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Conformation and Intramolecular Hydrogen Bonding of 2-Chloroacetamide as Studied by Microwave Spectroscopy and Quantum Chemical Calculations

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The microwave spectrum of 2-chloroacetamide ($ClCH_2CONH_2$) has been investigated at room temperature in the 19−80 spectral range. Spectra of the $^{35}ClCH_2CONH_2$ and $^{37}ClCH_2CONH_2$ isotopomers of one conformer, which has a symmetry plane (C_s symmetry), were assigned. The amide group is planar, and an intramolecular hydrogen bond is formed between the chlorine atom and the nearest hydrogen atom of the amide group. The ground vibrational state, six vibrationally excited states of the torsional vibration about the CC bond, as well as the first excited state of the lowest bending mode were assigned for the $^{35}ClCH_2CONH_2$ isotopomer, whereas the ground vibrational state of $^{37}ClCH_2CONH_2$ was assigned. The CC torsional fundamental vibration has a frequency of 62(10) cm^{-1}, and the bending vibration has a frequency of 204(30) cm^{-1}. The rotational constants of the ground and of the six excited states of the CC torsion were fitted to the potential function $V(z) = 16.1(\langle z^4\rangle + 2.3\langle z^2\rangle)$ cm^{-1}, where z is a dimensionless parameter. This function indicates that the equilibrium conformation has C_s symmetry. Rough values of the chlorine nuclear quadrupole coupling constants were derived as $\chi_{aa} = -47.62(52)$ and $\chi_{bb} = 8.22(66)$ MHz for the ^{35}Cl nucleus and $\chi_{aa} = -34.6(10)$ and $\chi_{bb} = 6.2(11)$ MHz for the ^{37}Cl nucleus. Ab initio and density functional theory quantum chemical calculations have been performed at several levels of theory to evaluate the equilibrium geometry of this compound. The density functional theory calculations at the B3LYP/6-311++G(3df,2pd) and B3LYP/cc-pVTZ levels of theory as well as ab initio calculations at the MP2(F)/cc-pVTZ level predict correct lowest-energy conformation for the molecule, whereas the ab initio calculations at the QCISD(FC)/6-311G(d) and MP2(F)/6-311++G(d,p) levels predict an incorrect equilibrium conformation.

Introduction

Intramolecular hydrogen (H) bonds are important in chemistry and biology. The peptide linkage, −C(O)NH−, found in amides is an essential feature of proteins. Gas-phase studies of amides and of molecules possessing internal H bonds by microwave (MW) spectroscopy and gas electron diffraction (GED) are major research interests of the MW and GED laboratoties in Oslo, owing to their fundamental significance.

It is important to perform investigations of amides and H-bonded compounds in the gas phase at low pressures rather than in condensed phases, since perturbations caused by neighboring molecules often occur in the fluid phase or in crystals, obscuring the properties of the compounds under investigation. GED and MW spectroscopy both offer the possibility of studying molecules at low pressures and are therefore ideal for studies of this kind.

The GED and MW laboratories in Oslo have a long tradition of studying intramolecular H bonding as well as amides. Recent examples of investigation of the former effect include cyclopropylmethylselenol ($C_3H_5CH_2SeH$),[1] cyclopentadienylphosphine ($C_5H_5PH_2$),[2] 1,1,1-trifluoro-2-propanol ($CF_3CH(OH)CH_3$),[3] cyclopropylmethylphosphine ($C_3H_5CH_2PH_2$),[4] 1-fluorocyclopropylcarboxylic acid (C_3H_4FCOOH),[5] and 3-buteneselenol ($H_2C{=}CHCH_2CH_2SeH$).[6] Further microwave studies are found in reviews.[7−9] A comprehensive review literature of intramolecular H bonding in condensed phases is also available.[10−12]

Examples of recent gas-phase studies of amides are formamide ($HCONH_2$),[13] urea $CO(NH_2)_2$,[14] acetamide (CH_3CONH_2),[15] 2,2-dichloroacetamide ($CHCl_2CONH_2$)[16] formic hydrazide ($H_2NNHCHO$),[17] acrylamide ($H_2C{=}CHCONH_2$),[18] 2-chloro-2,2-difluoroacetamide ($CF_2ClCONH_2$),[19] 2,2-difluoroacetamide (CF_2HCONH_2),[20] and 2,2,2-trichloroacetamide (CCl_3CONH_2).[21] In this work, our investigations are extended to include a MW investigation of 2-chloroacetamide ($CH_2ClCONH_2$), which has not previously been studied by MW spectroscopy.

Rotation about the CC bond in the title compound may lead to rotational isomerism. A model of the title compound with atom numbering is depicted in Figure 1. The O1C2C6Cl7 chain of atoms is in an *antiperiplanar* (ap) arrangement in this figure, allowing an internal H bond to be formed between the Cl7 and H5 atoms.

The structural and conformational properties of 2-chloroacetamide have been subjected to several previous studies. The pure quadrupole spectra of the crystalline compound were measured by Allen.[22,23] The dipole moment in a dioxane solution was found to be 2.94 D by Soundararajan,[24] who concluded that a conformer with the O1C2C6Cl7 dihedral angle in 10−30° range from ap, or an “unlimited proportions of rotational isomers”, could account for the observed dipole moment. Katayama[25] performed an X-ray investigation of 2-chloroacetamide and found that there are two forms of the compound in the crystalline state, one being more stable than the other. The amide moieties are connected by *inter*molecular H bonds in both forms. The O1C2C6Cl7 dihedral angle is about 21° from ap in both conformers.[25] A gas-phase GED diffraction study was made by Kimura et al.,[26] who concluded that there is only one conformer of 2-chloroaceamide in the gaseous state and that the O1C2C6Cl7 dihedral angle is about 15° from ap. A more recent GED study was reported by Samdal and Seip,[27]

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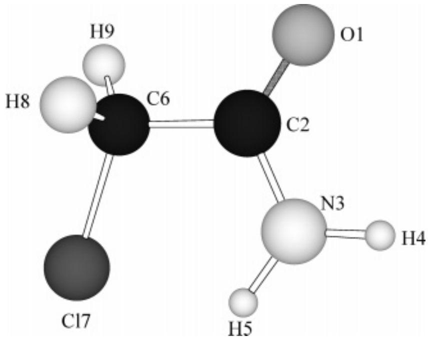

Figure 1. Model of 2-chloroacetamide with atom numbering. The O1C2C6Cl7 dihedral angle is antiperiplanar (180°) in the conformation shown here.

who came to a similar conclusion as that of Kimura et al.[26] The O1C2C6Cl7 dihedral angle was determined to be 17.8-(14)° from ap in the more recent GED work,[27] in which it was claimed that the said dihedral angle is undoubtedly nonzero.

