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Microwave Spectrum, Conformation, Intramolecular Hydrogen Bonding and *Ab Initio* Calculations for 2-Nitroethanol

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The microwave spectrum of 2-nitroethanol has been investigated in the 26.5–39.0 GHz spectral region at room temperature. The spectra of the ground and of six excited states of the torsional vibration of the nitro group of one rotamer were assigned and could be fitted to the ordinary Watson Hamiltonian to within the experimental accuracy. The nitro group is *not* rotating freely but has a low torsional frequency determined to be 34(10) cm^{-1} by relative intensity measurements. The identified conformer has a *gauche* arrangement for the O–C–C–N chain of atoms and is stabilized by a weak six-membered intramolecular O–H···O hydrogen bond formed between the hydrogen atom of the hydroxyl group and one of the oxygen atoms of the nitro group. The N–O bond (where the oxygen atom is involved in intramolecular hydrogen bonding), and the C–C bond are about 17° from being completely eclipsed. This rotamer is at least 4 kJ mol^{-1} more stable than any other rotameric form of the molecule. The microwave work has been assisted by *ab initio* computations made at the MP2/6–31++G** level of theory.

The conformational properties of 2-nitroethanol have attracted the interest of several workers.[1–7] The compound has been studied by infrared (IR),[1–5,7] Raman,[5] and nuclear magnetic resonance spectroscopy (NMR).[6] *Ab initio* computations have been reported[7] and photorotamerization studies have been carried out.[7] All authors agree that free 2-nitroethanol prefers a O–C–C–N *gauche* (about 60° from *syn*=0°) conformation which is stabilized by a six-membered intramolecular hydrogen (H) bond as its most stable form. The exact shape of the H bond was not evident in the early infrared studies and might involve one or both oxygen atoms of the nitro group.[3] A freely rotating nitro group with no definite location, as has been found for nitroethane,[8] is another possibility.

Studies of dilute CCl_4 solutions reveal that the O–H stretching frequency is rather complex with *three* distinct peaks.[3,4] It was therefore assumed that three distinct conformers, two with O–C–C–N *gauche* arrangements and one with an *anti* arrangements exist in solution.[4] Temperature studies of the complex O–H stretching band[4] yielded enthalpy differences of −1.6(4) and −2.9(4) kJ mol^{-1}, respectively, between the most stable H-bonded *gauche* form and each of the two other conformers.

However, in the gas phase only *two* peaks at 3628 and 3670 cm^{-1} were observed for the O–H stretching vibration,[5] and they were assigned to the H-bonded *gauche* conformer and to an *anti* form, respectively. The enthalpy difference between the two could not be obtained owing to experimental difficulties.[5]

The H-bonded *gauche* rotamer is clearly preferred in nitrogen and rare gas matrices.[7] Irradiation with infrared and ultraviolet radiation creates substantial amounts of other form(s) assumed to be *anti* form(s).[7]

Interestingly, the *six*-membered O–H···O hydrogen bond appears to be remarkably *weak* in this molecule as judged by a red shift of the O–H stretching frequency of only 42 cm^{-1} (from 3670 to 3628 cm^{-1}) in the gas phase.[5] The stabilization of the H-bonded rotamer by a few kJ mol^{-1} has been inferred from this red shift[3–5] as well as from the temperature studies of the O–H stretching frequency band[4] and the NMR study.[6] The rather low-level *ab initio* computations[7] yielded energy differences much higher than this (in the 19.1–24.9 kJ mol^{-1} range for various *gauche* and *anti* conformations considered in this work[7]).

No microwave (MW) spectrum has been reported for 2-nitroethanol. The present combined MW and high-level *ab initio* work was undertaken to determine the

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geometry of the preferred O–C–C–N *gauche* conformer with special attention to the conformation and dynamics of the nitro group. The possible existence of additional high-energy rotamers and their structures, relative energies and dynamics are other themes of this investigation.

Experimental

The sample utilized in this work was purchased from Fluka. It was distilled before use. The MW spectrum was studied in the 26.5–39 GHz spectral region using the Oslo spectrometer which is described in Ref. 9. 2-Nitroethanol has a vapour pressure of only a few Pa at room temperature at which the spectra were taken. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 3–8 Pa when the spectra were recorded and stored using the computer programs written by Waal.[10] The accuracy of the spectral measurements is presumed to be better than ± 0.10 MHz.

