The Structure of Gaseous 2-Azetidinone as Studied by Microwave Spectroscopy, Electron Diffraction and *Ab Initio* Calculations

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The simplest four-member β-lactam, 2-azetidinone, has been studied by microwave spectroscopy, electron diffraction and *ab initio* quantum chemical computations at the 6-31G** level. An accurate r_g structure has been determined by making use of rotational constants from five isotopic species and electron diffraction data in a joint analysis. The molecule is planar (apart from the methylene group hydrogen atoms) in the gas phase. The dipole moment and ^{14}N quadrupole coupling constants have been determined. Numerous vibrationally excited states have also been assigned for the parent and one deuterated species. The ring-puckering potential was determined from the vibrationally excited states of the puckering vibration.

2-Azetidinone is the simplest four-membered lactam. There is great biological interest attached to this compound, because it is part of a series of antibiotics such as e.g. penicillins and cephalosporins.[1] The biological activity shown by these antibiotics is presumed to depend on the β-lactam moiety.[1]

The structural properties of 2-azetidinone have received considerable attention, and very recently its crystal structure was determined with high accuracy.[2] The molecule is completely planar in the crystal. In the crystal structure, the molecules are paired into centrosymmetric dimers linked by N–H···O hydrogen bonds. The planes of the two molecules are parallel but not quite coplanar, being mutually displaced by 36 pm.[2] The infrared and Raman spectra of parent 2-azetidinone as well as several isotopomers have also been studied recently both in the crystalline phase and in solution, and a force field was determined.[3] MNDO quantum chemical calculations have been made for the title compound,[4] as have *ab initio* computations.[5] In the most recent of these,[5b] the rather large 6-31G basis set with full geometry optimization was employed.

No structural studies in the gas phase using microwave (MW) or electron diffraction (ED) have been reported. Due to the rather great chemical and biological interest in β-lactams, such studies were thought to be worthwhile.

Ab initio calculations using the elaborate 6-31G** basis set with full geometry optimization were also made in order to benefit from the chemical insight such high-level computations offer. Special attention was paid to the question of whether this molecule has a planar heavy-atom ring skeleton in the free state, and whether the atomic arrangement around the nitrogen atom is planar.

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Experimental

Microwave experiment. The samples used both in the MW and ED experiments were purchased from Aldrich Chemical Co. The samples, which were stated to be 99 % pure, were used as received. The vapour pressure is only a few Pa at room temperature. This makes it impossible to study 2-azetidinone much below this temperature with our instrument. The MW spectra were thus recorded at room temperature at a pressure of about 1 Pa. The spectrometer employed was an improved version of the one described in Ref. 6. With this instrument quadrupole splittings greater than about 0.60 MHz were resolved in favourable cases. The 18.0–38.0 GHz spectral region was studied extensively. The hydrogen atom attached to the nitrogen atom exchanges easily with deuterium using heavy water. This N-deuterated species was thus produced by exchange with heavy water in the absorption cell.

Electron diffraction experiment. The electron-diffraction data were recorded on a Balzers Eldigraph KD-G2 apparatus[7] using Kodak Electron Image photographic plates. The experiment was carried out using nozzle-to-plate distances of 497.95 and 248.02 mm. The nozzle temperatures were approximately 135 °C for the long camera distance, and 148 °C for the middle camera distance. The wave length of the electron beam was 5.898 pm in all experiments. Five plates for both camera distances were used in the structure analysis. The optical densities (D) were recorded on a Joyce Loebl densitometer and processed in the usual way employing a blackness correction of $1 + 0.03D + 0.09D^2 + 0.03D^3$.[8] The molecular scattering intensities were modified with $s/|f_C'||f_O'|$ (Ref. 8), and the backgrounds were subtracted from the modified form

utilizing polynomials of the 9th degree for both camera distances. The intensity data cover the $12.50 \leq s \leq 150.00\ \text{nm}^{-1}$ range with data intervals $\Delta s = 1.25\ \text{nm}^{-1}$ for the long camera distance, and $30.00 \leq s \leq 300.00\ \text{nm}^{-1}$ for the middle camera distance with data intervals $\Delta s = 2.50\ \text{nm}^{-1}$. The elastic scattering factors were calculated by the partial wave method[9] based on analytical Hartree-Fock potentials in the cases of carbon, nitrogen and oxygen.[10] In the case of hydrogen, the electron density for bonded hydrogen was used.[11] The inelastic scattering factors were those of Tavard *et al.*[12]

Method of calculation. The *ab initio* quantum chemical computations were performed using the GAMESS[13] program package. The program used in the present calculations is a revised version prepared by M. W. Schmidt of North Dakota State University and S. Elbert of Iowa State University. The computations were made employing a FPS-164 computer. In order to investigate theoretically whether 2-azetidinone has a planar ring structure, a large and flexible basis set is to be preferred. The rather large basis set 6-31G** (Ref. 14) meets this requirement and was utilized in all the present *ab initio* computations. This basis set has *d*-polarization functions for the first-row elements (C, N, and O) and *p*-polarization functions for hydrogen. The calculated equilibrium geometry was optimized at the Hartree-Fock level of theory by calculating the analytical energy gradients. This geometry was used for calculation of the vibrational frequencies, the dipole moment components along the principal inertial axes and the quadrupole coupling constants. The quadrupole coupling constants for the ^{14}N nucleus were calculated from the components of the electric field gradient along the principal inertial axes at the position of the nitrogen nucleus. A value for the quadrupole moment Q of $2.00 \times 10^{-30}\ \text{m}^2$ was assumed[15] for the ^{14}N nucleus.

Results

Theoretical computations. The *ab initio* calculations predict both the heavy atoms as well as the hydrogen atom attached to the nitrogen nucleus to be completely planar to within less than 1×10^{-3} pm. The parameters for the fully optimized structure are shown in Table 1, which also includes some other parameters of interest obtained from the theoretical computations. The atom numbering is given in Fig. 1.

Microwave spectrum and assignment. The results of the theoretical calculations summarized in Table 1 indicate 2-azetidinone to be a prolate asymmetric rotor with Ray's asymmetry parameter[16] $\varkappa \approx -0.70$, and with a large dipole moment component along the *a* inertial axis and a much smaller one along the *b* axis. The component along the *c* axis is zero since the molecule possesses a symmetry plane and the *c* axis is perpendicular to this plane. It is also predicted (Table 1) that the heavy-atom ring-puckering

Table 1. Structure, total energy, dipole moment, ^{14}N nuclear quadrupole coupling constants and low-frequency vibrational frequencies calculated using *ab initio* calculations employing the 6-31G** basis set.[a]

Bond length / pm		Angle / °	
N1–C2	135.8	∠C2N1C4	96.2
C2–C3	153.3	∠N1C2C3	91.2
C3–C4	154.9	∠C2C3C4	85.6
C4–N1	145.5	∠C3C4N1	87.0
C2–O5	118.6	∠O5C2C3	135.9
N1–H6	99.4	∠H6N1C4	133.0
C3–H7	108.1	∠C2C3H7	114.1
C4–H8	108.4	∠N1C4H8	114.2
		∠H7C3C2O5	63.8[b] from *syn*
		∠H8C4N1H6	63.5[b] from *syn*

Energy of calculated structure / 10^5 kJ mol^{-1}

−6.4571254

Principal inertial axis dipole moment components[c,d] / 10^{-30} C m

μ_a = 13.746 μ_b = 1.298

Quadrupole coupling constants of ^{14}N nucleus / MHz

χ_{aa} = 2.37 χ_{bb} = 2.30

Vibrational frequencies of the three lowest modes of the parent species / cm^{-1}

Ring puckering:	111
N1–H6 out-of-plane vibration:	417
Lowest heavy-atom in-plane vibration:	516

Vibrational frequencies of the three lowest modes of the N1 deuterated species / cm^{-1}

Ring puckering:	108
N1–D6 out-of-plane vibration:	326
Lowest heavy-atom in-plane vibration:	505

[a] See text. [b] Dihedral angle. [c] The principal axes are those calculated from the structure in this table.
[d] 1 Debye = 3.33564×10^{-30} C m.