MW spectroscopy is characterized by a superior accuracy and resolution, and it is therefore well suited to determine definitely whether the O1C2C6Cl7 dihedral angle is indeed different from the *exact* ap conformation. Moreover, this method can provide evidence as to whether the amide group is planar or not.

Comparatively few gas-phase studies of compounds stabilized by internal H bonds involving the chlorine atom have been performed. Investigations into this atom's ability to involve itself in such interactions are clearly of interest. These were the main motivations to undertake the present MW and quantum chemistry investigation.

Quantum chemical calculations at various levels of theory have been performed in addition to the MW study for two reasons. First, such calculations provide a number of useful predictions that aids the spectroscopic investigations. Second, it is possible to compare the ability of different levels of calculation to reproduce the experimental findings. Experience gained in this manner may prove useful in future studies.

Experimental

A commercial sample of 2-chloroacetamide was used. The compound was purified by recrystallization several times from acetic acid ethyl ester and its purity checked by NMR spectroscopy. Its MW spectrum was studied in the 19−80 GHz spectral region using the Oslo Stark modulated MW spectrometer, whose main features have been described elsewhere.[2,5] The resolution of this instrument is about 0.4 MHz. In addition to conventional Stark-spectroscopy studies, microwave radio frequency double resonance experiments were performed as described by Wodarczyk and Wilson.[28] The spectrum was recorded at room temperature. The vapor pressure is roughly 1−2 Pa at this temperature, which is less than the optimum pressure of approximately 5 Pa. It is not possible to increase the temperature above room temperature when using the current apparatus. A higher temperature would have produced a higher vapor pressure than 1−2 Pa, resulting in a stronger spectrum than that observed.

Results

Quantum Chemical Calculations. A series of quantum chemical calculations were performed at the HP Superdome facility in Oslo, employing the Gaussian 03 suite of programs.[29]

Several ab initio and density functional theory (DFT) calculations were undertaken using wave functions of at least triple-ζ quality. The ab initio calculations performed here include quadratic configuration interaction calculations with single and double substitutions (QCISD)[30] using the 6-311G(d) basis set and with the inner-shell electrons excluded (FC), as well as Møller−Plesset second-order perturbation calculations[31] with all electrons participating (MP2(F)). The 6-311++G(d,p) basis set and Dunning's correlation-consistent triple-ζ basis set with polarized valence electrons, cc-pVTZ,[32,33] were used in the MP2-(F) calculations. DFT calculations were performed using the B3LYP functional of Becke et al.[34,35] with the 6-311++G-(3df,2pd) and cc-pVTZ basis sets.

The geometries were fully optimized in all the calculations. The structures obtained this way are collected in Table 1, where the GED structure[27] is included for comparison. The rotational constants calculated from the theoretical structures are listed in Table 2, where the dipole moments, its components along the principal inertial axes and the value of $I_a + I_b - I_c$, where I_a, I_b and I_c are the principal moments of inertia, are given. The value of $I_a + I_b - I_c$ is included because it is exactly zero for a planar molecule and approximately 3.15×10^{-20} u m^2 for a compound having a symmetry plane (C_s symmetry) and two sp^3-hybridized out-of-plane H atoms.

Inspection of Table 1 reveals that there are small differences between the calculated and the ED bond lengths and bond angles regardless of the computational procedure. It is therefore not possible to decide which computational procedure that predicts the most accurate structure of the title compound from this comparison alone.

It is further noted that an unusually large value of 116.4(2)° is found experimentally for the C2C6Cl7 angle. The theoretical predictions of this angle are all very similar to this value. The distance between the Cl7 and N3 atoms is about 300 pm in these calculations and in the GED experiment,[27] compared with the sum of the van der Waals radii of chlorine (180 pm) and nitrogen (150 pm), which is 330 pm.[36] Repulsion between the Cl7 and the N3 atoms may therefore at least partly explain this unusually large bond angle.

Significant differences are, however, predicted in the theoretical calculations (Table 1) for the important O1C2C6Cl7 dihedral angle. The ab initio QCISD(FC)/6-311G(d) and MP2(F)/6-311++G(d,p) calculations predict this angle to deviate 14−19° from a completely ap structure, while exact C_s symmetry is found in the MP2(F)/cc-pVTZ and B3LYP calculations. It is also noted that the two first of these calculations predict a nonplanar amide group, whereas this group is planar in the B3LYP and MP2(F)/cc-pVTZ calculations. It is concluded that the most elaborate ab initio calculations (MP2(F)/cc-pVTZ) as well as the DFT calculations predict C_s symmetry for 2-chloroacetamide, whereas the remaining ab initio calculations predict a hump at the C_s conformation. The computed value of $I_a + I_b - I_c$ (Table 2) is about 3.14×10^{-20} u m^2 in the those cases where an exact C_s symmetry is predicted for 2-chloroacetamide and larger in the other cases.