Results and discussion

Ab initio calculations. The Gaussian 92 program package[11] running on the IBM RS6000 cluster in Oslo was employed in all the *ab initio* computations of the conformational and structural properties of the title molecule. The 6-31++G** basis set provided with the program was used. Electron correlation was included using the second-order Møller–Plesset (MP2) perturbation theory[12] as implemented with the Gaussian 92 program.

Rotational isomerism in 2-nitroethanol may arise by rotating around the O1–C1, C1–C2 and C2–N1 bonds (Fig. 1). A large number of 'stable' conformers corresponding to energy minima on the potential energy surface may thus exist. A freely rotating nitro group might complicate the conformational analysis further.

Experience indicates that stable forms, if they existed at all for this compound, are most likely for *gauche* ($\pm 60°$ from *syn*) and *anti* (180° from *syn*) orientation of the O1–C1–C2–N1 and of the H1–O1–C1–C2 chains of atoms. Searches for energy minima on the conformational energy surface were made starting with the 'normal' values for the O1–C1–C2–N1 and H1–O1–C1–C2 dihedral angles (± 60 or 180°). Several different orientations of the nitro group were used as the starting point in the present computations. The geometry was fully optimized in each case. The vibrational frequencies were calculated for each stable rotamer to ensure that a true minimum had been found (all frequencies were positive[13]).

Six stable conformers were predicted in these MP2/6-31++G** computations; three of them having the *gauche* orientation for the O1–C1–C2–N1 link of atoms, and three having *anti* orientation. These six forms are drawn in Fig. 1. Their geometries are listed in Table 1

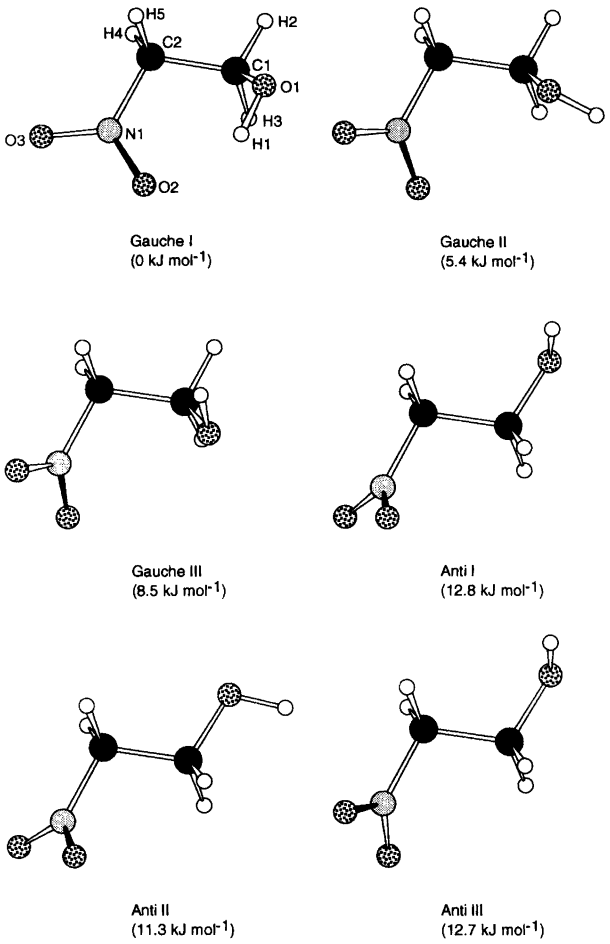

Fig. 1. The rotameric forms of 2-nitroethanol found to be energy minima ('stable') on the energy surface in the MP2/6-31++G** calculations. Atom numbering is given for *Gauche I*. This conformer, which is stabilized by a O1–H1···O2 hydrogen bond, was assigned in this work and shown to be at least 4 kJ mol^{-1} more stable than any other conformation.

together with some other parameters of interest. It should be noted that the same minima were always found in these high-level *ab initio* computations with widely different starting geometries for the nitro group and the same initial values for the H1–O1–C1–C2 and O1–C1–C2–N1 dihedral angles. It is therefore assumed that the six conformers shown in Fig. 1 indeed represent all the *stable* forms of 2-nitroethanol.

