^{14}N quadrupole coupling in the microwave spectra of N-vinylformamide

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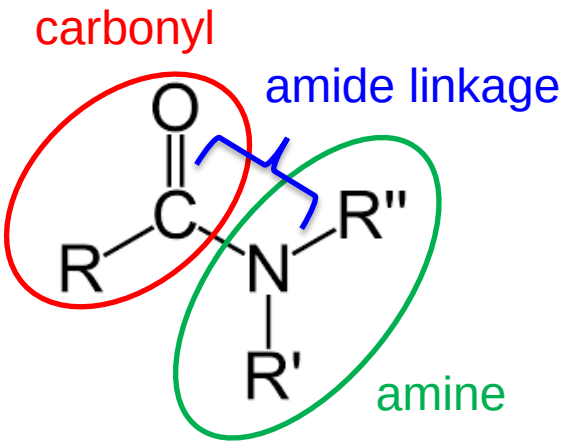
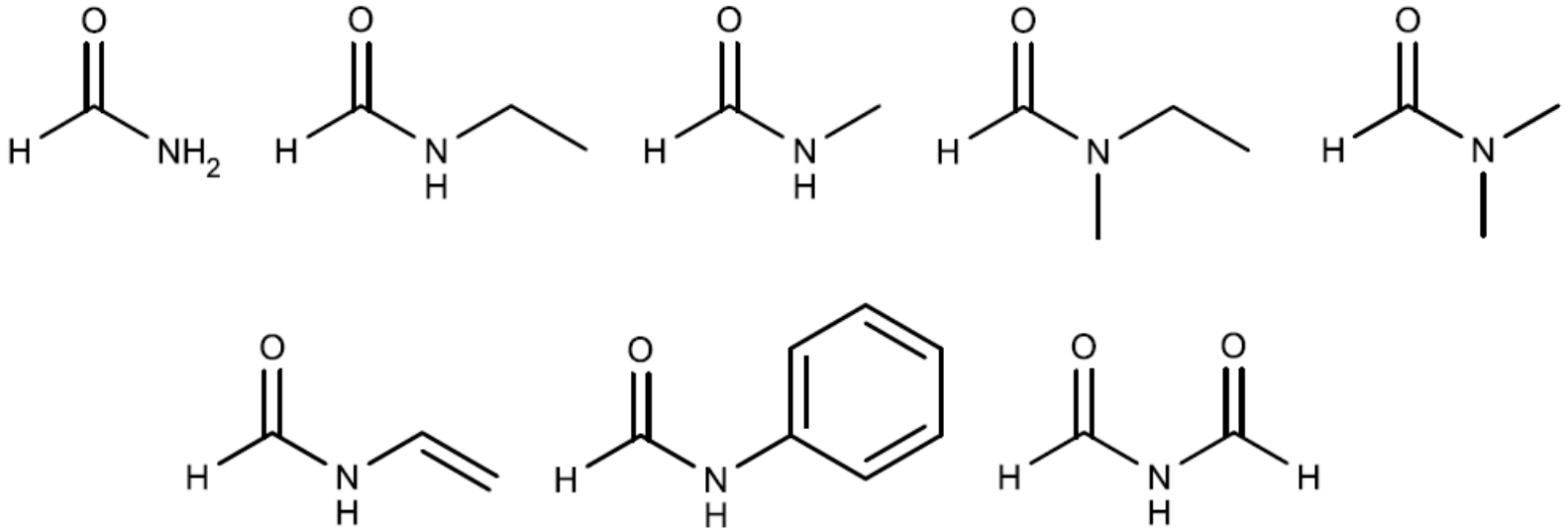
Motivation