The potential function for rotation about the C2C6 bond was also calculated employing the B3LYP/6-311++G(3df,2pd) procedure. The O1C2C6Cl7 dihedral angle was varied in steps of 20°, while allowing all remaining structural parameters to be optimized. A sketch of the potential function based on these calculations is shown in Figure 2. There is no indication in this function for the existence of a second minimum on the potential energy hypersurface, corresponding to a second "stable" rotameric form of 2-chloroacetamide. This is in agreement with results of the GED studies.[26,27] An sp conformation of the O1C2C6Cl7 chain of atoms, which means that the C2O1 and

TABLE 1: Experimental and Quantum Chemistry Geometries of $^{35}ClCH_2CONH_2$[a]

	GED(r_g)[b]	QCISD(FC)/6-311G(d)	B3LYP/6-311++G(3d f,2pd)	MP2(F)/6-311++G(d,p)	B3LYP/cc-pVTZ	MP2(F)/cc-pVTZ
			Bond Lengths			
O1=C2	122.2(2)	121.6	121.5	122.1	121.6	121.7
C2−N3	136.2(2)	136.0	134.9	136.1	134.8	136.4
C2−C6	152.3(3)	153.0	152.6	152.5	152.6	151.4
C6−Cl7	178.8(2)	179.4	180.4	178.1	181.2	177.9
N3−H4	103.9(12)[c]	100.6	100.6	100.9	100.5	100.2
N3−H5	103.9(12)[c]	100.4	100.5	100.7	100.4	100.1
C6−H8	111.3(7)[d]	109.2	108.5	109.1	108.5	108.1
C6−H9	111.3(7)[d]	109.0	108.5	108.8	108.5	108.1
			Bond Angles			
O1C2N3		124.1	124.4	124.1	124.6	124.7
O1C2C6	118.8(3)	118.0	117.5	118.6	117.4	117.9
N3C2C6	118.0(2)	117.8	118.1	117.1	118.0	117.3
C2N3H4	118.7	116.6	118.4	116.4	118.4	118.2
C2N3H5	120.4	121.4	121.6	119.7	121.4	121.2
H4N3H5		118.2	120.0	118.1	120.1	120.6
C2C6Cl7	116.4(2)	116.5	116.7	115.6	116.7	116.3
C2C6H8	108.1(8)[e]	108.0	108.2	107.8	108.3	107.8
C2C6H9	108.1(8)[e]	107.5	108.2	107.5	108.3	107.8
Cl7C6H8		107.6	107.3	107.9	107.1	107.9
Cl7C6H9		108.0	107.3	108.6	107.1	107.9
H8C6H9	108.0	109.1	109.0	109.4	109.1	108.9
			Dihedral Angles			
O1C2N3H4		9.6	−0.0	12.2	0.1	0.0
O1C2N3H5		167.3	180.0	164.9	179.9	179.9
O1C2C6Cl7	−162.2(14)	−165.8	180.0	−161.0	180.0	179.9

[a] Distances are given in picometers, and angles are given in degrees. Dihedral angles are zero for *synperiplanar* conformations. [b] Gas electron diffraction r_g structure. Uncertainties represent one standard deviation.[27] [c−e] Refined together.

TABLE 2: Rotational Constants, Moments of Inertia, and Dipole Moments Obtained in Quantum Chemical Calculations[a]

	QCISD(FC)/6-311G(d)	B3LYP/6-311++G(3d f,2pd)	MP2(F)/6-311++G(d,p)	B3LYP/cc-pVTZ	MP2(F)/cc-pVTZ
		Rotational Constants			
A	9504.6	9688.5	9460.5	9683.2	9810.7
B	2369.8	2366.6	2402.3	2359.2	2422.2
C	1932.8	1924.8	1963.0	1919.7	1966.1
$I_a + I_b - I_c$	4.95	3.14	6.34	3.14	3.11
		Dipole Moment			
μ_a	1.15	1.21	1.55	1.05	1.55
μ_b	1.79	1.81	1.73	1.79	1.77
μ_c	0.15	0.0	0.30	0.0	0.0
μ_{tot}	2.13	2.17	2.34	2.08	2.35

[a] $^{35}ClH_2CONH_2$ species. Rotational Constants are in MHz, the moments of inertia are in 10^{-20} u m^2, and the dipole moments are in debye.

C6Cl7 bonds eclipse each other, represents the maximum of the potential energy function, which is calculated to lie 19.0 kJ/mol above the energy ap conformer.

The same B3LYP method was used to calculate the vibrational frequencies (not given in Tables 1 or 2), which were all positive. This is independent indication that the C_s rotamer is a minimum on the potential energy hypersurface.[37] Watson's quartic centrifugal distortion constants[38] and the vibration−rotation interaction constants have also been calculated at this level of theory and will be compared below with their experimental counterparts.

Microwave Spectrum and Assignment. The quantum chemical calculations above indicate that four normal modes (not given in Tables 1 or 2) have frequencies lower than 500 cm^{-1} and will therefore have a significant Boltzmann factor at room temperature. Moreover, the uncorrected B3LYP/6-311++G-(3df,2pd) value for the torsion about the C2C6 bond is only 60 cm^{-1}, resulting in a Boltzmann factor as large as 0.75 at room temperature. The rotational constants are predicted to be about $A \approx 9.5$, $B \approx 2.4$, and $C \approx 1.9$ GHz (Table 2) in all the theoretical calculations. 2-Chloroacetamide must therefore have a comparatively large partition function at room temperature, which is one factor resulting in a weak spectrum.

Both a- and b-type transitions are expected for this compound, since the corresponding dipole moment components along the principal inertia axes are predicted to be sizable (Table 2). The perpendicular b-type spectra are very rich in the investigated spectral range (19−80 GHz). Moreover, there are two isotopes of chlorine, ^{35}Cl (75.78% abundance) and ^{37}Cl (24.22% abundance), both of which have spin = $^3/_2$. The ^{14}N isotope makes up more than 99% of naturally occurring nitrogen and has a spin of 1. Each MW transition will consequently have a very complicated hyperfine structure caused by quadrupole coupling of the spins of the chlorine and nitrogen nuclei with the overall rotation of the molecule. The low vapor pressure of 2-chloroacetamide, as well as the other factors mentioned above, should lead to a dense and relatively weak MW spectrum at room temperature, and such a spectrum was observed. Absorption lines occur every few MHz throughout the whole MW region. Many lines were obviously split into two or more components, while others were broad and/or skew, presumably owing to nuclear quadrupole interactions.