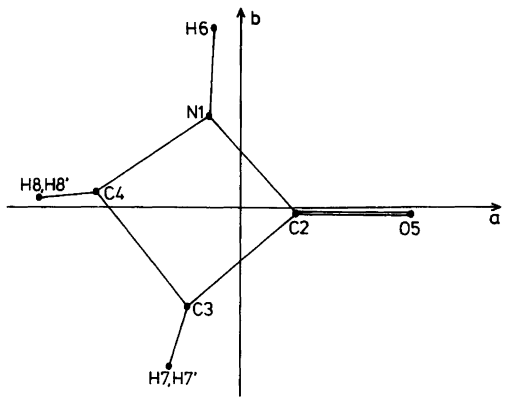

Fig. 1. Projecting of 2-azetidinone in the inertial *a–b* principal axis plane. Atom numbering is indicated.

Table 2. Ground vibrational state spectrum for the parent species of 2-azetidinone.

Transition[a,b]	Observed frequency/MHz	Obs.-calc. frequency/MHz	Centrifugal distortion/MHz
$2_{1,1} \leftarrow 1_{1,0}$	18725.76	0.01	−0.05
$3_{0,3} \leftarrow 2_{0,2}$	25538.46	0.05	−0.05
$3_{1,2} \leftarrow 2_{1,1}$	27982.59	−0.01	−0.13
$3_{1,3} \leftarrow 2_{1,2}$	24132.24	−0.08	−0.07
$3_{2,1} \leftarrow 2_{2,0}$	26776.02	−0.08	−0.19
$3_{2,2} \leftarrow 2_{2,1}$	26157.33	0.12	−0.17
$4_{0,4} \leftarrow 3_{0,3}$	33417.14	0.05	−0.15
$4_{1,3} \leftarrow 3_{1,2}$	37094.79	0.07	−0.26
$4_{1,4} \leftarrow 3_{1,3}$	32017.78	0.02	−0.15
$4_{2,2} \leftarrow 3_{2,1}$	36210.85	0.00	−0.35
$4_{2,3} \leftarrow 3_{2,2}$	34752.42	−0.01	−0.29
$4_{3,1} \leftarrow 3_{3,0}$	35232.63	−0.05	−0.48
$4_{3,2} \leftarrow 3_{3,1}$	35159.45	−0.08	−0.47
$4_{2,3} \leftarrow 4_{0,4}$	33319.72	0.09	−0.45
$5_{2,4} \leftarrow 5_{0,5}$	35602.18	0.05	−0.64
$5_{1,4} \leftarrow 5_{1,5}$	18976.83	−0.07	−0.37
$6_{1,5} \leftarrow 6_{1,6}$	26060.54	0.04	−0.61
$7_{1,6} \leftarrow 7_{1,7}$	33727.52	0.04	−0.92
$8_{3,5} \leftarrow 8_{2,6}$	29985.79	−0.04	−1.56
$8_{2,6} \leftarrow 8_{2,7}$	20733.10	−0.04	−1.13
$9_{3,6} \leftarrow 9_{2,7}$	29380.02	−0.02	−1.91
$9_{2,7} \leftarrow 9_{2,8}$	28352.28	0.14	−1.73
$10_{3,7} \leftarrow 10_{2,8}$	30193.50	−0.08	−2.42
$10_{2,8} \leftarrow 10_{2,9}$	36734.62	−0.09	−2.50
$11_{3,8} \leftarrow 11_{2,9}$	32696.60	0.10	−3.13
$11_{3,8} \leftarrow 11_{3,9}$	20370.51	0.07	−2.25
$12_{3,9} \leftarrow 12_{2,10}$	37011.50	−0.13	−4.09
$12_{3,9} \leftarrow 12_{3,10}$	28313.33	0.03	−3.36
$13_{3,10} \leftarrow 13_{3,11}$	37260.15	0.04	−4.77
$14_{4,10} \leftarrow 14_{4,11}$	18575.80	0.01	−3.55
$15_{4,11} \leftarrow 15_{4,12}$	26512.29	0.05	−5.30
$16_{4,12} \leftarrow 16_{4,13}$	35742.31	−0.05	−7.51
$18_{5,13} \leftarrow 18_{5,14}$	23511.29	−0.09	−7.28
$19_{5,14} \leftarrow 19_{5,15}$	32656.91	0.01	−10.41
$21_{6,15} \leftarrow 21_{6,16}$	19869.50	−0.02	−9.01
$22_{6,16} \leftarrow 22_{6,17}$	28526.44	−0.08	−13.11
$25_{7,18} \leftarrow 25_{7,19}$	23892.24	−0.04	−15.28
$26_{7,19} \leftarrow 26_{7,20}$	33633.04	−0.11	−21.62
$28_{8,20} \leftarrow 28_{8,21}$	19252.55	−0.03	−16.65
$29_{8,21} \leftarrow 29_{8,22}$	28031.31	0.05	−24.14
$32_{9,23} \leftarrow 32_{9,24}$	22536.23	−0.02	−25.48
$33_{9,24} \leftarrow 33_{9,25}$	32287.76	−0.02	−36.17
$36_{10,26} \leftarrow 36_{10,27}$	25941.33	0.00	−37.27
$37_{10,27} \leftarrow 37_{10,28}$	36662.71	0.11	−51.98
$39_{11,28} \leftarrow 39_{11,29}$	20200.82	0.02	−36.68
$40_{11,29} \leftarrow 40_{11,30}$	29467.14	0.02	−52.57
$43_{12,31} \leftarrow 43_{12,32}$	22976.40	0.02	−50.99
$44_{12,32} \leftarrow 44_{12,33}$	33113.11	0.03	−72.01
$47_{13,34} \leftarrow 47_{13,35}$	25865.46	0.01	−69.04
$48_{13,35} \leftarrow 48_{13,36}$	36878.82	0.08	−96.22
$50_{14,36} \leftarrow 50_{14,37}$	19677.82	0.02	−63.80
$51_{14,37} \leftarrow 51_{14,38}$	28867.61	0.03	−91.41
$54_{15,39} \leftarrow 54_{15,40}$	22015.12	0.00	−83.85
$55_{15,40} \leftarrow 55_{15,41}$	31982.52	0.04	−118.74
$58_{16,42} \leftarrow 58_{16,43}$	24453.68	−0.03	−108.27
$59_{16,43} \leftarrow 59_{16,44}$	35209.95	0.00	−151.70
$61_{17,44} \leftarrow 61_{17,45}$	18282.95	0.03	−95.69
$62_{17,45} \leftarrow 62_{17,46}$	26993.60	−0.10	−137.67
$65_{18,47} \leftarrow 65_{18,48}$	20236.99	0.02	−121.19
$66_{18,48} \leftarrow 66_{18,49}$	29635.18	−0.10	−172.69
$69_{19,50} \leftarrow 69_{19,51}$	22278.88	−0.03	−151.54
$70_{19,51} \leftarrow 70_{19,52}$	32378.60	−0.08	−214.03
$73_{20,53} \leftarrow 73_{20,54}$	24409.27	−0.02	−187.35
$77_{21,56} \leftarrow 77_{21,57}$	26628.82	0.14	−229.28