Interestingly, the torsional frequencies of the nitro group (torsion around the C2–N1 bond) is computed to be 24 cm^{-1} in *Gauche I* and approximately 50 cm^{-1} in the other five rotamers (Table 1). A freely rotating nitro group would have torsional frequencies much closer to zero. The present computations thus indicate that *none* of nitroethanol's rotamers possesses a freely rotating nitro group. This contrasts the findings made for nitroethane mentioned above.[8] The substitution of one of the H atoms in the methyl group in nitroethane with a hydroxyl group is thus predicted to increase the barrier

Table 1. Ab initio structure, rotational constants, dipole moments, torsional frequencies of the nitro group and energy differences of the six stable rotamers of $HOCH_2CH_2NO_2$ as calculated at the MP2/6–31++G** (frozen core) level.

Conformer:[a]	*Gauche I*	*Gauche II*	*Gauche III*	*Anti I*	*Anti II*	*Anti III*
Distance/pm						
H1–O1	96.8	96.5	96.7	96.6	96.6	96.6
C1–O1	142.0	142.7	142.2	142.4	142.8	142.4
C1–H2	109.0	109.4	109.4	108.9	109.4	108.7
C1–H3	109.4	109.1	108.7	109.1	109.1	109.4
C1–C2	151.6	150.8	151.9	152.8	151.9	152.8
C2–H4	108.8	109.0	109.0	108.5	108.5	108.7
C2–H5	109.0	108.6	108.7	108.9	108.8	108.7
C2–N1	150.1	149.8	149.4	149.1	149.1	149.1
N1–O2	124.7	124.3	124.3	124.6	124.5	124.6
N1–O3	124.1	124.3	124.4	124.5	124.5	124.5
Angle/°						
H1–O1–C1	106.6	109.1	109.3	108.8	108.7	108.9
O1–C1–H2	106.2	111.2	112.1	106.2	111.3	106.5
O1–C1–H3	111.7	111.7	105.7	112.2	111.9	111.8
O1–C1–C2	112.8	106.5	112.0	109.8	104.7	109.9
C1–C2–H4	112.8	111.3	111.0	111.4	111.6	110.4
C1–C2–H5	111.0	111.9	112.7	111.2	110.6	112.2
C1–C2–N1	112.4	110.2	109.3	109.1	109.3	109.0
C2–N1–O2	118.1	117.0	116.6	116.4	116.6	118.0
C2–N1–O3	116.9	117.5	117.7	118.1	118.1	116.5
Dihedral angle[b]/°						
H1–O1–C1–H2	186.6	−83.3	55.0	199.8	−67.6	197.0
H1–O1–C1–H3	−55.6	39.2	173.4	−41.3	55.0	44.2
H1–O1–C1–C2	69.1	158.8	−67.1	81.3	173.8	78.3
O1–C1–C2–H4	169.3	177.5	185.7	59.8	58.9	62.4
O1–C1–C2–H5	46.0	52.9	61.0	−64.8	−65.3	62.2
O1–C1–C2–N1	−71.8	−64.9	−56.8	177.9	177.0	180.1
C1–C2–N1–O2	17.3	−48.2	−61.9	66.8	58.2	111.2
C1–C2–N1–O3	−164.1	133.3	117.4	−110.9	−121.0	66.4
Non-bonded distances[c,d]/pm						
H1···O2	220	369	400	440	474	463
H1···O3	399	433	350	503	527	477
Rotational constants[c]/MHz						
A	8060.9	6401.3	6100.3	8919.9	9098.2	8888.9
B	2483.7	2531.1	2610.8	1970.2	1992.0	1977.3
C	2049.8	2409.0	2430.6	1761.7	1761.6	1761.2
Principal-axis dipole moment component[e]/10^{-30}C m						
μ_a	4.94	14.21	11.97	10.61	13.24	10.14
μ_b	9.41	0.57	2.13	2.10	1.17	6.60
μ_c	2.47	10.14	14.61	6.24	0.50	1.60
Torsional frequency of the nitro group[f]/cm^{-1}						
	23.9	57.1	56.7	47.1	46.0	47.6
Energy difference[g]/kJ mol^{-1}						
	0	5.4	8.5	12.2	11.3	12.7

