(0,29)	1485.586	-0.000
9(5,4)-8(5,3)	1464.769	0.002	17(6,12)-16(6,11)	1475.122	0.018	30(1,30)-29(1,29)	1485.586	-0.000
11(1,11)-10(1,10)	1464.769	-0.008	16(6,10)-15(6,9)	1475.122	0.000	27(5,22)-26(5,21)	1485.926	-0.004
9(3,6)-8(3,5)	1465.189	0.013	18(4,14)-17(4,13)	1475.529	-0.010	27(6,22)-26(6,21)	1485.926	-0.004
10(2,8)-9(2,7)	1465.418	0.002	18(5,14)-17(5,13)	1475.529	0.027	30(1,29)-29(1,28)	1486.277	-0.022
11(2,10)-10(2,9)	1465.575	-0.001	17(7,11)-16(7,10)	1475.529	0.024	28(5,24)-27(5,23)	1486.277	0.003
11(1,10)-10(1,9)	1465.575	-0.006	21(1,21)-20(1,20)	1475.672	-0.012	28(4,24)-27(4,23)	1486.277	0.003
12(0,12)-11(0,11)	1465.851	-0.012	21(0,21)-20(0,20)	1475.672	-0.012	31(0,31)-30(0,30)	1486.671	-0.008
12(1,12)-11(1,11)	1465.851	-0.012	19(3,16)-18(3,15)	1475.791	-0.005	27(7,21)-26(7,20)	1486.671	-0.008
10(5,6)-9(5,5)	1465.983	-0.026	17(8,9)-16(8,8)	1475.791	-0.007	31(1,31)-30(1,30)	1486.671	-0.011
10(7,4)-9(7,3)	1465.983	0.002	20(2,18)-19(2,17)	1476.097	-0.010	28(6,23)-27(6,22)	1487.008	0.002
10(7,3)-9(7,2)	1465.983	0.000	18(6,13)-17(6,12)	1476.097	-0.010	28(5,23)-27(5,22)	1487.008	0.002
10(8,3)-9(8,2)	1465.983	0.000	19(6,13)-18(6,12)	1476.221	-0.017	29(4,25)-28(4,24)	1487.385	0.027
11(2,9)-10(2,8)	1466.421	-0.020	17(6,11)-16(6,10)	1476.452	0.013	31(2,30)-30(2,29)	1487.385	-0.014
12(2,11)-11(2,10)	1466.652	-0.005	21(1,20)-20(1,19)	1476.452	0.014	31(1,30)-30(1,29)	1487.385	-0.014
10(4,6)-9(4,5)	1466.652	-0.008	19(5,15)-18(5,14)	1476.580	0.002	28(6,22)-27(6,21)	1487.747	-0.001
12(1,11)-11(1,10)	1466.957	0.006	21(2,20)-20(2,19)	1476.580	-0.013	28(7,22)-27(7,21)	1487.747	-0.000
13(0,13)-12(0,12)	1466.957	0.006	19(4,15)-18(4,14)	1476.580	-0.007	29(6,24)-28(6,23)	1488.088	0.005
11(5,7)-10(5,6)	1467.360	0.021	21(3,19)-20(3,18)	1477.186	-0.007	29(5,24)-28(5,23)	1488.088	0.005
11(6,6)-10(6,5)	1467.360	-0.024	21(2,19)-20(2,18)	1477.186	-0.007	32(2,31)-31(2,30)	1488.490	-0.010
11(7,5)-10(7,4)	1467.360	0.011	19(6,14)-18(6,13)	1477.359	0.015	32(1,31)-31(1,30)	1488.490	-0.010
11(7,4)-10(7,3)	1467.360	0.005	18(8,10)-17(8,9)	1477.359	-0.002	30(6,25)-29(6,24)	1489.166	0.005
11(8,4)-10(8,3)	1467.360	0.026	22(1,21)-21(1,20)	1477.546	0.016	30(5,25)-29(5,24)	1489.166	0.005
11(8,3)-10(8,2)	1467.360	0.026	22(2,21)-21(2,20)	1477.546	0.016	33(2,32)-32(2,31)	1489.583	-0.019
12(2,10)-11(2,9)	1467.470	-0.017	20(4,16)-19(4,15)	1477.650	-0.007	32(4,28)-31(4,27)	1490.634	0.021
12(3,10)-11(3,9)	1467.470	0.018	20(5,16)-19(5,15)	1477.650	-0.000	32(5,28)-31(5,27)	1490.634	0.021
11(3,8)-10(3,7)	1467.470	0.006	22(2,20)-21(2,19)	1478.260	-0.020			
11(6,5)-10(6,4)	1467.470	0.004						
13(2,12)-12(2,11)	1467.742	0.001						

microwave data [1], these lines could be unambiguously assigned.

Keeping the molecular constants for the ground state fixed, the constants for the level $\nu_3 = 1$ were refined by the least-squares method and the above procedure repeated with successively larger sets of assigned transitions. At each step of the assignment procedure, the experimental spectrum was compared with the computed one, obtained by a Lorentz line-shape function convoluted with a rectangular line shape function and adjusting thereby with the experimental parameters.

In Table 2, the molecular constants obtained from the least-squares analysis of more than 500 assigned transitions are reported. The standard deviation of the fit (0.014 cm^{-1}) is compatible with the resolution of the spectrum. The assignment of the transitions was completed up to $K_a = 8$ and $J = 35$. Due to the medium resolution of the spectrum, the quartic constant Δ_K and the sextic centrifugal distortion constants could not be included in the least-squares analysis.

Table 3 reports the observed values of the assigned transitions included in the fitting procedure together with the difference between these values and those computed from the adjusted constants of Table 2. The difference between the observed and calculated line positions is consistent with the instrumental resolution. A part of the spectrum in the P branch region of the ν_3 band compared with the

computed spectrum is shown in Figure 4. Considering the fact that the ν_3 band of $\text{H}_2\text{C}^{14}\text{N}^{15}\text{N}$ and no hot bands of $\text{H}_2\text{C}^{15}\text{N}_2$ have been taken into account the computed spectrum simulates the observed one very well.

The determination of the rotational and centrifugal distortion constants for the first vibrational state of the methylene bending fundamental in $^{15}\text{N}_2$ -diazirine has confirmed the validity of the methods developed for the analysis of this asymmetric top molecule. The extension of the investigation to the other fundamental modes of diazirine and its isotopomers will give a complete representation of these molecules in their vibrational states. The molecular parameters obtained from these analyses will be also helpful for the determination of the molecular force field in the normal coordinate analysis of diazirine [11].

Acknowledgements

The authors would like to express their thanks to Prof. Dr. Manfred Winnewisser for stimulating discussions and Dr. Brenda P. Winnewisser for critically reading the manuscript. The experimental work was supported by funds of Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie. Calculations were carried out at the Hochschulrechenzentrum of the Justus Liebig University of Giessen.

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