[a] ±0.10 MHz. [b] See text for "correction" to quadrupole splittings.

vibration is the only very low-frequency vibration, with a frequency of about 111 cm^{-1} which is close to the value of 94 cm^{-1} calculated by the Japanese workers.[3] The *a*-type *R*-branch spectra of the ground and several excited states of the ring-puckering vibration were thus expected to be the dominant feature of this MW spectrum. These strong ^aR spectra are centered around frequencies given by approximately $(J+1)\times(B+C)/2$. In addition to these ^aR spectra, *a*-type *Q*-branch transitions belonging to the ground as well as to excited states were expected to be scattered all over the investigated spectral range and to occur with considerable intensities, since there are three rather low-frequency normal modes, as shown in Table 1. These *Q*-branch spectra are much richer, but somewhat weaker than the comparatively strong ^aR spectra of the same vibrational state. A relatively dense and strong spectrum was thus predicted for 2-azetidinone and this was also found to be the case.

The assignment of this spectrum was easily made. The ground vibrational state spectrum is summarized in Table 2.* It was found, as expected, that the strongest transitions present are the *a*-type *R*-branch $J = 4 \leftarrow 3$ transitions whose low-K_{-1} members have peak absorption coefficients of roughly 2×10^{-6} cm^{-1} at room temperature. As can be seen in Table 2, the highest J value which could be assigned was $J = 77$. Higher-J *a*-type *Q*-branch lines were searched for but they could not be identified, presumably because of insufficient intensities caused by unfavourable Boltzmann factors. Several of the ^aQ-branch lines with intermediate values for the J quantum number were found to be split or to posses "shoulders", due to quadrupole interaction. "Corrections" for quadrupole interactions were made in several cases for the intermediate-J *Q*-branch lines which displayed the largest quadrupole splittings, employing Rudolph's formula.[17] The "corrected" frequencies were then used in the least-squares fit. Some of the frequencies appearing in Table 2 have been "corrected", and the frequencies listed in this table may deviate slightly from those actually observed. The *b*-type transitions are all very weak since $\mu_b = 1.26(11)\times10^{-30}$ C m (see dipole moment section below). The strongest *b*-type transitions are the intermediate-J *Q*-branch transitions. Their frequencies could be predicted very accurately from the strong *a*-type transitions. Identifications of these *b*-type lines could be made only for the strongest ones belonging to the ground vibrational state. A search was made for the strongest *b*-type lines of the low-J ^bR-branch transitions as well, but they were too weak to be assigned, although their frequencies could be very accurately predicted. A total of 64 transitions were ultimately identified, as shown in Table 2.

The spectroscopic constants (*A*-reduction I^r-representation[18]) found by a least-squares fit of the transitions shown in Table 2 are listed in Table 3. The centrifugal distortions of the observed transitions are comparatively small, as seen in Table 2. Only quartic centrifugal distortion constants were therefore employed in the fitting procedure. The centrifugal distortion constants (Table 3) are rather poorly determined with the exception of δ_J. Some of them are also strongly correlated. This is presumably a result of the fact that rather few types of transitions are present with sufficient intensities in this spectrum.

Table 3. Spectroscopic constants[a,b] for the ground state of the parent and deuterated species of 2-azetidinone.

Species	Parent	Deuterated
No. of transitions	64	48
R.m.s.[c]/MHz	0.066	0.092
A_0/MHz	12161.348(12)	11129.123(47)
B_0/MHz	5003.341(11)	4998.833(17)
C_0/MHz	3715.787(11)	3611.599(17)
Δ_J/kHz	0.79(37)	2.29(59)
Δ_{JK}/kHz	3.39(21)	3.98(66)
Δ_K/kHz	7.2(11)	1.0(29)
δ_J/kHz	0.1314(66)	0.161(27)
δ_K/kHz	2.70(14)	1.94(53)
$I_a + I_b - I_c$[d]/10^{-20} m² u	6.55583(14)	6.55766(40)

[a]Uncertainties represent one standard deviation. [b]*A*-reduction I^r-representation. [c]Root-mean square deviation. [d]Conversion factor 505379.05×10^{-20} m² u MHz.

Vibrationally excited states. The ground-state transitions were accompanied by several intense satellite transitions presumably belonging to vibrationally excited states of the molecule. Many of the low-J ^aR-branch transitions displayed resolved Stark effects and their assignments were straightforward. A total of nine vibrationally excited states were assigned, as shown in Tables 4 and 5 which list the spectroscopic constants obtained for them. High-J *Q*-branch lines of the *a*-type variety were identified for most of these excited states, as noted in the legend to Table 4. The centrifugal distortion constants given in Table 5 are generally of a rather poor quality, presumably for reasons similar to those discussed above for the ground-state transitions.

It is seen in Tables 4 and 5 that five successively excited states of the ring-puckering vibration have been identified. The reasons for these assignments are rather obvious: The first excited state was found to be 93(10) cm^{-1} higher in energy than the ground state, as determined by relative intensity measurements performed as described in Ref. 19. This is close to the theoretical value presented in Table 1 (111 cm^{-1}) and nearly identical with the value (94 cm^{-1}) found in the force-field calculation.[3] The frequency observed in the Raman spectrum of the solid is 119 cm^{-1} (Ref. 3). It should be remembered[2] that 2-azetidinone is strongly hydrogen-bonded in the crystalline state, so that the puckering vibration is expected to have a somewhat different frequency in the gaseous state than in the crystal.

*The spectra of vibrationally excited states and of the isotopic species are available from the authors upon request, or from the Molecular Spectra Data Center, Bldg. 221, Room B 268, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A., where they have been deposited.

Table 4. Rotational constants[a,b] (MHz) and Δ[c] (10^{-20} m^2 u) for vibrationally excited states of the parent species of 2-azetidinone.