In the experience of the authors, it is generally easier to assign a-type spectra than b-type. The fact that high K_{-1} ^aR transitions are modulated at Stark field strengths of a few V/cm was used in making the first assignments. The $J = 14 \leftarrow 13$ series of the

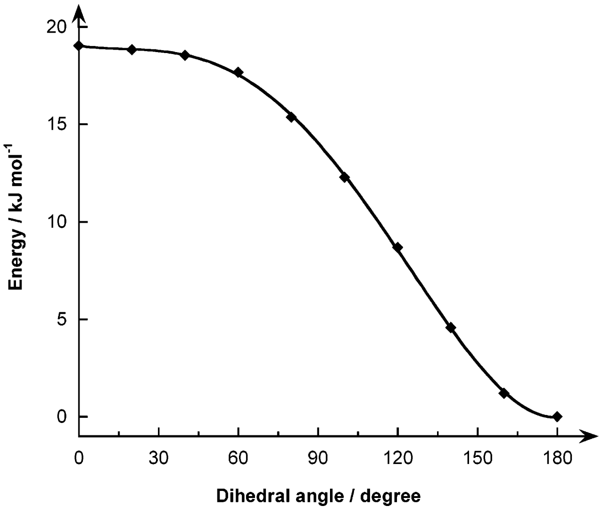

Figure 2. B3LYP/6-311++G(3df,2pd) potential function of rotation about the C2C6 bond. Dots indicate values for which calculations have been performed.

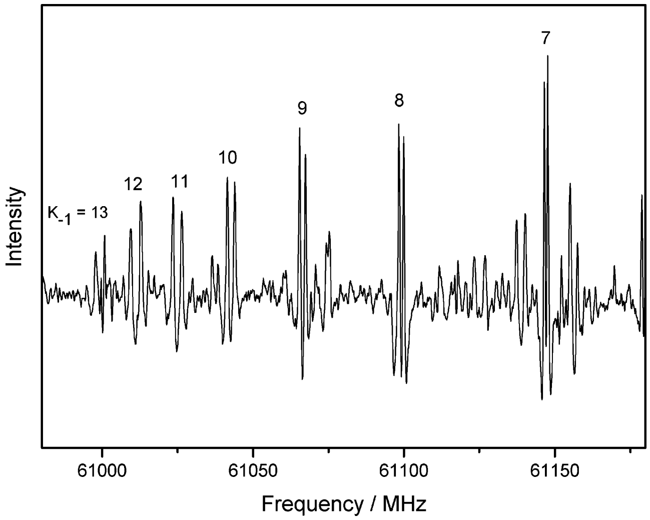

Figure 3. High-K_{-1} *a*-type $J = 14 \leftarrow 13$ transitions. The splitting into two resolved components of approximately equal intensity for each value of the pseudo quantum number K_{-1} is caused by nuclear quadrupole coupling of spin of the ^{35}Cl nucleus with the overall rotation of the molecule. The quadrupole splitting increases with the value of K_{-1}. The values of K_{-1} are indicated above each line pair. This spectrum was taken using a Stark-modulation voltage of about 45 V/cm.

$^{35}ClH_2CONH_2$ isotopomer, which appears near 61 GHz, is shown in Figure 3. The Stark modulation voltage was approximately 45 V/cm in this case. A characteristic feature of these lines is that they are split by quadrupole interaction into two well-resolved peaks of approximately the same intensity, a feature that is clearly visible in Figure 3. These splittings increase with K_{-1}. No further splittings were observed for these ^{a}R branch lines, since the resolution of our spectrometer is no better than 0.4 MHz. The average frequency of each pair of peaks was taken as an approximation of the unperturbed transition frequency in the absence of the nuclear quadrupole interaction. In the cases where no resolved quadrupole hyperfine structure was observed, no corrections to the observed frequencies of the observed peaks were made. It is estimated that the transition frequencies obtained this way represent the frequencies unperturbed by quadrupole interaction to within ±0.20 MHz.

These transitions were subjected to a least-squares analysis using Sørensen's Rotfit program.[39] Additional low-K_{-1} ^{a}R lines were gradually included in the least-squares fit. The fact that low-K_{-1} lines are modulated at higher field strengths than the high-K_{-1} lines was useful in the assignment procedure. The assignments of some of the ^{a}R transitions were also confirmed by radiofrequency microwave double-resonance experiments.[28] The *B* and *C* rotational constants are accurately determined from the ^{a}R lines. A fairly accurate *A* rotational constant could also be determined from them, since the molecules is not too close to the prolate (Ray's asymmetry parameter[40] $\kappa = -0.84$). This allowed the b-type lines to be readily identified, as they were found close to their predicted frequencies. No splittings due to quadrupole interactions were observed for most b-type lines. Some of them were, however, split into two components of equal intensities, as was the case for the high-K_{-1} ^{a}R-lines mentioned above. The frequencies of the centers of these doublets were used in the fitting procedure. About 270 transitions were ultimately assigned. Of these, with a maximum value of $J = 50$, 239 were used to determine the spectroscopic constants (A reduction I^r representation[38]) shown in Table 3. The MW spectrum is listed in Table 1S in the Supporting Information. Only quartic centrifugal distortion constants were employed in the least-squares fit, which had a root-mean-square deviation of 0.160 MHz, comparable to the estimated accuracy of the unperturbed frequency of ±0.20 MHz. An estimate of the quadrupole perturbation of each transition caused by the chlorine atom can be calculated from the nuclear quadrupole coupling constants obtained as described in a later section.

TABLE 3: Spectroscopic Constants[a] of the Ground Vibrational State of $^{35}ClCH_2CONH_2$ and of the Ground Vibrational State of $^{37}ClCH_2CONH_2$

	$^{35}ClCH_2CONH_2$	$^{37}ClCH_2CONH_2$
A (MHz)	9640.4724(87)	9639.8557(96)
B (MHz)	2402.1687(15)	2337.7981(21)
C (MHz)	1948.3733(15)	1905.7781(20)
Δ_J (kHz)	0.3591(34)	0.3548(45)
Δ_{JK} (kHz)	1.6738(69)	1.6160(87)
Δ_K (kHz)	8.47(24)	6.34(25)
δ_J (kHz)	0.07512(39)	0.07274(37)
δ_K (kHz)	1.156(24)	1.426(24)
$I_a + I_b - I_c$ [b] (10^{-20} u m^2)	3.42201(12)	3.42084(17)
rms[c] (MHz)	0.160	0.162
no.[d]	239	178

[a] A, reduction; I, representation.[38] Uncertainties represent one standard deviation. [b] Principal moments of inertia. Conversion factor: 505379.05 × 10^{-20} MHz u m^2. [c] Root-mean-square deviation. [d] Number of transitions.