[a] See Fig. 1 for definition. [b] Measured from *syn*=0°. Positive dihedral angle corresponds to clockwise rotation. [c] Calculated from the structure given in this table. [d] Sum of van der Waals radii:[14] O···O 280 pm; O···H 260 pm. [e] 1 D=3.335 64 × 10^{-30} C m. [f] Only the torsional frequency of the nitro group is given in this table. [g] The total energy of conformer *Gauche I* was calculated to be −941 501.48 kJ mol^{-1} (−358.598 962 1 hartree). [g] Energy difference between *Gauche I* and each of the other conformations.

to internal rotation of the nitro group quite considerably even in conformations where there is no H bonding between the H atom of the hydroxyl group and one of the oxygen atoms of the nitro group which could have 'locked' the conformation of this group. The *lowest* torsional frequency is computed for *Gauche I*. The strained structure (see below) of this rotamer might perhaps explain why the torsional frequency of the nitro group is lowest in just this form of the molecule.

Table 1 reveals some further interesting predictions: The H-bonded *Gauche I* rotamer is predicted to be the most stable conformation, as expected. The H bond in this conformation is characterized by a non-bonded H1···O2 distance of ca. 220 pm, which is 40 pm shorter than the sum of the van der Waals distances of oxygen (140 pm) and hydrogen (120 pm).[14] The non-bonded O1···O2 distance is 285 pm, close to twice the van der Waals distance of oxygen (280 pm).[14] The non-bonded H1···O3 distance is about 399 pm, much longer than the sum of the van der Waals distances of oxygen and hydrogen (260 pm[14]). The H1 is thus undoubtedly bonded to only one of the oxygen atoms of the nitro group, viz. the O2 atom. A non-bonded interaction between the H1 atom and the N1 atom is unlikely to be large, since this distance (not given in Table 1) with 278 pm, compared with 270 pm, which is the sum of the van der Waals radii of hydrogen and nitrogen.[14] The O1–H1···O2 angle is 123°, far from the ideal linear (or near-linear) arrangement (180°). The structure of the O1–H1···O2 hydrogen bond clearly shows that it must be rather weak, as has already been pointed out.[2–7]

A striking structural feature of *Gauche I* is the unusual value predicted for the C1–C2–N1–O2 dihedral angle (17°; Table 1). The C1–C2 and N1–O2 bonds are thus nearly eclipsing one another. This near-eclipsed arrangement is likely to be repulsive, and it is not found in any of the five other non-hydrogen bonded conformations shown in Fig. 1. Typically, in these five high-energy forms one C2–H bond and one N1–O bond is almost eclipsing one another. It is likely that there is weak attraction between these two bonds. The unusual orientation of the nitro group seen in *Gauche I* is believed to be largely a result of H bonding. This effect would tend to have the O2 atom as close to H1 as possible energetically and does so by rotating the nitro group into a rather unfavourable near-eclipsed conformation.

Another unusual structural feature is the rather large O1–C1–C2–N1 dihedral angle (71.8°; Table 1). The 'normal' value is about 60°, so it is possible that the large value seen in *Gauche I* reflects some repulsive interaction, perhaps to be traced back to the H bonding with the nitro group.

The energy difference between *Gauche I* and the rotamer with the second lowest energy (*Gauche II*) is predicted to be only 5.4 kJ mol^{-1}. This rather modest energy difference is another indication that the six-membered O–H···O hydrogen bond is quite weak in 2-nitroethanol. Moreover, the relatively large energy difference of 6–7 kJ mol^{-1} between the *Gauche II* rotamer and the three *anti* forms is a strong indication that the second lowest energy rotamer of 2-nitroethanol is indeed a non H-bonded *gauche* form and *not* an *anti* rotamer, contrary to what has often been assumed.[2–7] The present computational results perhaps reflect the general tendency for 1,2-disubstituted ethane derivatives to prefer the *gauche* orientation when the substituents are strongly electronegative,[15] as is the case in 2-nitroethanol.