Vib. state	*A*	*B*	*C*	Δ
$P=1$[d]	12091.230(34)	5013.1724(97)	3725.9105(98)	6.96831(22)
$P=2$[e]	12030.772(76)	5020.804(16)	3734.850(16)	7.34978(45)
$P=3$[f]	11982.170(91)	5026.394(15)	3742.246(15)	7.67564(49)
$P=4$[g]	11936.31(41)	5031.7186(97)	3749.388(10)	7.9885(18)
$P=5$[h]	11890.2(15)	5037.110(39)	3756.591(32)	8.3037(68)
$0=1$[i]	12121.338(92)	5004.507(17)	3718.441(17)	6.76657(53)
$I=1$[j]	12169.304(23)	5004.1513(44)	3710.6693(44)	6.32476(16)
$P=1+0=1$[k]	12053.35(67)	5013.368(18)	3728.181(20)	7.1783(31)
$P=1+I=1$[l]	12100.08(94)	5013.829(25)	3720.612(25)	6.7313(42)

[a,b]Comments as for Table 3. [c]$\Delta = I_a + I_b - I_c$. Same conversion factor as used for this entry in Table 3. [d]First excited state of ring-puckering vibration (r–p). 48 transitions with a maximum value of $J=69$ and a root-mean square deviation of 0.059 MHz were used to derive these rotational constants. For the remainder of the entries of this table the corresponding parameters are: [e]Second excited r–p; 39; $J=57$; 0.093 MHz. [f]Third excited r–p; 34; $J=50$; 0.093 MHz. [g]Fourth excited r–p; 9; $J=4$; 0.069 MHz. [h]Fifth excited r–p; 6; $J=4$; 0.189 MHz. [i]First excited state of N1–H6 out-of-plane vibration; 37; $J=58$; 0.105 MHz. [j]First excited state of lowest in-plane vibration; 27; $J=59$; 0.090 MHz. [k]First excited r–p plus first excited state of the second lowest out-of-plane vibration; 7; $J=4$; 0.168 MHz. [l]First excited r–p plus first excited state of the lowest in-plane vibration; 8; $J=4$; 0.118 MHz.

The second excited state of the puckering vibration is 200 (15) cm^{-1}, and the third excited state is 327(50) cm^{-1} above the ground vibrational state, as determined by relative intensity measurements.[19] Moreover, $\Delta = I_a + I_b - I_c$ is seen in Table 4 to increase successively as the puckering mode becomes successively excited. This is typical for an out-of-plane vibration.[20]

Excited states of two other normal modes have also been assigned as shown in Table 4. The first excited state of the second lowest out-of-plane fundamental was found to have a frequency of 367(60) cm^{-1} by relative intensity measurements.[19] This is rather close to the value of 417 cm^{-1} found in the theoretical computations (Table 1) for the normal mode, which can best be described as the N1–H6 out-of-plane bending mode. In the crystal, this mode occurs at 690 cm^{-1} according to the IR investigation.[3] This high value is not surprising, since H6 is involved in hydrogen bonding in the crystal.[2] Moreover, Δ is 6.76657(53)$\times 10^{-20}$ m^2 u (Table 4) for this excited state, slightly higher than the value of 6.55584(14)$\times 10^{-20}$ m^2 u found for the ground vibrational state (Table 3), which is typical for an out-of-plane vibration.[20]

The first vibrationally excited state of the lowest heavy-atom in-plane vibration is characterized by the fact that $\Delta = 6.32476(16)\times 10^{-20}$ m^2 u (Table 4), which is lower than the ground-state value of 6.55584(14)$\times 10^{-20}$ m^2 u. Such a decrease is typical for in-plane vibrations.[20] Relative intensity measurements[19] yield a value of 440(60) cm^{-1} for this mode, as compared to 516 cm^{-1} obtained in the *ab initio* calculations (Table 1). The Raman frequency of this normal mode of solid 2-azetidinone is assigned as 479 cm^{-1} (Ref. 3).

It is noted that the frequencies of the three lowest vibrational modes determined by relative intensity measurements[19] are lower than the *ab initio* values in Table 1. It has been found[21] that the 6-31G** basis set generally yields vibrational frequencies which are too high by 10–15 %, in accord with the present findings.

Finally, Table 4 contains rotational constants for the combination states of the puckering and the N1–H6 bend-

Table 5. Centrifugal distortion constants[a–c] (kHz) for vibrationally excited states of the parent species of 2-azetidinone.

Vib. state	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
$P=1$	0.88(36)	6.29(46)	−10.4(26)	0.240(15)	0.17(39)
$P=2$	0.77(58)	4.18(82)	1.7(48)	0.175(29)	1.82(77)
$P=3$	1.21(55)	8.1(12)	−22.7(67)	0.310(40)	−2.2(11)
$P=4$[d]	0.79	3.39	7.2	0.1314	2.70
$P=5$[d]	0.79	3.39	7.2	0.1314	2.70
$0=1$	0.94(62)	5.1(11)	−2.1(64)	0.200(38)	1.45(99)
$I=1$[e]	0.79	3.414(66)	7.2	0.1359(26)	2.70
$P=1+0=1$[d]	0.79	3.39	7.2	0.1314	2.70
$P=1+I=1$[d]	0.79	3.39	7.2	0.1314	2.70

[a,b]Comments as for Table 3. [c]Vibrationally excited states designated the same way as in Table 4. [d]Kept constant at ground-state values shown in Table 3. [e]Only Δ_{JK} and δ_J fitted with the rest of the centrifugal constants kept at the ground-state values listed in Table 3.

Table 6. Rotational constants (MHz) and $\Delta^{a-c}/(10^{-20}\ m^2\ u)$ for vibrationally excited states of the deuterated species of 2-azetidinone.

Vib. state	*A*	*B*	*C*	Δ
$P=1^d$	11077.900(70)	5009.083(21)	3622.518(22)	7.00256(57)
$P=2^e$	11032.658(36)	5016.9798(85)	3631.6140(83)	7.38023(31)
$P=3^f$	10990.47(63)	5023.694(20)	3639.830(21)	7.7356(35)
$P=4^g$	10955.3(19)	5030.031(42)	3646.614(49)	8.0148(94)
$0=1^i$	11109.3(11)	5000.685(30)	3613.492(28)	6.6944(52)
$I=1^j$	11136.8(16)	5000.158(89)	3606.954(63)	6.3391(98)

[a-c]Comments as for Table 4. [d]First excited state of r−p; 37; $J=63$; 0.104 MHz. [e]Second excited r−p; 22; $J=43$; 0.164 MHz. [f]Third excited r−p; 8; $J=4$; 0.124 MHz. [g]Fourth excited r−p; 4; $J=4$; 0.238 MHz. [i]First excited state of N1−H6 out-of-plane bending vibration; $J=4$; 0.144 MHz. [j]First excited state of in-plane bending vibration; 4; $J=4$; 0.180 MHz.

Table 7. Centrifugal distortion constants[a-c](kHz) for vibrationally excited states of the deuterated species of 2-azetidinone.

Vib. state	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
$P=1$	1.19(76)	4.9(10)	−3.4(45)	0.201(40)	1.24(82)
$P=2^{d,e}$	2.29	4.11(18)	1.	0.1793(87)	1.94

[a-c]Comments as for Table 4. [d]Only Δ_{JK} and δ_J fitted with the rest of the centrifugal distortion constants kept at the ground-state values listed in Table 3. [e]The centrifugal distortion constants were kept constant at the ground-state values shown in Table 3 for the rest of the vibrationally excited states whose rotational constants are listed in Table 6.

ing vibrations, and for the puckering and the lowest heavy-atom in-plane vibration. The intensities of these combination excited state vibrations were so low that no accurate quantitative relative intensity measurements could be made.