The spectrum of the $^{37}ClCH_2CONH_2$ species, being about $^1/_3$ as intense as the ^{35}Cl species, was assigned in a manner analogous to that of the $^{35}ClCH_2CONH_2$. A total of 200 transitions were assigned, 178 of which were used to determine the spectroscopic constants displayed in Table 3. The lines employed to obtain this result are listed in Table 9S in the Supporting Information.

Comparison of the experimental rotational constants of $^{35}ClCH_2CONH_2$, shown in Table 3, with the corresponding to theoretical values in Table 2 reveals that the differences are no larger than 2% in all cases. Rotational constants alone cannot therefore be used to determine which computational scheme is more accurate. However, it can be seen from Table 3 that $I_a + I_b - I_c = 3.42201(12) \times 10^{-20}$ u m^2 for $^{35}ClCH_2CONH_2$, which is almost identical to the value of $3.42084(37) \times 10^{-20}$ u m^2 found for the $^{37}ClCH_2CONH_2$ species. This strongly suggests that the molecule has C_s symmetry.

It is noted that the B3LYP and the MP2(F)/cc-pVTZ calculations (Table 2), which both predict C_s symmetry, yield $I_a + I_b - I_c \approx 3.1 \times 10^{-20}$ u m^2, while the QCISD(FC)/6-

TABLE 4: Spectroscopic Constants[a] of Vibrationally Exited States of $^{35}ClCH_2CONH_2$

	first torsion	second torsion	third torsion	fourth torsion	fifth torsion	sixth torsion	first bending
A (MHz)	9569.6868(95)	9500.6247(90)	9432.7773(86)	9365.9316(90)	9299.725(18)	9234.655(26)	9656.209(16)
B (MHz)	2403.9542(22)	2405.7640(22)	2407.6092(34)	2409.5215(40)	2411.486(11)	2413.564(11)	2397.4778(58)
C (MHz)	1954.8190(22)	1961.1695(22)	1967.5008(34)	1973.8822(40)	1980.358(11)	1986.931(11)	1942.5496(58)
Δ_J (kHz)	0.3799(50)	0.3977(51)	0.3993(69)	0.4096(95)	0.435(25)	0.457(24)	0.369(11)
Δ_{JK} (kHz)	1.638(12)	1.617(11)	1.614(10)	1.630(16)	1.621(41)	1.779(47)	1.676(16)
Δ_K (kHz)	6.50(23)	6.89(21)	7.01(19)	7.89(20)	6.70(35)	11.74(92)	5.70(38)
δ_J (kHz)	0.07046(47)	0.06809(43)	0.06487(32)	0.06292(55)	0.0650(13)	0.0655(15)	0.07253(59)
δ_K (kHz)	1.471(29)	1.496(25)	1.510(21)	1.432(34)	1.323(87)	1.43(11)	1.455(32)
$I_a + I_b - I_c$[b] (10^{-20} u m^2)	4.50880(17)	5.57168(15)	6.62254(17)	7.66876(20)	8.71924(45)	9.76599(63)	2.97059(33)
rms[c] (MHz)	0.202	0.183	0.186	0.173	0.238	0.220	0.219
no.[d]	197	185	149	119	56	40	88

[a] A, reduction; I, representation.[38] Uncertainties represent one standard deviation. [b] Principal moments of inertia. Conversion factor: 505379.05 × 10^{-20} MHz u m^2. [c] Root-mean-square deviation. [d] Number of transitions.

311G(d) and MP2(F)/6-311++G(d,p) calculations predict significantly larger values for this quantity. The value 3.1 × 10^{-20} u m^2 is valid for a completely rigid molecule, whereas a compound possessing a low-frequency out-of-plane vibration is expected to have a somewhat larger value for this combination of moments of inertia,[41] in agreement with the present findings (Table 3).

Moreover, it is possible to determine the substitution coordinates of the chlorine atom using the moments of inertia of the ^{35}Cl and ^{37}Cl species in Kraitchman's equations.[42] The values found in this manner for the principal inertial axis coordinates are $|a| = 172.2(2)$ and $|b| = 4.6(7)$ pm, whereas a small imaginary value ($1.75i$ pm) was found for the c coordinate, which should be zero for symmetry reasons. The error limits reported for the a and b coordinates are Costain uncertainties, which have been calculated using the K values suggested by van Eijck.[43] The values of the substitution coordinates agree well with those calculated from the B3LYP/6-311++G(3df,2pd) structure ($|a| = 174.0$, $|b| = 3.8$, and $|c| = 0$ pm). This provides additional evidence that the stable form of 2-chloroacetamide has a symmetry plane including a planar amide group.

It is possible to suggest a preferred structure based on the previous ED work[27] and the present calculations: 2-chloroacetamide has C_s symmetry. The bond lengths and bond angles involving heavy atoms are accurately determined by ED, as shown in Table 2. Bond lengths and bond angles involving hydrogen atoms obtained in the quantum chemical calculations are assumed to be more accurate than their experimental counterparts. There are small differences in these parameters in the various calculations (see Table 2). The preferred values are those predicted in the MP2(F)/cc-pVTZ calculations, because these calculations predict the correct conformation and because MP2 calculations with a large basis set are known to predict accurate equilibrium structures.[44]

A comparison between the observed and calculated quartic centrifugal distortions constants is in order. The B3LYP/6-311++G(3df,2pd) quartic centrifugal distortion constants were $\Delta_J = 0.375$, $\Delta_{JK} = 1.583$, $\Delta_K = 4.82$, $\delta_J = 0.0742$, $\delta_K = 1.458$ kHz, compared to the experimental values (Table 3) $\Delta_J = 0.3591(34)$, $\Delta_{JK} = 1.6738(69)$, $\Delta_K = 8.47(24)$, $\delta_J = 0.07512(39)$ and $\delta_K = 1.156(24)$ kHz. The agreement between theory and experiment is satisfactory for Δ_J, Δ_{JK}, and δ_J, whereas Δ_K and δ_K deviate significantly for unknown reasons.

Vibrationally Excited States. The ground-state transitions are accompanied by several series of lines that have the same quadrupole patterns as the ground-state lines but lower intensities. The transitions of the first excited state of the most intense series have approximately 75% of the intensity of the corresponding ground-state counterparts. This series of lines was assigned in a manner similar to that of the ground state. The spectroscopic constants obtained for this state are shown in Table 4, while the 197 transitions used to derive them are listed in Table 2S in the Supporting Information.