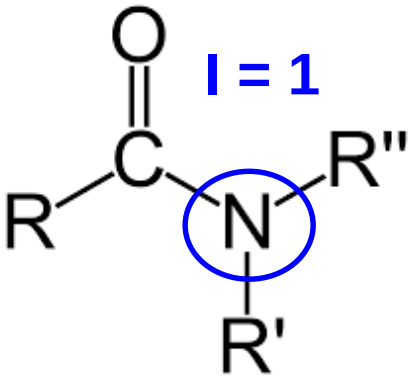
- Amides: general interest in chemistry and molecular biology; complex electronic configurations
- Formamides: contain the planar sub-unit H(C=O)N





^{14}N nuclear quadrupole coupling effect

- Origin: interaction of the electric quadrupole moment of the nucleus with the electricfield gradient (EFG)

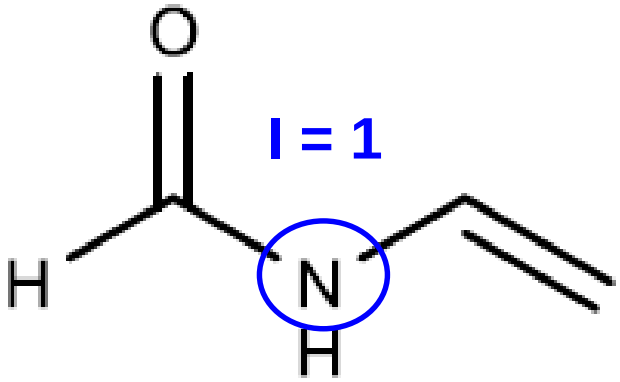


- Only electrons associated with the nucleus have major contributions to the EFG
- Only valence p electrons need be considered, thereby establishing a link between chemical bonding and nuclear quadrupole coupling (Townes and Dailey)

→ Information on the EFG and the nature of the chemical bond

N-Vinylformamide

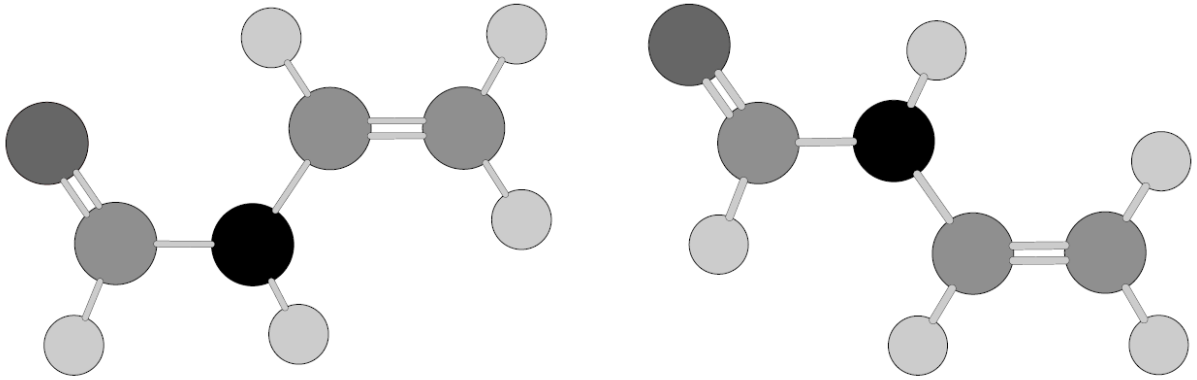
- Møllendal and Samdal: room temperature spectra from 18 to 75 GHz, resolution about 0.5 MHz, estimated accuracy 0.10 MHz for isolated lines (*J. Phys. Chem. A* **116** (2012) 12073)



- Spectra attributed to two conformers were assigned.
- Quadrupole splittings of the ^{14}N nucleus not resolvable

→ Remeasurements of the the spectra at higher resolution to gain information on the nuclear quadrupole coupling

Conformational preferences



trans *cis*

- Møllendal and Samdal: B3LYP and CCSD(T)/6-311++G(d,p): *cis* conformer is more stable than the *trans* by 0.3 and 2.8 kJ/mol, respectively.
- Our work: MP2/6-311++G(d,p): *trans* conformer is more stable by 1.8 kJ/mol

Nuclear quadrupole coupling constants

- Single-point EFG calculations at the B3PW91/6-311+G(df,pd)//MP2/6-311++G(d,p) level and a calibration factor of eQh^{-1} of 4.5586(40) MHz $a.u.^{-1}$ (W. C. Bailey, *Chem. Phys*. **252** (2000) 57.)

