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^{14}N Quadrupole Coupling in the Microwave Spectra of N-Vinylformamide

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Abstract

The microwave spectra of two conformers, *trans* and *cis*, of the title compound were recorded using two molecular beam Fourier transform microwave spectrometers operating in the frequency range 2 GHz to 40 GHz, and aimed at analyses of their ^{14}N quadrupole hyperfine structures. Rotational constants, centrifugal distortion constants, and nuclear quadrupole coupling constants χ_{aa} and $\chi_{bb} - \chi_{cc}$, were all determined with very high accuracy. Two fits including 176 and 117 hyperfine transitions were performed for the *trans* and *cis* conformers, respectively. Standard deviations of both fits are close to the measurement accuracy of 2 kHz. Complementary quantum chemical calculations - MP2/6-311++G(d,p) rotational constants, MP2/cc-pVTZ centrifugal distortion constants, and B3PW91/6-311+G(d,p)//MP2/6-311++G(d,p) nuclear quadrupole coupling constants - give spectroscopic parameters in excellent agreement with the experimental parameters.

Keywords: Microwave spectroscopy, N-Vinylformamide, Nuclear quadrupole coupling constants, Quantum chemical calculations

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1. Introduction

Amides are nitrogen containing functional groups of general interest in chemistry and molecular biology. Due to conjugation between the carbonyl π -electrons and the lone electron pair of the nitrogen, their electronic configurations are rather complex. It is this character of the amide bond that is the origin of its behavior in chemical reactions and biological processes.

Formamides are a sub-class of amides which contain the planar sub-unit $\text{H}(\text{C}=\text{O})\text{N}$. Spectroscopic investigations of several formamides have been reported, aimed at determining their rotational structures. The simplest amide, formamide [1], as well as N-methylformamide [2], N-ethylformamide [3], N,N-dimethylformamide [4], and N,N-methylethylformamide [5] were thoroughly studied. Reports on the microwave spectra of three unsaturated formamides, N-phenylformamide [6, 7], N-vinylformamide [8], and diformamide [9] are available in the literature. Such unsaturated molecules are very interesting, since π -electron conjugation between the double bond(s), the lone electron pair of the nitrogen, and the carbonyl bond is possible.

The microwave spectrum of N-vinylformamide, $\text{HC}(=\text{O})\text{N}(\text{H})\text{CH}=\text{CH}_2$, was recently investigated by Møllendal and Samdal [8], at room temperature from 18 to 75 GHz. Spectra attributed to the *trans* and *cis* forms shown in Fig. 1 were assigned, and it was concluded from the inertial defects that each is completely planar. However, with a resolution of about 0.5 MHz and an estimated accuracy of 0.10 MHz for isolated lines, it was not possible to resolve the quadrupole splittings of the ^{14}N nucleus.

Therefore, we decided to remeasure the spectra at higher resolution to gain information on the nuclear quadrupole coupling in this molecule. The origin of this effect is the interaction of the electric quadrupole moment of the nucleus with the electric field gradient (EFG) at the site of the nucleus due to all other charges in the molecule. However, since the EFG due to a charge at a distance r from the nucleus in question is proportional to $1/r^3$, only electrons associated with the nucleus have major contributions to the EFG. Indeed, the seminal work of Townes and Dailey [10] argues that only valence p electrons need be considered, thereby establishing a link between chemical bonding and nuclear quadrupole coupling. Thus, analysis of the quadrupole hyperfine structure yields information not only on the EFG at the site of the nitrogen nucleus, but also on the nature of the chemical bond.

Quantum chemical calculations were undertaken to complement this work. These are discussed in Section 2. Experimental techniques and results are

discussed in Section 3.

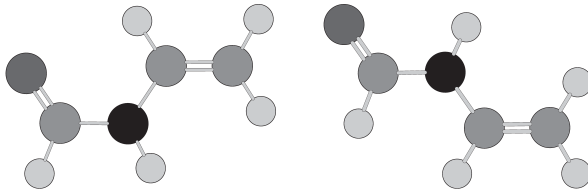


Figure 1: Observed *trans* (left) and *cis* (right) conformers of N-vinylformamide.

2. Theoretical

Quantum chemical calculations were undertaken to complement this experimental investigation. These calculations concern the rotational constants, inertial axes components of the ^{14}N nuclear quadrupole coupling constants (NQCCs), and quartic centrifugal distortion constants (CDCs), and were made with the GAUSSIAN 09 suite of programs [11].

2.1. Conformational Preferences

Quantum chemical calculations by Møllendal and Samdal identified four stable conformers. Only the two most stable (Fig. 1) were found in their experimental spectrum - and in ours. At the B3LYP and CCSD(T) levels of theory, each in conjunction with cc-pVTZ bases, Møllendal and Samdal calculate the *cis* conformer more stable than the *trans* by 0.3 and 2.8 kJ/mol, respectively. In this work, at the MP2/6-311++G(d,p) level, *trans* is found more stable by 1.8 kJ/mol. This point will be revisited in the Section 3. (The MP2 optimized atomic coordinates in the principal inertial axis system are given in the Supplementary Material in Tables S1 and S2.)