Relative intensity measurements yielded 65(15) cm^{-1} for this vibration, close to the uncorrected B3LYP/6-311++G(3df,2pd) value (60 cm^{-1}) calculated for the torsional vibration about the C2C6 bond. It is seen in Table 2 that the value of $I_a + I_b - I_c$ is larger in the excited state than in the ground state. This is typical for an out-of-plane vibration, for example a torsional vibration.[41] This increase of $I_a + I_b - I_c$ upon excitation can be used to get an estimate of the torsional frequency using the formula $\omega = 67.5/\Delta$ cm^{-1},[41] where Δ is the increase of $I_a + I_b - I_c$ upon excitation. This formula is derived assuming no coupling with other normal harmonic modes. Only weak coupling is expected in our case since the three lowest vibrational frequencies are predicted at 60, 237 and 334 cm^{-1} in the B3LYP/6-311++G(3df,2pd) calculations.

Δ is calculated to be 1.087 × 10^{-20} u m^2 from the entries in Tables 3 and 4, which yields $\omega = 62$ cm^{-1} for the lowest torsional normal mode, a value that is close to the theoretical value (60 cm^{-1}) and relative intensity measurement result 65(15) cm^{-1}. Our best estimate of the torsional fundamental is therefore 62(10) cm^{-1}.

The spectroscopic vibration−rotation constant α_X is given by $\alpha_X = X_0 - X_1$, where X_0 is the X rotational constant in the ground vibrational state and X_1 is the corresponding constant of the first excited state of a normal vibration.[45] The values of the α_X calculated from the entries in Tables 3 and 4 for the lowest torsional mode are $\alpha_A = 70.79(1)$, $\alpha_B = -1.786(3)$, and $\alpha_C = -6.446(3)$ MHz, compared to 66.23, −1.25, and −6.00 MHz, respectively, obtained from the B3LYP/6-311++G(3df,2pd) calculations.

It was possible to assign 5 additional excited states of this torsional mode. Their spectroscopic constants are listed in Table 4; the spectra are found in Tables 3S−7S in the Supporting Information. It is noted that the rotational constants vary almost linearly and that the values of $I_a + I_b - I_c$ increase approximately linearly. These properties are characteristic for a nearly harmonic mode.[41]

Finally, a seventh vibrationally excited state was assigned. Its spectroscopic constants are displayed in Table 4, while the spectrum is found in Table 8S. The value of $I_a + I_b - I_c = 2.97059(33) \times 10^{-20}$ u m^2, which is lower for this excited state than for the ground vibrational state (Table 3). This is typical for bending vibration having A′ symmetry in a compound with C_s symmetry. Relative intensity measurements yielded 204(40) cm^{-1} for this mode, in fair agreement with the B3LYP value of 238 cm^{-1} for the lowest bending vibration.

The values of the α_X calculated from the rotational constants in Tables 3 and 4 are $\alpha_A = -15.74(2)$, $\alpha_B = 4.69(1)$, and $\alpha_C =$

TABLE 5: Least-Squares Fit of the Rotational Constants[a] to the Expression $\langle z^4\rangle + 2.3\,\langle z^2\rangle$

vibrational state	A_v calcd	A_v calcd − obsd	B_v calcd	B_v calcd − obsd	C_v calcd	C_v calcd − obsd
0	9640.95	0.48	2402.19	0.02	1948.39	0.02
1	9568.74	−0.95	2403.92	−0.04	1954.80	−0.02
2	9500.22	−0.41	2405.75	−0.17	1961.15	−0.02
3	9433.94	1.17	2407.59	−0.17	1967.42	−0.08
4	9366.32	0.39	2409.56	0.04	1973.95	0.07
5	9298.91	−0.81	2411.57	0.08	1980.53	0.17
6	9234.79	0.14	2413.49	−0.08	1986.79	−0.14

derived function for the rotational constants[b]

$A_v = 9679.2(13) - 131.0(26)\langle z^2\rangle - 22.98(67)\langle z^4\rangle$
$B_v = 2401.328(92) + 2.65(18)\langle z^2\rangle + 0.912(47)\langle z^4\rangle$
$C_v = 1945.09(17) + 10.87(34)\langle z^2\rangle + 2.590(88)\langle z^4\rangle$

[a] In MHz. [b] Uncertainties represent one standard deviation.

5.82(1) MHz, which compare favorably with the corresponding values, −20.23, 5.09, and 6.05 MHz, respectively, obtained from the B3LYP/6-311++G(3df,2pd) calculations.

Potential Function for the C2C6 Torsion. Following Gwinn and co-workers,[46] a reduced potential function of the form

$$V(z) = A(\langle z^4\rangle + B\langle z^2\rangle) \tag{1}$$

can be used to describe the torsion. A and B (not to be confused with the rotational constants) are parameters to be fitted. A may have the dimension cm^{-1}. B and z are dimensionless. The molecule will have C_s symmetry as its equilibrium conformation provided B is positive. A double minimum potential with a hump at the C_s conformation will exist if B is negative, resulting in C_1 symmetry for the equilibrium conformation of the compound.

It is possible to expand the rotational constants, β_v, in a power series involving the expectation value of the dimensionless coordinate z

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

where β_v is the A_v, B_v, or C_v rotational constants in the vth state of the torsional mode. β_0, β_2, and β_4 are empirical parameters adjusted to give the best fit. The values of $\langle z^2\rangle_v$ and $\langle z^4\rangle_v$ in eq 1 depend only on the value of B.[46]

Computer programs by Møllendal[47] based on these concepts were employed. The rotational constants of successively excited states of the torsion were fitted for a range of values of B to eq 2 using the least-squares method. It was found that the value $B = 2.3$ yielded the best overall fit. All rotational constants were given the same weight in the fit. The results are given in Table 5.

It is seen in this table that a fit with a *positive B* is able to reproduce the rotational constants very well. This is another indication that the equilibrium conformation of the O1C2C6Cl7 link of atoms is indeed planar and has an exact ap conformation.