After the above assignments had been made, no strong unassigned lines remained in the spectrum. According to the theoretical computations described above, the fourth lowest normal mode (not reported in Table 1) is predicted to be 614 cm^{-1} higher in energy than the ground vibrational state. The intensities of the transitions of the first excited state of this mode should then be approximately only 4 % of the corresponding intensities of the ground vibrational state. Assignment of such relatively weak transitions is not always easy, because they may often be overlapped by stronger lines. It is thus concluded that the major excited states have properly been accounted for.

Isotopic species. The assignment of the spectrum of the deuterated species (atom No. 6 in Fig. 1) was straightforward. The spectroscopic constants for the ground vibrational state are found in Table 3, whereas the corresponding constants for the vibrationally excited states are given in Tables 6 and 7. The vibrational frequencies as determined by relative intensity measurements[19] were as follows: 97 (10) cm^{-1} for the first excited state of the ring-puckering vibration, 338(70) cm^{-1} for the N1−D6 out-of-plane bending vibration, and 460(80) cm^{-1} for the lowest in-plane bending vibration.

The ^{13}C species were studied in natural abundance. Only the ground-state ^aR transitions were sufficiently strong to be assigned. The spectroscopic constants are found in Table 8.

^{14}N Nuclear quadrupole coupling constants. The selected transitions appearing in Table 9 were used to determine the quadrupole coupling constants for the ^{14}N nucleus following the procedure of Ref. 22. The resulting quadrupole coupling constants shown in this table are not very accurate, due to the fact that only rather limited experimental data were available. Comparison of the ^{14}N quadrupole coupling constants in Table 9 with those computed by the *ab initio* method and listed in Table 1 reveals reasonably good agreement. The quadrupole coupling constants for the vibrationally excited states and for the deuterated species were assumed to be the same as for the ground vibrational state (Table 9). "Corrections" due to quadrupole

Table 8. Spectroscopic constants[a-d] for the ground state of the ^{13}C species of 2-azetidinone.

Species	2-^{13}C	3-^{13}C	4-^{13}C
No. of transitions	6	5	6
R.m.s.[c]/MHz	0.124	0.110	0.116
A_0/MHz	12161.60(78)	11822.84(96)	12158.05(77)
B_0/MHz	4987.533(23)	4989.321(23)	4891.867(21)
C_0/MHz	3707.035(23)	3676.132(21)	3653.651(21)
$\Delta^e/10^{-20}\ m^2\ u$	6.5540(37)	6.5624(41)	6.5558(36)

[a-c]Comments as for Table 3. [d]Centrifugal distortion constants fixed at ground-state values shown in Table 3. See text. [e]$\Delta = I_a + I_b - I_c$.

Table 9. ^{14}N quadrupole splittings[a] (E_q) and diagonal elements of the quadrupole coupling tensor for the ground-vibrational state of 2-azetidinone.

Transition	$F' \leftarrow F$	E_q(obs.)/MHz	$[E_q(\text{obs.}) - E_q(\text{calc.})]$/MHz
$5_{1,4} \leftarrow 5_{1,5}$	5 ← 5	−1.31(2)	−0.04
	6 ← 6	0.47(3)	−0.02
$5_{2,4} \leftarrow 5_{0,5}$	5 ← 5	−0.65(2)	0.05
	6 ← 6	0.32(2)	0.05
$7_{1,6} \leftarrow 7_{1,7}$	7 ← 7	−1.19(2)	−0.08
$8_{2,6} \leftarrow 8_{2,7}$	8 ← 8	−0.76(2)	0.07
	9 ← 9	0.33(3)	−0.02
$9_{2,7} \leftarrow 9_{2,8}$	9 ← 9	−0.79(2)	0.08
	10 ← 10	0.39(2)	0.03
$12_{3,9} \leftarrow 12_{3,10}$	11 ← 11	0.30(3)	−0.07
	12 ← 12	−0.59(2)	0.07
	13 ← 13	0.30(2)	0.01
$13_{3,10} \leftarrow 13_{3,11}$	12 ← 12	0.36(3)	−0.02
	13 ← 13	−0.71(2)	−0.03
	14 ← 14	0.36(2)	0.06
$16_{4,12} \leftarrow 16_{4,13}$	15 ← 15	0.28(3)	−0.03
	16 ← 16	−0.55(2)	0.02
	17 ← 17	0.28(2)	0.02
^{14}N quadrupole coupling constants/MHz			
χ_{aa} = 1.9(5)	χ_{bb} = 1.7(2)		

[a]Uncertainties represent one standard deviation.

interaction, and discussed above, were calculated using the quadrupole coupling constants of Table 9.

Dipole moment. The dipole moment determined in the ordinary manner[22] is given in Table 10. Comparison of the experimental principal-axes dipole moment components (Table 10) with the theoretical values (Table 1) reveals rather good agreement. The total dipole of $12.77(13)\times10^{-30}$ C m is almost the same as that of formamide[23] [$12.38(20)\times10^{-30}$ C m].

Table 10. Stark coefficients[a] and dipole moment[a] of 2-azetidinone.

Transition		$\Delta\nu\ E^{-2}/10^{-6}$ MHz V^{-2} cm^2	
		Obs.	Calc.
$3_{1,3} \leftarrow 2_{1,2}$	$M = 0$	−3.61(3)	−3.58
$3_{0,3} \leftarrow 2_{0,2}$	$M = 1$	−3.42(5)	−3.16
$3_{1,2} \leftarrow 2_{1,1}$	$M = 0$	−2.52(3)	−2.68
	$M = 1$	−22.1(4)	−21.3
$2_{1,1} \leftarrow 1_{1,0}$	$M = 0$	47.9 (5)	48.7
$4_{1,4} \leftarrow 3_{1,3}$	$M = 0$	−2.13	−2.12
Dipole moment/10^{-30} C m			
μ_a = 12.71(12)	μ_b = 1.26(11)	$\mu_{tot.}$ = 12.77(13)	

[a]Uncertainties represent one standard deviation.
1 Debye = 3.33564×10^{-30} C m.

Ring-puckering potential function and ring planarity. According to Gwinn and coworkers,[24] the changes of the rotational constants upon excitation of the ring-puckering mode provide accurate information about the ring-puckering potential function (see reviews by Gwinn and Gaylord,[24] and by Legon[25]). The approach used by most workers is briefly the following: The simplest one-dimensional Schrödinger equation appropriate to the ring-puckering vibration is given by

$$-(h^2/2\mu)(d^2\psi/dx^2) + V(x)\psi = E\psi. \quad (1)$$

Here, μ is the reduced mass of the puckering vibration, and it has been assumed that the large-amplitude puckering mode can be separated from the remaining high-frequency small-amplitude vibrations. For almost all cases investigated in which the planar ring has a plane of symmetry it has been possible to interpret the observables associated with the ring-puckering mode very successfully by using a simple one-dimensional potential function $V(x)$ of the type[24,25]

$$V(x) = ax^4 + bx^2 \quad (2)$$

The following transformations[26]

$$z = (2\mu/\hbar^2)^{1/6}\, a^{1/6}\, x, \qquad B = (2\mu/\hbar^2)^{1/3}\, a^{-2/3}\, b, \tag{3}$$

and

$$\lambda = (2\mu/\hbar^2)^{2/3}\, a^{-1/3}\, E$$

results in the dimensionless eigenvalue problem

$$d^2\psi/dz^2 + (\lambda - z^4 - Bz^2) = 0 \tag{4}$$

By defining[26]

$$A = (\hbar^2/2\mu)^{2/3}\, a^{1/3} \tag{5}$$

the following reduced potential becomes[26]

$$V = A(\langle z^4\rangle + B\langle z^2\rangle) \tag{6}$$

In most calculations A is in units of cm^{-1}, while B and z are dimensionless. The molecule will have a symmetry plane in the equilibrium configuration provided B is positive. A double minimum will exist if B is negative.