2.2. Spectroscopic Parameters

Spectroscopic parameters predicted for both *trans* and *cis* conformers are collected in Table 1, along with the experimental parameters. Rotational constants and ^{14}N inertial axes NQCCs were calculated on MP2/6-311++G(d,p) optimized molecular structures. Quartic CDCs were calculated at the MP2/cc-pVTZ level of theory.

2.3. Nuclear Quadrupole Coupling Constants

Components of the NQCC tensor, χ_{ij} are related to those of the EFG tensor, q_{ij} by

$$\chi_{ij} \text{ (MHz)} = (eQ/h) \times q_{ij} \text{ (a.u.)}, \quad (1)$$

where e is the fundamental electric charge, Q is the electric quadrupole moment of the nucleus, and h is Planck’s constant. Calibration of a particular computational model for the calculation of NQCCs is achieved by taking the coefficient eQ/h as a best-fit parameter determined by linear regression analysis of calculated q_{ij} on the experimental structures of a number of molecules versus the corresponding experimental χ_{ij} [12]. The premise that underlies this procedure is that errors inherent in the level of theory are systematic and can be corrected, at least in part, by the best fit parameter eQ/h . Thus was undertaken calibration of the B3PW91/6-311+G(d,p) model, the result of which is illustrated in Fig. 2. Further details are given in Supplementary Material. The best-fit parameter eQ/h , the slope of the line shown in the figure, is 4.599(12) MHz/a.u.

This model was used here for calculation of the NQCCs on MP2/6-311++G(d,p) optimized structures of both *trans* and *cis* conformers of N-vinylformamide. (The results of calculations on this and several other MP2, B3LYP, and HF optimized structures are shown in Table S3 in Supplementary Material.)

3. Experimental

At the beginning of the experimental work, some microwave transitions of *cis* and *trans* conformers given in Ref. [8] were remeasured with higher resolution using a molecular beam Fourier transform microwave (MB-FTMW) spectrometer operating in the frequency range from 26.5 GHz to 40 GHz [13]. N-Vinylformamide was purchase from TCI Deutschland GmbH, Eschborn, Germany, with a stated purity of over 98 % and used without further purification. A gas mixture containing 1 % substance in helium at a total pressure of about 100 kPa was used throughout. The helium - substance mixture was expanded through the pulsed nozzle into the cavity.

The hyperfine splittings were calculated using the predicted NQCCs, and could be completely resolved and assigned. We then used the fitted constants χ_{aa} and $\chi_{bb}-\chi_{cc}$ to predict and measure further low J – transitions using the program *XIAM* [14]. Some transitions in the frequency range from 2 GHz

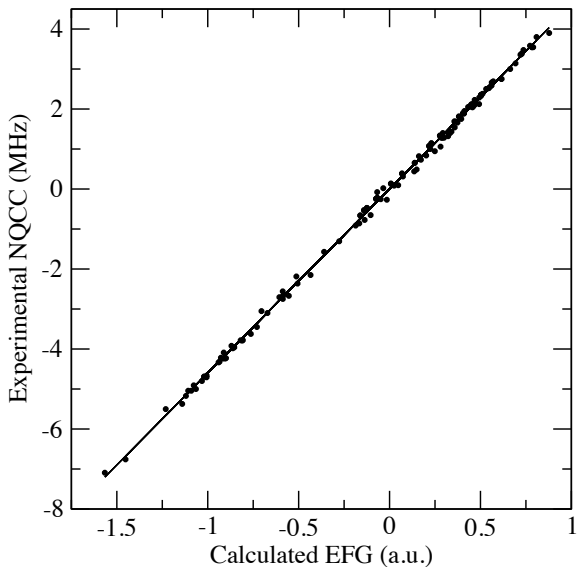


Figure 2: Linear regression of experimental NQCCs, χ_{ii} versus B3PW91/6-311+G(d,p) calculated EFGs, q_{ii} . The slope, eQ/h is 4.599(12) MHz/a.u. Standard deviation of the residuals is 0.086 MHz (3.8 % of average $|\chi_{ii}|$).

to 26.5 GHz were also recorded using another MB-FTMW spectrometer [15] and included in the fit.

The spectrum shown in Fig. 3 illustrates a typical high resolution measurement of the *trans* conformer with the characteristic hyperfine structure. A list including all assigned transitions of *trans* and *cis* are given in the Supplementary Material in Tables S4 and S5.