The leading terms in the expressions found for the rotational constants, 9679.2(13), 2401.328(92), and 1945.09(17) MHz (Table 5), are approximations of state in which the torsion is frozen. Interestingly, $I_a + I_b - I_c$ is calculated from them to be 2.85×10^{-20} u m^2 for this hypothetical state. This is fairly close to about 3.15×10^{-20} u m^2, which is expected for the equilibrium structure.

Finally, the A constant of eq 1 was adjusted to reproduce the fundamental frequency (62(10) cm^{-1}). A value of $A = 16.1$ cm^{-1} was found using a spacing of 62 cm^{-1} between the two first energy levels. The potential function is therefore

$$V(z) = 16.1(\langle z^4\rangle + 2.3\langle z^2\rangle)\ \mathrm{cm}^{-1} \tag{3}$$

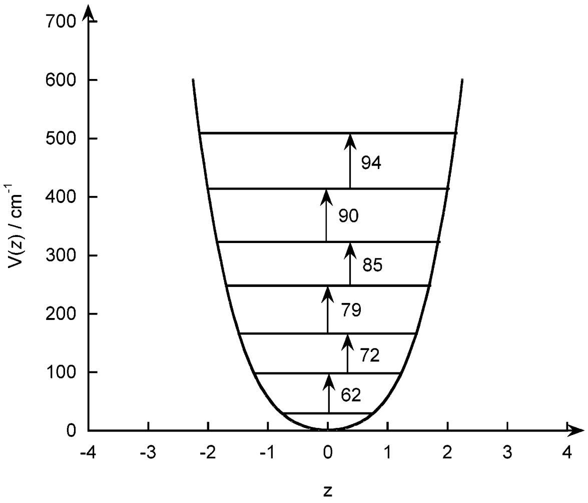

Figure 4. The potential function $V(z) = 16.1(\langle z^4\rangle + 2.3\langle z^2\rangle)$ cm^{-1} describing the torsional vibration about the C2C6 bond. The first few eigenstates are indicated.

This function is drawn in Figure 4. The first few eigenstates calculated from this potential function are indicated on this figure.

It is not straightforward to compare the potential functions shown in Figures 2 and 4 because the B3LYP potential function has been derived allowing a complete relaxation of the molecule apart from the torsion about the C2C6 bond, whereas the function shown in Figure 4 is two-dimensional, involving only the energy and the torsional motion about the C2C6 bond. The function in Figure 4 models the bottom of the well (the ap conformation) rather reliably, but yields no information about the maximum (the sp conformation), while the theoretical potential function in Figure 4 models the whole torsional motion about the C2−C6 bond.

Quadrupole Coupling Constants of the Chlorine Nucleus. The quadrupole interaction of the chlorine nucleus with the overall molecular rotation is much larger than the quadrupole effect of the ^{14}N nucleus. The quadrupole coupling originating from the nitrogen nucleus was therefore neglected, because there was no way this could be determined from the available experimental data. Rough values of principal-axis components of the coupling tensor were derived from the observed splittings listed in Tables 10S and 11S in the Supporting Information. The results of a least-squares fit using programs described previously[48] were $\chi_{aa} = -47.62(52)$ and $\chi_{bb} = 8.22(66)$ MHz for the ^{35}Cl nucleus and $\chi_{aa} = -34.6(10)$ and $\chi_{bb} = 6.2(11)$ MHz for the ^{37}Cl nucleus.

The principal nuclear quadrupole coupling constants are available for the $CH_3{}^{35}Cl$ (−74.7514(11) MHz) and $CH_3{}^{37}Cl$ species (−58.9116(34) MHz).[49] By use of these values and assumption that the nuclear quadrupole tensor is symmetrical about the C6Cl7 bond, $\chi_{aa} = -46.8$ and $\chi_{bb} = 9.4$ MHz were calculated for $^{35}ClCH_2CONH_2$ using the B3LYP/6-311++G(3df,2pd) structure. Likewise, $\chi_{aa} = -37.0$ and $\chi_{bb} = 7.5$ MHz were obtained for the $^{37}ClCH_2CONH_2$ species. The procedure outlined by Gordy and Cook[45] was used to derive these values. The agreement between the experimental and calculated values for χ_{aa} and χ_{bb} is satisfactory.

Discussion

It is assumed that 2-chloroacetamide takes a conformation where the O1C2C6Cl7 chain of atoms is exactly ap as a result of several intramolecular interactions. A sp arrangement for the said link of atoms would bring the electronegative chlorine and oxygen atoms into close proximity resulting in repulsion. Not surprisingly, the sp conformer represents a transition state in the B3LYP/6-311++G(3df,2pd) calculations.

The observed exact ap arrangement brings the chlorine atom into the closest possible proximity with the nearest atom of the amide group (H5), resulting in the formation of the strongest possible intramolecular H bond. The nonbonded interatomic distance between these two atoms is calculated using the B3LYP/6-311++G(3df,2pd) to be about 250 pm, 50 pm shorter than 300 pm, which is the sum of the van der Waals radii of chlorine (180 pm) and hydrogen (120 pm).[36] The N3−H5··· Cl7 bond angle is 110°, far from the ideal linear arrangement. The angle between the H5−N3 and Cl7−C6 bonds is about 4° from being parallel. The bond moments are thus only a few degrees from being antiparallel, which is ideal for stabilizing the H-bonded conformer via a dipole−dipole interaction. The H bond is not strong, but its strength is sufficient to outweigh the repulsion between the electronegative chlorine and nitrogen atoms, which are only 300 pm apart, compared to 330 pm, which is the sum of the van der Waals radii of chlorine (180 pm) and nitrogen (150 pm).[36]

Comparison with the results of the X-ray[25] and GED results[27] is in order. The conformation in the crystalline phase differs from the gas-phase conformation as the O1C2C6Cl7 dihedral angle is approximately 21° from the exact ap conformation in the crystal,[25] compared to 0° found in this investigation. It is likely that this difference is a result of crystal forces.

The GED finding of a dihedral angle of 17.8(14)° from ap for the said link of atoms resulted from a *static* treatment of the data.[27] This approach results in an *average* dihedral angle and cannot be used to decide whether the molecule has a C_s conformation or not. However, it is possible to estimate the average O1C2C6Cl7 dihedral angle using the potential function shown in Figure 2. Following the treatment outlined by Samdal,[50] a value of 22.9° was obtained. Inclusion of the shrinkage effect,[51−53] which was subsequently made, decreases this value somewhat, resulting in good agreement with the experimental value of 17.8(14)°.