→ Predicted NQCCs in almost exact agreement with experimental values for nitrogencontaining molecules

→ Significantly simplify the spectrum assignment

- http://nqcc.wcbailey.net/Publ_N.html

- Problem: NOT for N-vinylformamide and some other unsaturated amides! The B3PW91/6-311+G(d,p)//MP2/6-311++G(d,p) level worked better.

Nuclear quadrupole coupling constants

New calibration for unsarturated amides

- $\chi_{ij}\,(MHz) = \left(\frac{eQ}{h}\right) \times\ q_{ij}\,(a.u.)$

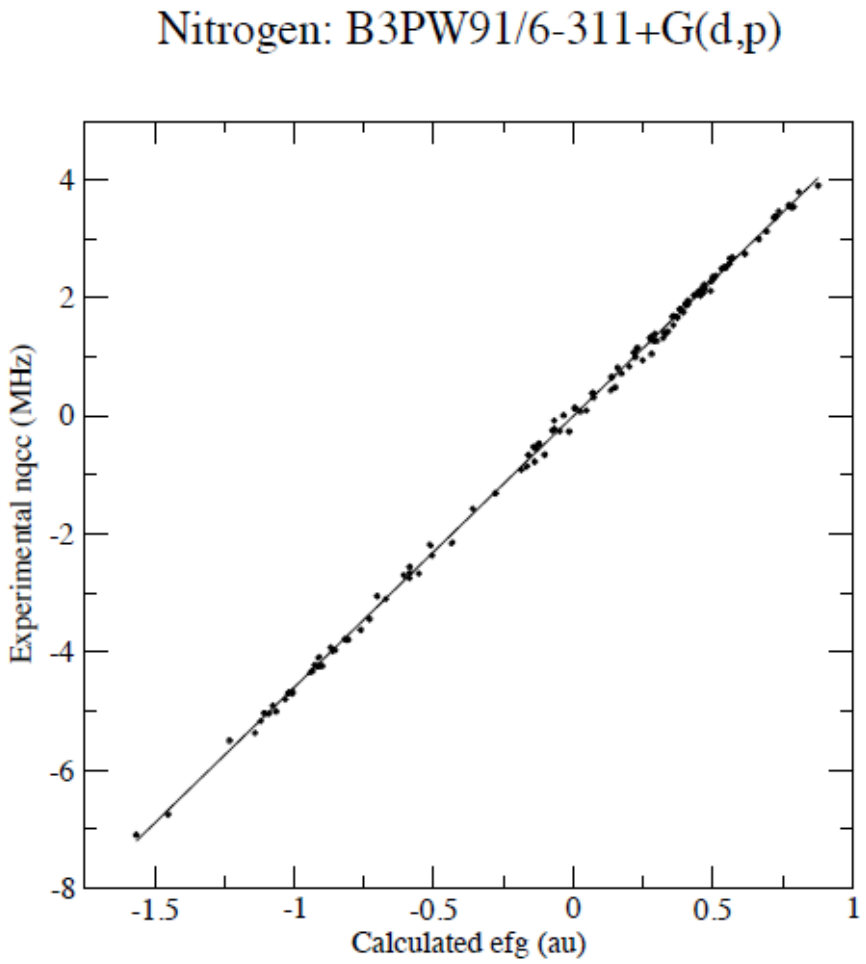
χ_{ij} : component of the NQCC tensor

q_{ij} : component of the EFG tensor

e : fundamental electric charge

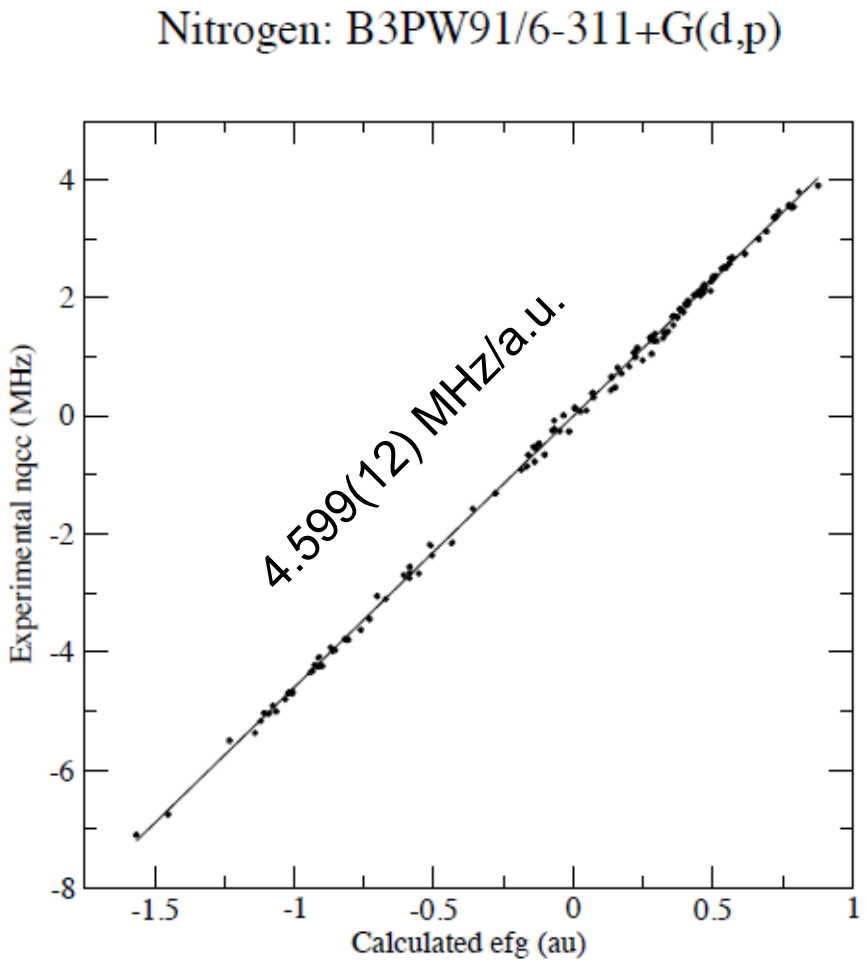
Q: electric quadrupole moment of the nucleus

h : Planck's constant



Nuclear quadrupole coupling constants

- Calibration for the calculation of NQCCs by taking 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}
- Standard deviation of the residuals is 0.086 MHz (3.8 % of average $|\chi_{ij}|$)