In the spectrum, only few transitions with low J and K quantum numbers could be measured for *cis*, and all transitions belonging to *cis* possess lower intensity in comparison to those of *trans*. We conclude, therefore, that *trans* is the more stable conformer under our molecular beam conditions, which is in agreement with the calculations at the MP2/6-311++G(d,p) level of theory.

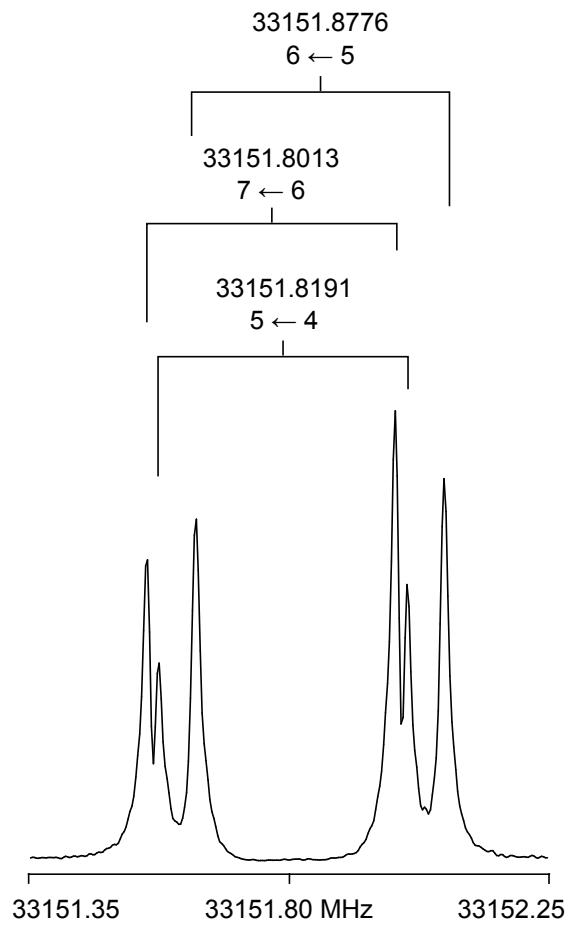


Figure 3: Three quadrupole components of the $6_{06} \leftarrow 5_{05}$ transition of the *trans* conformer of N-vinylformamide. The Doppler doublets are marked by brackets. The hyperfine transitions are given by $F' \leftarrow F$. For this spectrum, 225 decays were co-added.

Table 1: Rotational parameters from the program *XIAM* (Expt.) compared with theoretical parameters (Calc.) for the *trans* and *cis* conformers of N-vinylformamide.

	Unit	<i>trans</i>		<i>cis</i>	
		Expt. ^a	Calc. ^b	Expt. ^a	Calc. ^b
<i>A</i>	MHz	19723.24435(44)	19820.5	36996.2(22)	37208.0
<i>B</i>	MHz	2976.65870(56)	2943.6	2419.11090(19)	2400.1
<i>C</i>	MHz	2587.48251(52)	2562.9	2272.12989(18)	2254.6
Δ_J	kHz	0.6861(19)	0.681	0.20045(71)	0.190
Δ_{JK}	kHz	-8.905(11)	-9.05	-4.219(22)	-3.82
Δ_K	kHz	103.32(11)	104.		274.
δ_J	kHz	0.13929(79)	0.139	0.01564(92)	0.0162
δ_K	kHz	2.53(26)	2.63		1.10
χ_{aa}	MHz	1.70574(90)	1.714	1.8520(14)	1.847
$\chi_{bb} - \chi_{cc}$	MHz	5.5774(20)	5.624	5.4272(37)	5.365
χ_{bb}^c	MHz	1.9358(11)	1.955	1.7876(20)	1.759
χ_{cc}^c	MHz	-3.6416(11)	-3.669	-3.6396(20)	-3.606
σ^d	kHz	2.3		2.5	
N^e/N_q^f		43 / 176		31 / 117	

^a Parameters are given with one standard uncertainty in parentheses. Watson's A reduction and I^r representation were used.

^b See Section 2.

^c Derived parameter.

^d Standard deviation of the present fit.

^e Number of rigid rotor transitions used in the least square fit.

^f Number of hyperfine transitions.

4. Results and Discussion

Using the program *XIAM*, excellent fits for the *trans* and *cis* conformers with standard deviations of 2.3 kHz and 2.5 kHz, respectively, could be achieved, which are close to the measurement accuracy of about 2-3 kHz for N-vinylformamide. In both cases, the rotational constants, CDCs, and NQCCs were all determined with high accuracy. Inertial defects for *trans* and *cis* respectively are -0.0000873 and -0.0001461 u·Å², which confirms that the two conformers are definitely planar. Relative intensities in the spectrum of the *trans* and *cis* transitions clearly indicate that *trans* is the more stable conformer.