As shown by Gwinn and coworkers,[24] it is possible to expand the rotational constants in the various states of the ring-puckering in a power series involving the expectation values of the dimensionless coordinate z

$$\beta_v = \beta_0 + \beta_2\langle z^2\rangle_v + \beta_4\langle z^4\rangle_v \tag{7}$$

where β_v is the A_v, B_v or C_v rotational constant in the vth excited state of the puckering mode. β_0, β_2 and β_4 are empirical parameters adjusted to give the best fit to the data. This will be described below.

A computer program was written to calculate the eigenvalues of the potential function $V(z)$ of eqn. (6) and the expectation values for $\langle z^2\rangle_v$ and $\langle z^4\rangle_v$. The matrix elements for $V(z)$ were taken from Heilbronner *et al.*,[27] who use the harmonic oscillator wave functions as basis functions. The same matrix elements are also found in Ref. 28. 50×50 matrices for even as well as for odd values of the vibrational quantum number v were employed. The numerical results were checked against Laane's tabulations,[25] and found to be in very good agreement in all test cases. The matrix elements of the z^2 and z^4 matrices were taken from Wilson *et al.*[29] They were transferred to the energy basis by using the eigenvectors obtained in the diagonalization of the $V(z)$ matrix.

The values of $\langle z^2\rangle_v$ and $\langle z^4\rangle_v$ depend only on the values of B [eqn. (3)]. The rotational constants of successively excited states of the puckering vibration of the parent and deuterated species were fitted to eqn. (7) utilizing the least-squares method for a range of values of B. It was found that the value $B = 4.7$ yielded the best overall fit. The results of

Table 11. Comparison of calculated and observed rotational constants[a] (MHz) using the potential function $V(z) = 19.2\langle z^4\rangle + 4.7\langle z^2\rangle$.

v	A_v		B_v		C_v	
	calc	calc-obs	calc	calc-obs	calc	calc-obs
Parent species						
0	12161.68	0.33	5003.60	0.26	3715.88	0.09
1	12090.17	−0.06	5012.87	−0.30	3725.89	−0.02
2	12031.63	0.86	5020.33	−0.47	3734.54	−0.31
3	11981.83	−0.33	5026.54	0.14	3742.37	0.12
4	11936.04	−0.26	5032.23	0.51	3749.60	0.21
5	---[b]		5036.66	−0.46	3756.42	−0.16
Calculated rotational constants[c]/MHz						
$A_v = 12201.6(17) - 199.1(50)\langle z^2\rangle_v + 8.9(20)\langle z^4\rangle_v$						
$B_v = 4998.38(74) + 26.3(17)\langle z^2\rangle_v - 1.55(57)\langle z^4\rangle_v$						
$C_v = 3710.44(35) + 26.38(81)\langle z^2\rangle_v + 0.08(27)\langle z^4\rangle_v$						
Deuterated species						
0	11129.05	−0.07	4998.84	0.01	3611.58	−0.02
1	11077.83	−0.07	5008.91	−0.18	3622.57	0.06
2	11032.44	−0.22	5016.99	0.01	3631.67	0.06
3	10990.23	−0.24	5023.69	0.00	3639.50	−0.33
4	---[b]		5029.84	−0.19	3646.71	0.10
Calculated rotational constants[c]/MHz						
$A_v = 11156.53(58) - 131.1(20)\langle z^2\rangle_v - 3.75(92)\langle z^4\rangle_v$						
$B_v = 4993.17(29) + 20.57(88)\langle z^2\rangle_v - 1.72(35)\langle z^4\rangle_v$						
$C_v = 3605.47(40) + 30.3(12)\langle z^2\rangle_v - 1.09(48)\langle z^4\rangle_v$						

[a]See text. [b]Not used in least-squares fit due to rather large uncertainty. [c]Uncertainties represent one standard deviation.

the fitting procedure are shown in Table 11. All the rotational constants were given the same weights in the fitting procedure. The A_v rotational constants of the fifth excited puckering state of the parent species and of the fourth excited state of the deuterated species were not used in this least-squares fit because they have rather large standard deviations, as seen in Tables 4 and 6 above.

It is seen in Table 11 that a rather good fit has been obtained with $B = 4.7$. The worst fit is found for the second and third excited states of the A_v rotational constants of the parent species. It is suggested that a weak Coriolis interaction between the N1–H6 out-of-plane bending vibration and the ring-puckering vibration is responsible for this slight deviation. The fact that B adopts a positive value of 4.7 leads us to conclude that the equilibrium configuration of the heavy atoms of the ring is completely planar, just as predicted in the theoretical computations above.

The constant A of eqn. (5) was then adjusted to reproduce the observation that the first excited state of the puckering vibration is 93 cm^{-1} higher in energy than the ground state vibration. A value of $A = 19.2$ cm^{-1} was found. The puckering potential for the parent species is then

$$V(z) = 19.2(\langle z^4\rangle + 4.7\langle z^2\rangle) \quad (8)$$

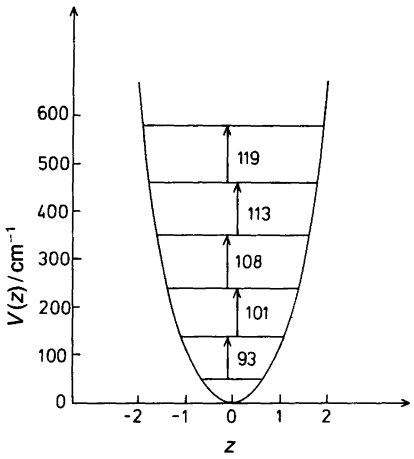

Fig. 2. Potential function $19.2(\langle z^4\rangle + 4.7\langle z^2\rangle)$ describing the puckering vibration of 2-azetidinone. Eigenstates are indicated.

This potential is drawn in Fig. 2. The deuterated species was found to have the same value for B, but a slightly different value for A.