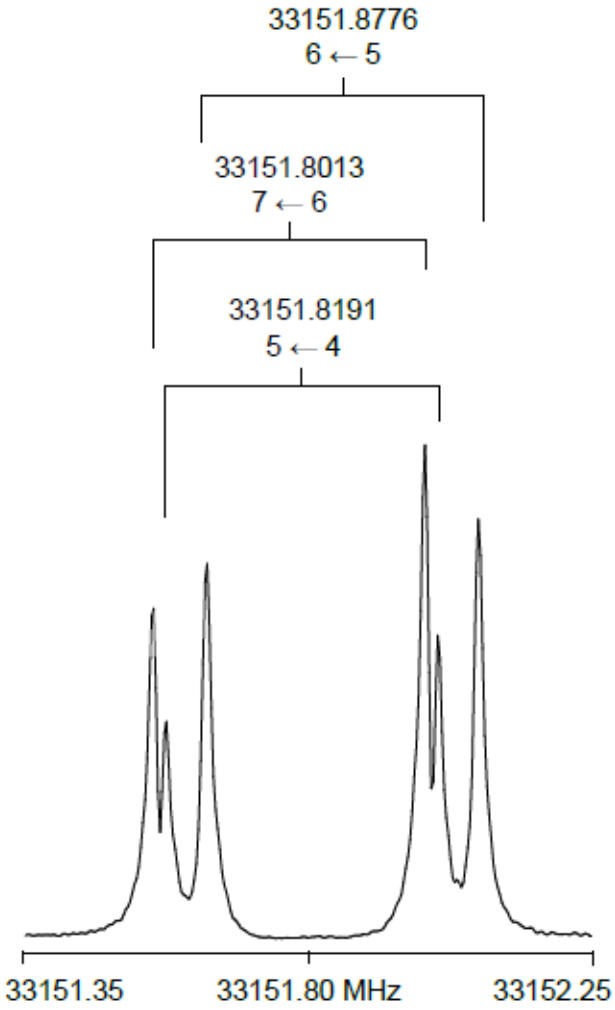
Nuclear quadrupole coupling constants

Unsaturated amides/nitrogen-containing molecules:
use B3PW91/6-311+G(d,p)//MP2/6-311++G(d,p)
and calibration factor 4.599 MHz/a.u.

Saturated amides/nitrogen-containing molecules:
use B3PW91/6-311+G(df,pd)//MP2/6-311++G(d,p)
and calibration factor 4.5586 MHz/a.u.

Microwave spectrum

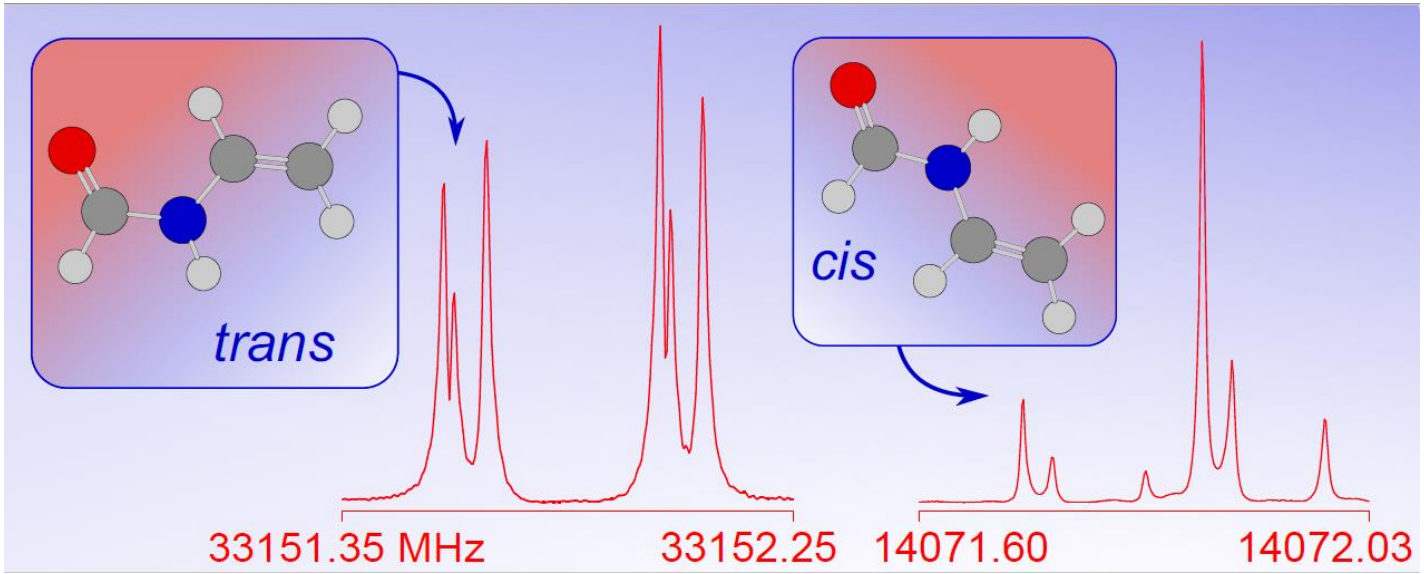
- Molecular beam FT microwave spectroscopy
- 2 – 26.5 GHz Cavity (Aachen) and 26.5 – 40 GHz Cavity (Paris)
- No broadband scans necessary; high resolution measurements
- Hyperfine splittings completely resolved and assigned