The weakness of the H bond manifests itself in yet another way, the red shift of the O–H stretching frequency which occurs upon H bond formation. This frequency is computed (not given in Table 1) to be 3850 cm^{-1} for *Gauche I* and 3892 cm^{-1} for *Gauche II*, respectively. The red shift is thus 42 cm^{-1}, which is the same as observed in the gas phase (see Introduction).[5] (It is noted that the calculated frequency for the O–H stretching vibration is too high by about 6% even at this rather high level of theory.)

MW spectrum and assignment of the ground vibrational state of Gauche I. The *ab initio* computations above predict that *Gauche I* is the most stable conformer. The theoretical rotational constants of Table 1 indicate that it is a prolate asymmetrical top with the asymmetry parameter $\kappa \approx -0.86$ and its largest dipole moment component along the *b*-inertial axis. Such a spectrum is typically dominated by many comparatively strong high-J ^bQ-transitions and a few somewhat weaker ^bR-transitions. A large number of much weaker high-J *P*- and *R*-branch transitions are also present in spectra of this kind provided no complications from a very low barrier to internal rotation exists.

The survey spectra revealed a rich spectrum of moderate intensity; the strongest lines seen, which turned out to be *b*-type *Q*-branch transitions as predicted, had peak absorption coefficients of roughly 2×10^{-7} cm^{-1} at room temperature. A trial spectrum of a rigid rotor was first predicted using the rotational constants and dipole moment components of *Gauche I* shown in Table 1. Attempts to assign the strongest lines of the spectrum as high-J *b*-type *Q*-branch transitions were soon successful, because they were located close to their predicted frequencies. The strongest *b*-type *R*-branch lines were searched for next. They were much harder to find owing to their lower intensities and the fact that there are so few of them in the spectrum. Ultimately, several very weak low-J ^aR- as well as high-J ^bR-branch transitions confirmed the assignments. No *c*-type transitions were assigned, although it is presumed that their hypothetical frequencies could be very accurately predicted. It is assumed that the reason for not seeing *c*-type lines is a small component of the dipole moment along the *c*-inertial axis producing insufficient intensity. This is in keeping with the theoretical prediction of μ_c (Table 1).

A total of about 100 transitions were assigned, some

Table 2. MW spectrum of the ground vibrational state of *Gauche I* of 2-nitroethanol.

Transition $J''_{K''-1,K''+1} \leftarrow J'_{K'-1,K'+1}$	Observed frequency[a]/MHz	Obs.−calc. freq./MHz
$5_{3,2} \leftarrow 5_{2,3}$	27 719.50	0.02
$6_{1,6} \leftarrow 5_{0,5}$	29 421.75	0.01
$7_{0,7} \leftarrow 6_{1,6}$	28 562.80	−0.02
$7_{5,2} \leftarrow 6_{5,1}$	32 237.46	0.02
$7_{5,3} \leftarrow 6_{5,2}$	32 237.46	0.04
$8_{1,8} \leftarrow 7_{0,7}$	36 737.93	0.00
$8_{4,5} \leftarrow 7_{4,4}$	36 902.72	0.00
$9_{0,9} \leftarrow 8_{1,8}$	38 030.46	−0.11
$10_{2,9} \leftarrow 10_{1,10}$	28 509.82	0.01
$12_{1,11} \leftarrow 12_{0,12}$	28 709.04	−0.03
$13_{2,12} \leftarrow 13_{1,13}$	35 827.62	0.02
$14_{4,10} \leftarrow 14_{3,11}$	34 491.86	0.05
$16_{2,14} \leftarrow 16_{1,15}$	30 533.16	0.01
$17_{2,15} \leftarrow 17_{1,16}$	34 263.89	0.15
$17_{4,13} \leftarrow 16_{5,12}$	32 089.37	−0.14
$18_{4,14} \leftarrow 17_{5,13}$	38 242.15	0.07
$19_{4,15} \leftarrow 19_{3,16}$	28 606.00	−0.05
$20_{3,17} \leftarrow 20_{2,18}$	31 572.40	−0.04
$21_{4,17} \leftarrow 21_{3,18}$	28 588.70	0.12
$22_{6,16} \leftarrow 21_{7,15}$	30 576.92	−0.05
$23_{5,18} \leftarrow 23_{4,19}$	37 589.02	−0.09
$24_{7,17} \leftarrow 23_{8,16}$	28 126.45	−0.10
$26_{5,21} \leftarrow 26_{4,22}$	34 945.01	0.04
$27_{8,19} \leftarrow 26_{9,18}$	30 820.15	−0.15
$29_{5,24} \leftarrow 29_{4,25}$	37 598.64	−0.05
Coalescing *P*- and *R*-branch transitions[b]		
$36_{12} \leftarrow 35_{13}$	27 054.93	0.14
$40_{13} \leftarrow 39_{14}$	34 650.17	0.10
$41_{14} \leftarrow 40_{15}$	27 696.70	−0.08
$48_{16} \leftarrow 47_{17}$	38 006.48	−0.05