The two MP2/6-311++G(d,p) optimized structures yield rotational constants which differ from the experimental values all by less than 1 %, while B3PW91/6-311+G(d,p) EFGs calculated on these optimized structures give NQCCs in almost exact agreement with the experimental deduced values, which confirms that this combination of methods is suitable for prediction of NQCCs in π -conjugated amides. MP2/cc-pVTZ calculated CDCs are in good agreement with the experimental results.

Comparing χ_{zz} constants in the several formamides shown in Table 2, we note two distinct groups. First, we see that the χ_{zz} values are about the same for N-ethylformamide (No. **2** in Fig. 4) and N-methylformamide (**3**), as well as for N,N-methylethylformamide (**4**) and N,N-dimethylformamide (**5**), gradually increasing in magnitude from 3.8510(11) MHz in formamide (**1**) to 4.364(2) MHz in N,N-dimethylformamide (**5**). We believe that this change depends on the increasing number of alkyl substitutions attached to the nitrogen atom. In the second group, the two conformers of N-vinylformamide (**6**) possess almost exactly the same χ_{zz} value, which is similar to that of N-phenylformamide (**7**) but different from those of the saturated formamides (**2** - **5**), and gradually decreasing in magnitude from 3.8510(11) MHz in formamide (**1**) to 3.41(7) MHz in diformamide (**8**). It is likely, in this second group, that π -electron conjugation from the substituent through the lone pair electrons of the nitrogen to the carbonyl bond affects the EFGs at the nitrogen nucleus, which affect is manifest in significant variation of the χ_{zz} constant.

Table 2: ^{14}N NQCC z-principal axis component, χ_{zz} (MHz) in the formamides given here and shown in Fig. 4.

	χ_{zz}	Ref.
Formamide	-3.8510(11)	[1]
N-Ethylformamide	-3.993(51) ^a	[3]
N-Methylformamide	-4.0358(28)	[2]
N,N-Methylethylformamide	-4.216(31) ^a	[5]
N,N-Dimethylformamide	-4.364(2)	[4]
N-Phenylformamide, <i>trans</i>	-3.671(22)	[6, 7]
N-Vinylformamide, <i>trans</i>	-3.6416(11) ^b	
N-Vinylformamide, <i>cis</i>	-3.6396(20) ^b	
Diformamide, <i>cis-trans</i>	-3.41(7)	[9]

^a Calculated from experimental diagonal components and theoretical off-diagonal components. See <http://nqcc.wcbailey.net/Amides.pdf>. [16].

^b This work.

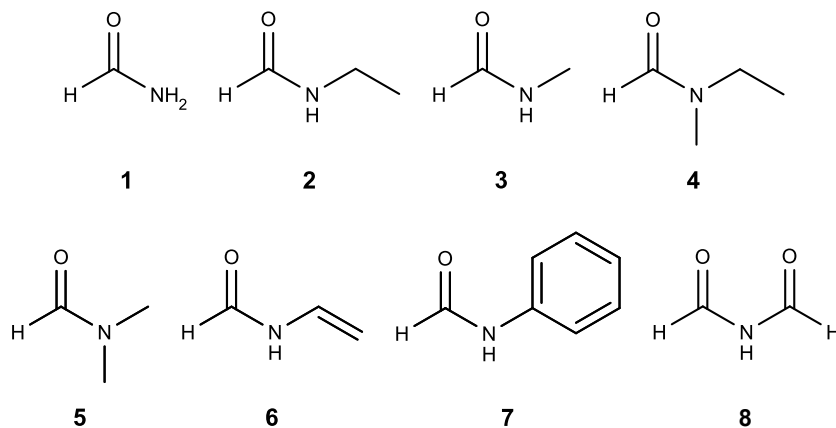


Figure 4: 1. Formamide, 2. N-Ethylformamide, 3. N-Methylformamide, 4. N,N-Methylethylformamide, 5. N,N-Dimethylformamide, 6. N-Vinylformamide, 7. N-Phenylformamide, 8. Diformamide

5. Conclusion

The quadrupole hyperfine structures in the microwave spectra of the *trans* and *cis* conformers of N-vinylformamide were assigned in the frequency range from 2 to 40 GHz, providing ^{14}N NQCCs with very high accuracy. The NQCCs of the two conformers are almost exactly the same, and are compared with values found for other saturated and unsaturated formamides.

B3PW91/6-311+G(d,p) calculated EFGs, in conjunction with $eQ/h = 4.599(12)$ MHz/a.u., yields more reliable NQCCs for formamides possessing conjugated π -electron systems than does the B3PW91/6-311+G(df,pd) model recommended in Ref. [12], whereas this latter performs better for aliphatic formamides [16]. We conclude from this that f-polarization functions on heavy atoms hinder rather than help with modeling of conjugated π -electron systems.

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Graphical Abstract