Planarity around the N1 atom. The question of whether the H6 atom is exactly coplanar with the heavy-atoms of the ring is an interesting one. The variations of $\Delta = I_a + I_b - I_c$ may partly answer this question. It is seen in Tables 3

Table 12. The root-mean-square amplitudes of vibration, *l*, and perpendicular correction coefficients, *K*, at 415 K and 0 K, respectively, for the parent species of 2-azetidinone.[a]

Atom pair[b]	*l* (415 K)/pm			*l* (0 K)/pm	*K* (415 K)/pm	*K* (0 K)/pm
	Calc.	Obs.		Calc.	Calc.	Calc.
N1–C2	4.43	5.4		4.37	0.323	0.207
C2–C3	5.31	6.3		5.06	0.220	0.177
C3–C4	5.37	6.3	(3)[c]	5.21	1.005	0.294
N1–C4	4.53	5.5		4.47	1.635	0.429
C2=O5	3.98	4.4		3.94	0.991	0.378
N1–H6	7.42[d]			7.41	4.007	2.348
C3–H7,7′	7.86[d]			7.85	2.092	1.607
C4–H8,8′	7.87[d]			7.86	3.033	1.677
N1 ··· C3	5.57	5.5	(2)[c]			
C2 ··· C4	5.61	5.5				
N1 ··· O5	5.05	5.5(3)				
C3 ··· O5	6.94	6.3(4)	(3)[c]			
C4 ··· O5	5.96	6.7(4)				
N1 ··· H7	12.23	13.5				
C2 ··· H8	12.17	13.5				
O5 ··· H6	11.89	13.2	(7)[c]			
O5 ··· H7	13.96	15.3				
N1 ··· H8	9.75	10.9				
C2 ··· H6	9.53	10.7				
C2 ··· H7	9.87	11.0				
C3 ··· H8	7.86	9.0	(7)[c]			
C4 ··· H6	8.97	10.1				
C4 ··· H7	11.71	12.9				

[a]The *l* and *K* values were calculated as described in the text. [b]See Fig. 1 for atom numbering. [c]Refined in one group. One standard deviation is given in parentheses. [d]Not refined.

and 8 that the ground-state values are approximately 6.55×10^{-20} m^2 u for the parent and the ^{13}C species. However, for the D6-deuterated species (Table 3) this value increases a little to 6.57769(40) (with the same units as above). A similar increase for the corresponding values has been found for other amides such as formamide[23,30] and 2-fluoroacetamide,[31] both of which were assumed to have C_s equilibrium symmetry. In a penetrating study[30c] of the large-amplitude motions of the $-NH_2$ group hydrogen atoms of formamide it was concluded that formamide has a planar equilibrium conformation. Since the behaviour of the value of Δ upon deuteration is so similar for formamide and 2-azetidinone, it is concluded that H6 is coplanar with the heavy-atoms of the ring in its equilibrium conformation.

Structure determination. The rotational constants obtained in the MW analysis described above were used together with the ED intensity data to determine the full geometrical structure of 2-azetidinone in the following manner: The molecule was assumed to have C_s symmetry in accord with the MW results presented above. The molecular geometry (Fig. 1) was described by fifteen independent parameters: r(N1−C2), r(C2−C3), r(C3−C4), r(N1−C4), r(C2−O5), r(N1−H6), r(C3−H7), r(C4−H8), ∠C2C3C4, ∠C3C2O5, ∠C4N1H6, ∠C4C3H7, ∠C3C4H8, ∠H7C3H7′ and ∠H8C4H8′.

It was found in the course of the analysis that insufficient experimental data were available to allow independent determination of the structural parameters of the methylene group hydrogen atoms. Ultimately, it was therefore assumed that r(C3−H7) = r(C4−H8), that ∠C3C4H8 = ∠C4C3H7, and that ∠H7C3H7′ = ∠H8C4H8′. These assumptions are supported by the theoretical predictions summarized in Table 1.

The root-mean-square amplitudes of vibration, l, and the perpendicular correction coefficients, K, used in the analysis were calculated employing the Urey-Bradley force field given in Ref. 3 and the normal coordinate program written by Hilderbrandt.[32] This force field was considered to be accurate enough for our purpose in spite of the fact that it was not derived for 2-azetidinone in the gaseous state. The results are found in Table 12. The asymmetry for bonded atom pairs were estimated from the diatomic approximation[33] as $al^4/6$, where a is the constant in the Morse potential, and is assumed to be 0.020 pm^{-1} for C−C, C−N and C=O bonds,[34] and 0.026 pm^{-1} for N−H and C−H bonds.[35,36] The asymmetries for all non-bonded atom pairs were ignored. Correction for shrinkage was incorporated by refining a geometrically consistent r_α structure.[36]

The rotational constants were used in the analysis after transferring the ground vibrational state constants β_0 (where $\beta_0 = A_0$, B_0 or C_0) into the zero-point rotational constants β_z using the relationship[36]

$$\beta_z \approx \beta_0 + \Delta\beta_{vib.} \qquad (9)$$

Table 13. Zero-point spectroscopic constants.[a]

	$\Delta\beta_{vib.}$/MHz	β_z^b/MHz	β_z^c/MHz
Parent molecule			
A	12.4	12173.8(12)	12172.8(11)
B	0.61	5003.95(6)	5003.96(7)
C	−0.90	3714.89(9)	3715.12(8)
6-D isotopomer			
A	12.1	11141.3(12)	11140.7(15)
B	0.89	4999.72(9)	4999.84(15)
C	−0.78	3610.88(8)	3610.82(12)
2-^{13}C isotopomer			
A	12.5	12174.1(13)	12172.9(11)
B	0.62	4988.15(6)	4987.94(7)
C	−0.89	3706.14(9)	3706.29(9)
3-^{13}C isotopomer			
A	11.3	11834.2(11)	11836.3(13)
B	0.57	4989.89(6)	4990.08(9)
C	−0.89	3675.24(9)	3675.64(10)
4-^{13}C isotopomer			
A	12.8	12170.8(13)	12170.0(11)
B	0.57	4892.44(6)	4892.38(10)
C	−0.89	3652.76(9)	3653.01(9)

[a]See text. [b]Calculated from β_0 rotational constants shown in Tables 3 and 8 in the manner described in the text. [c]Calculated from the r_α^0-structure. This structure, which is not shown in Table 14, was calculated from the r_g structure shown in Table 14 using eqn. (10).

where $\Delta\beta_{vib.}$ is the harmonic correction to the ground state rotational constants. These corrections were calculated using the force field of Ref. 3 and Hilderbrandts program.[32] The results are given in Table 13. No universally accepted procedure exists for weighting of the rotational constants versus the ED intensity data.[37] In this work, the weights of the ED and MW data were chosen so that the *standard deviations* of the rotational constants calculated from the r_α^0 structure (defined below) are nearly the same as the standard deviations of the β_z rotational constants, estimated to be roughly 10 % of $\Delta\beta_{vib.}$ (cf. Table 13 and Ref. 37).