[a] ±0.10 MHz. [b] The K_{-1} energy levels coalesce for high values of J and K_{-1}.

of which are listed in Table 2.* Eighty-seven transitions were used to determine the spectroscopic constants shown in Table 3 (*A*-reduction *I*^{r}-representation[16]). Only quartic centrifugal distortion constants were employed in the least-squares fit, which had a root-mean-square deviation of ±0.085 MHz, comparable to the experimental uncertainty of ±0.10 MHz. No large vibration–rotation interactions of the kind seen in nitroethane[8] and ascribed to nearly free rotation of the nitro group[8] were encountered for 2-nitroethanol. This is an important indication that the barrier to internal rotation of the said group is much higher in the present case than in the case of nitroethane[8] for whatever reason.

The nitrogen atom has a spin of 1. Quadrupole interaction with the molecular rotation is then possible. However, no lines were seen to be split by this interaction.

Attempts to determine the dipole moment by Stark effect measurements failed because the low-*J* transitions were too weak to allow quantitative measurements to be made.

Vibrationally excited states of Gauche I. The ground-state spectrum was accompanied by several satellite spectra which could obviously be ascribed to vibrationally excited states of the torsional vibration of the nitro group. The rotational transitions of the successively excited states of this mode were seen to be separated by roughly constant frequency intervals with the intensities decreasing by about 20% upon excitation by one vibrational quantum. This behaviour is typical for a nearly harmonic vibration.[17] A total of six such states were assigned. Both *R*- and *Q*-branch transitions were assigned for the five first excited states, allowing all rotational constants to be determined as seen in Table 3. Assignment of seven *Q*-branch lines of the sixth excited state of the same vibration yielded $A_v - C_v = 5\,495.13(11)$ MHz and $\kappa = -0.859\,889$. Relative intensity measurements using selected transitions of the ground and the first excited state of this mode were performed largely as described in Ref. 18, and yielded 34(10) cm^{-1} for this vibration, compared to 24 cm^{-1} calculated by *ab initio* (Table 1).

The torsional frequency of 34(10) cm^{-1} definitely rules out a freely rotating nitro group. Unfortunately, there is insufficient information to derive the potential function for the rotation of the nitro group, but the frequency of 34(10) cm^{-1} indicates that the barrier heights are only a few kJ mol^{-1}.

The second lowest vibration is the torsion around the C1–C2 bond. Its frequency was calculated (not given in Table 1) to be 186 cm^{-1}. Attempts to assign the first excited state of this mode failed, presumably because it is rather weak.

MW search for further conformations. The above assignments include all the strongest lines as well as the large majority of transitions of intermediate intensity seen in the MW spectrum. Many weak lines were also assigned. Rotamers other than *Gauche I*, especially *Gauche II* predicted (Table 1) to be less stable than *Gauche I* by 5.4 kJ mol^{-1}, were searched for, but none was found. It is seen in Table 1 that all the other conformers are predicted to have at least one dipole moment component that is larger than μ_b of *Gauche I*. The spectra of rotamers other than *Gauche I* would thus have been quite intense provided such rotamer(s) were present in considerable amounts. Their obvious absence is one indication that *Gauche I* is considerably more stable than any other rotameric form. Our final conclusion is that *Gauche I* is at least 4 kJ mol^{-1} more stable than any other rotameric form of 2-nitroethanol. This estimate is considered to be conservative and is in agreement with the theoretical predictions in Table 1, and previous reports.[2–7]

Structure. It is seen from Table 3 that the experimental rotational constants of *Gauche I* in the ground vibrational

* The full ground-state spectrum and the spectra of the vibrationally excited states are available from the authors upon request, or from the Molecular Spectra Data Center, National Institute of Standards and Technology, Molecular Physics Division, Bldg. 221, Room B265, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 3. Spectroscopic constants[a,b] of the ground ($v_T=0$) and successively excited states of the torsion around the C2–N1 bond of 2-nitroethanol.