A lesson has been learned from the quantum chemical calculations, namely, that MP2 calculations employing relatively limited basis sets underestimates H bond interactions and at the same time are unable to predict the correct planar conformation of the amide group in this molecule.

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Supporting Information Available: Tables showing microwave spectra for $^{35}ClCH_2CONH_2$ and $^{37}ClCH_2CONH_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Cole, G. C.; Møllendal, H.; Guillemin, J.-C. *J. Phys. Chem. A* **2006**, *110*, 2134.
(2) Møllendal, H.; Cole, G. C.; Guillemin, J.-C. *J. Phys. Chem. A* **2006**, *110*, 921.
(3) Møllendal, H. *J. Phys. Chem. A* **2005**, *109*, 9488.
(4) Cole, G. C.; Mollendal, H.; Guillemin, J.-C. *J. Phys. Chem. A* **2005**, *109*, 7134.
(5) Møllendal, H.; Leonov, A.; de Meijere, A. *J. Phys. Chem. A* **2005**, *109*, 6344.
(6) Petitprez, D.; Demaison, J.; Wlodarczak, G.; Guillemin, J.-C.; Møllendal, H. *J. Phys. Chem. A* **2004**, *108*, 1403.
(7) Møllendal, H. *J. Mol. Struct.* **1983**, *97*, 303.
(8) Wilson, E. B.; Smith, Z. *Acc. Chem. Res.* **1987**, *20*, 257.
(9) Møllendal, H. *NATO ASI Ser., Ser. C* **1993**, *410*, 277.
(10) Tichy, M. *Adv. Org. Chem.* **1965**, *5*, 115.
(11) Aaron, H. S. *Top. Stereochem.* **1979**, *11*, 1.
(12) Desiraju, G.; Steiner, T. *The Weak Hydrogen Bond: Applications to Structural Chemistry and Biology*, 1999.
(13) Brown, R. D.; Godfrey, P. D.; Kleiboemer, B. *J. Mol. Spectrosc.* **1987**, *124*, 34.
(14) Godfrey, P. D.; Brown, R. D.; Hunter, A. N. *J. Mol. Struct.* **1997**, *413−414*, 405.
(15) Yamaguchi, A.; Hagiwara, S. n; Odashima, H.; Takagi, K.; Tsunekawa, S. *J. Mol. Spectrosc.* **2002**, *215*, 144.
(16) Gundersen, S.; Samdal, S.; Seip, R.; Strand, T. G. *J. Mol. Struct.* **2004**, *691*, 149.
(17) Samdal, S.; Møllendal, H. *J. Phys. Chem. A* **2003**, *107*, 8845.
(18) Marstokk, K.-M.; Møllendal, H.; Samdal, S. *J. Mol. Struct.* **2000**, *524*, 69.
(19) Gundersen, S.; Novikov, V. P.; Samdal, S.; Seip, R.; Shorokhov, D. J.; Sipachev, V. A. *J. Mol. Struct.* **1999**, *485−486*, 97.
(20) Gundersen, S.; Samdal, S.; Seip, R.; Shorokhov, D. J. *J. Mol. Struct.* **1999**, *477*, 225.
(21) Samdal, S.; Seip, R. *J. Mol. Struct.* **1997**, *413−414*, 423.
(22) Allen, H. C., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 6074.
(23) Allen, H. C., Jr. *J. Phys. Chem.* **1953**, *57*, 501.
(24) Soundararajan, S. *Trans. Faraday Soc.* **1957**, *53*, 159.
(25) Katayama, M. *Acta Crystallogr.* **1956**, *9*, 986.
(26) Kimura, M.; Aoki, M.; Kurita, Y. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 360.
(27) Samdal, S.; Seip, R. *J. Mol. Struct.* **1979**, *52*, 195.
(28) Wodarczyk, F. J.; Wilson, E. B., Jr. *J. Mol. Spectrosc.* **1971**, *37*, 445.
(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.
(30) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
(31) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(32) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
(33) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548.
(34) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(35) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(36) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: New York, 1960.

(37) Hehre, W. J.; Radom, L.; Schleyer, P. v. R. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(38) Watson, J. K. G. *Vibrational Spectra and Structure*; Elsevier: Amsterdam, 1977; Vol. 6.

(39) Sørensen, G. O. *ROTFIT*; Personal communication, 1972.

(40) Ray, B. S. *Z. Phys.* **1932**, *78*, 74.

(41) Laurie, V. W.; Herschbach, D. R. *J. Chem. Phys.* **1962**, *37*, 1687.

(42) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17.

(43) Van Eijck, B. P. *J. Mol. Spectrosc.* **1982**, *91*, 348.

(44) Helgaker, T.; Gauss, J.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **1997**, *106*, 6430.

(45) Gordy, W.; Cook, R. L. *Techniques of Chemistry, Vol. 56: Microwave Molecular Spectra*; John Wiley & Sons: New York, 1984; Vol. XVII.

(46) Gwinn, W. D.; Gaylord, A. S. *Int. Rev. Sci.: Phys. Chem., Ser. 2* **1976**, *3*, 205.

(47) Marstokk, K.-M.; Møllendal, H.; Samdal, S.; Uggerud, E. *Acta Chem. Scand.* **1989**, *43*, 351.

(48) Marstokk, K.-M.; Møllendal, H. *J. Mol. Struct.* **1969**, *4*, 470.

(49) Wlodarczak, G.; Boucher, D.; Bocquet, R.; Demaison, J. *J. Mol. Spectrosc.* **1986**, *116*, 251.

(50) Samdal, S. *J. Mol. Struct.* **1994**, *318*, 133.

(51) Almenningen, A.; Bastiansen, O.; Munthe-Kaas, T. *Acta Chem. Scand.* **1956**, *10*, 261.

(52) Bastiansen, O.; Trætteberg, M. *Acta Crystallogr.* **1960**, *13*, 1108.

(53) Morino, Y. *Acta Crystallogr.* **1960**, *13*, 1107.