Microwave spectrum

- Only few transitions with low *J* and *K* measurable for *cis*
- All transitions belonging to *cis* have lower intensity in comparison to those of *trans*.

→ *trans* is the more stable conformer under our molecular beam conditions (in agreement with MP2/6-311++G(d,p) calculations)



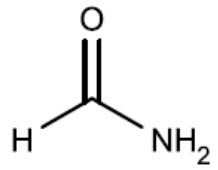
Molecular parameters

		trans		*cis*	
	Unit	Expt.[a]	Calc.[b]	Expt.[a]	Calc.[b]
A	MHz	19723.24435(44)	19820.5	36996.2(22)	37208.0
B	MHz	2976.65870(56)	2943.6	2419.11090(19)	2400.1
C	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
χ_{bb} - χ_{cc}	MHz	5.5774(20)	5.624	5.4272(37)	5.365
$\chi_{bb}{}^c$	MHz	1.9358(11)	1.955	1.7876(20)	1.759
$\chi_{cc}{}^c$	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	

Inertial defect: *trans* –0.0000873, *cis* –0.0001461 uÅ^2 → denitely planar

χ_{zz} in the formamides

	χ_{zz}
Formamide	–3.8510(11)
N-Ethylformamide	–3.993(51)[a]
N-Methylformamide	–4.0358(28)
N,N-Methylethylformamide	–4.216(31)[a]
N,N-Dimethylformamide	–4.364(2)
N-Phenylformamide, *trans*	–3.671(22)
N-Vinylformamide, *trans*	–3.6416(11)[b]
N-Vinylformamide, *cis*	–3.6396(20)[b]
Diformamide, *cis-trans*	–3.41(7)



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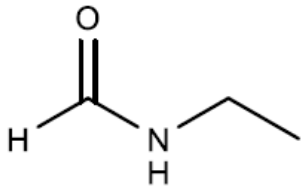

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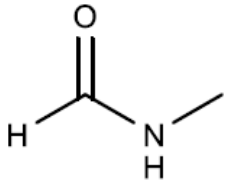

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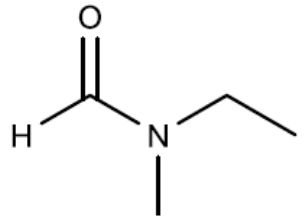

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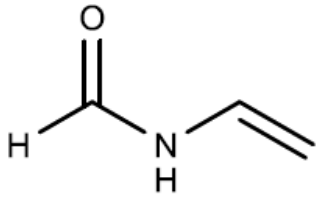

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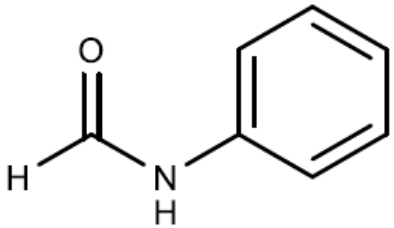

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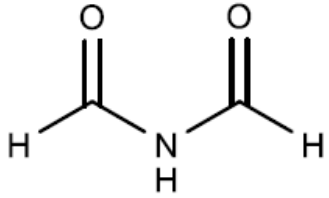

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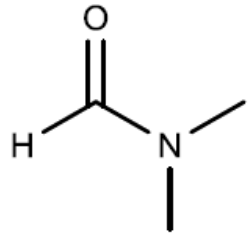

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