Vibrational state:	$v_T=0$	$v_T=1$	$v_T=2$	$v_T=3$	$v_T=4$	$v_T=5$
No. of transitions:	87	54	46	43	46	35
R.m.s. dev.[c]/MHz:	0.085	0.084	0.082	0.095	0.098	0.094
A_v/MHz	7946.777 1(50)	7912.292 4(94)	7873.280(10)	7827.571(13)	7772.441(14)	7706.692(21)
B_v/MHz	2498.704 5(14)	2500.996 0(68)	2503.957 5(84)	2507.774(10)	2512.706 1(88)	2518.686(18)
C_v/MHz	2095.686 8(13)	2101.350 7(66)	2107.167 2(82)	2113.376 8(96)	2120.563 7(86)	2129.357(18)
Δ_J/kHz	1.209 7(17)	1.053(48)	1.340(55)	1.256(65)	1.215(59)	1.02(13)
Δ_{JK}/kHz	−5.365(20)	−4.735(38)	−4.194(40)	−3.783(53)	−3.422(36)	−3.393(56)
Δ_K/kHz	39.036(38)	32.19(62)	25.82(69)	23.04(83)	18.04(65)	15.40(92)
δ_J/kHz	−0.0875 3(92)	−0.085 2(11)	−0.083 6(11)	−0.071 5(16)	−0.043 9(14)	−0.004 5(16)
δ_K/kHz	6.777(41)	6.991(52)	7.409(48)	7.711(76)	7.740(69)	7.538(75)

[a] *A*-reduction, *I*^{r}-representation.[16] [b] Uncertainties represent one standard deviation. [c] Root-mean-square deviation.

state are close to those calculated from the MP2/6–31++G** structure (Table 1). In fact, the agreement is better than about 2% for all three constants. Differences of this order magnitude are to be expected because the rotational constants are 'contaminated' with zero-point vibrational interaction while the *ab initio* rotational constants are calculated from an approximation of the equilibrium structure. Moreover, the structural parameters in Table 1 are very similar to their experimental counterparts in ethanol[19] and nitromethane.[20] No experimental data are at hand that could really improve the MP2/6–31++G** structure of *Gauche I*. The *ab initio* structure shown in Table 1 is therefore adopted as a *plausible* structure for this conformer. It is expected that this structure will be very close to any experimental structure that might be determined in the future.

Conclusions

The present MW investigation confirms the finding of the previous studies[1–7] by other methods that 2-nitroethanol prefers the H-bonded *Gauche I* conformation. Two effects are thought to be responsible for this choice. The first is the *gauche effect*[15] that would favour a *gauche* arrangement for the O1–C1–C2–N1 link of atoms. The fact that the *ab initio* computations above find that all three *gauche* forms are more stable than any of the *anti* forms is just what this effect would predict.

The second effect is H bonding, which undoubtedly makes *Gauche I* the most stable conformer amongst the three *gauche* rotamers of Fig. 1. The hydrogen atom of the hydroxyl group, H1, is undoubtedly bonded to one and not to both oxygen atoms of the nitro group. The nitrogen atom is too far away (approximately 278 pm; see above) to be of importance. The peculiar conformation of the nitro group (the C1–C2–N1–O2 dihedral angle is about 17°) is clearly a result of H bonding. This interaction would tend to bring the H1 and O2 atoms into the closest possible proximity, and this is achieved with the unusual dihedral angle of 17°.

There is much evidence that the six-membered H bond is weak: the non-bonded H1···O2 distance is approximately only 40 pm shorter than the sum of the van der Waals radii of hydrogen and oxygen,[14] the O1–H1···O2 is about 57° from being linear, the small red shift of the 42 cm^{-1} of the O–H stretching vibration,[5] and the fact that *Gauche I* is calculated to be only 5.4 kJ mol^{-1} more stable than *Gauche II*.

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