The conversion from r_a to r_α^0 is given by[36]

$$r_\alpha^0 = r_g - 1.5a(l_T^2 - l_0^2) - K_0 \qquad (10)$$

where $r_g = r_a - l_T^2/r$ and l_T and l_0 are the root-mean-square amplitudes of vibration at temperatures T and 0 K, respectively. The zero-point isotopic change in bond distances defined as $\delta r_z = r_z$ (isotopomer) − r_z (parent species) was accounted for using the following formula[36]

$$\delta r_z = 1.5a[l_0^2(\text{isotop.}) - l_0^2(\text{par.})] - [K_0(\text{isotop.}) - K_0(\text{par.})] \qquad (11)$$

Table 14. Geometrical structure of 2-azetidinone.

	r(ED + MW)[a]	r(equilibrium)[b]	r(X-Ray)[c]	r(*ab initio*)[d]
Bond distances[e]/pm				
N1–C2	138.0(2)	137.1	133.1	135.8
C2–C3	153.7(3)	152.6	152.2	153.3
C3–C4	155.3(5)	154.1	153.8	154.9
N1–C4	147.9(3)	147.0	146.7	145.5
C2=O5	120.1(1)	119.5	122.5	118.6
N1–H6	99.0(3)	96.8		99.4
C3–H7,7′	110.5 } (5)	107.5		108.1
C4–H8,8′	110.5 }	107.5		108.4
Bond angles[e]°				
∠N1C2C3	91.1(2)		91.7	91.2
∠C2C3C4	86.0(2)		85.9	85.6
∠C3C4N1	87.6(1)		86.2	87.0
∠C4N1C2	95.3(2)		96.2	96.2
∠C4N1H6	131.0(6)			133.0
∠C3C2O5	136.6(3)		135.9	135.9
∠C2C3H7	115.1(8)			114.1
∠N1C4H8	114.4(9)			114.2
∠C4C3H7	114.5(9)			
∠H7C3H7′	110.0(3)			
Dihedral angles[e]°				
∠H7C3C2O5	64.8(10) from *syn*			63.8
∠H8C4N1H6	64.1(9) from *syn*			63.5
R factor[f]				
R = 5.58[g]				

[a]The bond distances are r_g values, while the bond angles are r_α values. This table contains both the structurally independent parameters as given in the text, as well as the structurally dependent parameters. Temperature 415 K. Uncertainties represent one standard deviation. [b]Estimated equilibrium structure. See text. [c]Taken from Ref. 2. [d]This work. [e]Atom numbering given in Fig. 1. [f]Defined in Ref. 8. [g]For ED data only.

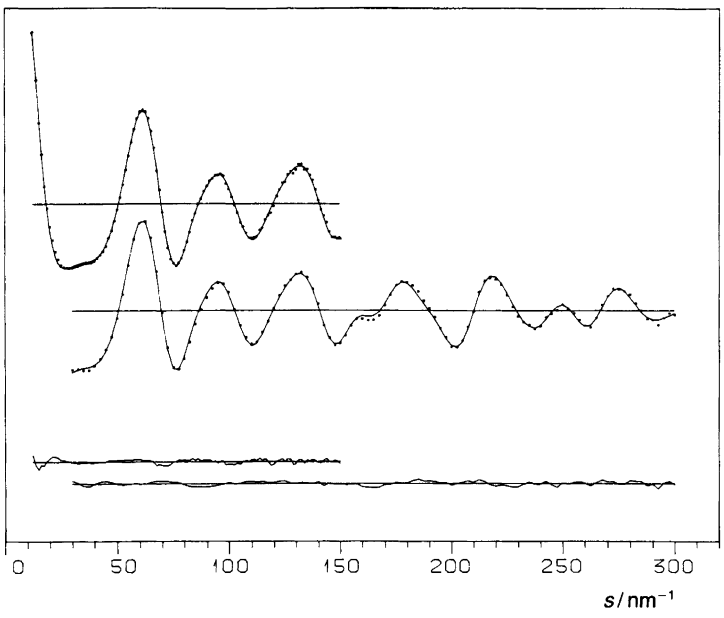

Fig. 3. Experimental (dots) and theoretical (full line) intensity curves for 2-azetidinone, and the corresponding difference curves.

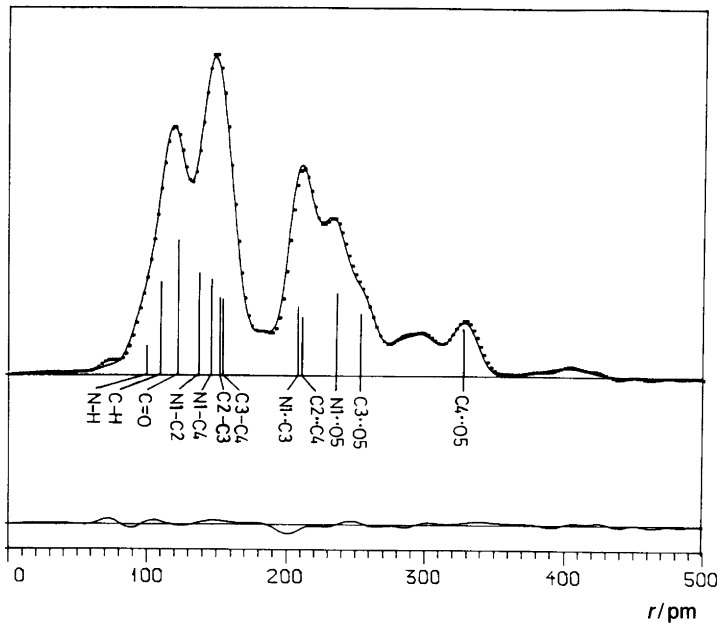

Fig. 4. Experimental (dots) and theoretical (full line) radial distribution functions with an artificial damping constant $B = 17$ pm^2. The position and approximate area (length of the bar) of the peaks corresponding to the most important distances are shown together with the difference curve. Theoretical intensities have been used below $s = 20.00$ nm^{-1}.

which gives identical equilibrium geometries for all isotopic species when the equilibrium bond distances are estimated from the diatomic approximation as

$$r_\alpha^0 = r_e + 1.5al_0^2 - K_0 \qquad (12)$$

Table 14 summarizes the parameters for r_q structure and those estimated for the corresponding r_e structure, calculated using the formula given in eqn. 12. The estimated equilibrium structure appears to be reasonable, apart from the C−H and N−H bond distances which seem to be rather short. The X-ray structure of solid 2-azetidinone as well as the *ab initio* structure are also included in this table for comparison purposes. The intensity curves are shown in Fig. 3, and the radial distribution curves are drawn in Fig. 4.

Discussion

As far as we know, this is the first gas-phase structural study of a lactam, and comparison with the structures of other free lactams cannot be made. However, comparison with the accurate X-ray structure[2] (Table 14) reveals several notable differences between the crystal[2] and the gas-phase structures of 2-azetidinone. The hydrogen atom (H6 of Fig. 1) and the oxygen atom are involved in intermolecular hydrogen bonding in the crystal.[2] The fact that the C2=O5 bond is about 25 pm shorter and the N1−C2 bond is approximately 50 pm longer in the gas phase than in the crystal is probably a result of hydrogen bonding and increased π-electron resonance in the crystalline state. This finding is very similar to what has been observed for several amides.[38]

It is also interesting to note that the C2−C3, C3−C4 and N1−C4 bonds are slightly shorter by 10–20 pm in the gas phase than in the crystal (Table 14), while the bond angles are rather similar in both phases.

The estimated equilibrium structure of the title molecule (Table 14) and the *ab initio* structure (Tables 1 and 14) are in good agreement. No differences in bond lengths larger than approximately 20 pm are seen for the two structures. It is noteworthy that the 6-31G** basis set is capable of reproducing the structure of this rather strained molecule so well.

There is also a striking structural similarity between the simplest amide, i.e. formamide, and 2-azetidinone. It was noted above that the dipole moments of formamide and 2-azetidinone are very similar. This is also the case for the C=O and C−N bonds. The C=O bond length is 121.2 (3) pm and the C−N bond length is 136.8(3) pm in formamide,[39,30b,c] as compared to 120.1(1) pm and 138.0(2) pm for the corresponding two distances in the title compound (Table 14).

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