DOI: 10.1002/anie.200805104

Adducts of NH_3 with the Conformers of Glycidol: A Rotational Spectroscopy Study**

*Barbara M. Giuliano, Sonia Melandri, Assimo Maris, Laura B. Favero, and Walther Caminati**

Various chemical problems, difficult to unravel with other techniques, were solved recently by rotational spectroscopy experiments in supersonic jets. The investigations of molecular complexes with this technique gave indications on the nature of the forces which bind the constituent molecules, on the preferred sites of interaction, and on the widely unexplored interactions in the intermediate regime between bonding and nonbonding. Molecular recognition, molecular aggregation, rare-gas atoms forming covalent bonds, and many more phenomena are investigated with this techniques without having to rely heavily on ab initio calculations—although their support is of great help in guiding spectroscopic searches and interpreting the spectra. Many of the complexes investigated involve one or more molecules of water linked to organic or biomolecules. Water participates in several kinds of hydrogen bonds, acting either as a proton acceptor or a proton donor. The most common hydrogen bonds in these systems are of the type $O{-}H_w{\cdots}O$, $O{-}H{\cdots}O_w$, $O{-}H_w{\cdots}N$, $N{-}H{\cdots}O_w$,[1–4] where the subscript indicates an atom belonging to the water molecule. These hydrogen bonds are moderately strong, in the range 15–25 $kJ\,mol^{-1}$.

Less information is available on molecular complexes of ammonia with organic molecules. The only systems investigated in which ammonia could play the dual proton-donor/proton-acceptor role are $F_3CH{\cdots}NH_3$,[5] $CH_3OH{\cdots}NH_3$,[6] pirrole$\cdots NH_3$,[7] and *tert*-butanol$\cdots NH_3$.[8] All the rotational spectra of its complexes with organic molecules revealed only conformers where ammonia, unlike water, acts exclusively as a proton acceptor.

A few rotationally resolved electronic-spectroscopy studies on adducts of ammonia with larger molecules confirm this behavior, such as in the case of 1-naphtol$\cdots NH_3$,[9] hydroquinone$\cdots NH_3$,[10] and aniline$\cdots NH_3$.[11]

This trend is in agreement also with the different pK_{HB} values, 0.64 and 1.86, respectively, for water and ammonia. K_{HB} is the equilibrium constant for the association reaction with a proton reference donor, namely 4-fluorophenol.[12] The higher value for ammonia shows that ammonia is a stronger hydrogen bond acceptor than water.

The formation of molecular complexes can result in various relative conformations. Interesting equatorial/axial equilibria have been encountered while investigating the microwave (MW) spectra of adducts of hydrohalogenic acids with organic molecules. For example, in saturated cyclic ethers, such as tetrahydropyran, two different lone pairs (axial and equatorial) are available at the ether oxygen atom to accept a proton. Alonso and collaborators could assign the supersonic-jet Fourier-transform microwave (FTMW) spectra of both axial and equatorial complexes in the case of tetrahydropyran$\cdots$HCl,[13] tetrahydropyran$\cdots$HF,[14] and pentamethylene sulfide$\cdots$HF,[15] thus characterizing relative energies and structural differences. Three conformers have been observed for formamide$\cdots$water,[4] and six conformers in the molecular recognition study of the self-aggregation of propylene oxide.[16] However, no rotational spectra are available on different adducts originating from the different conformations of a given molecule with a ligand. Ammonia, thanks to its propensity to behave only as proton acceptor, can generate a small number of species in the conformational mixture of its adducts with organic molecules, and these species can therefore be detected by FTMW spectroscopy.

Glycidol (oxiranemethanol) is an interesting chiral molecule, which, in a sense, resembles the palm of a hand, and for this reason it has been used as a probe for molecular recognition in IR[17] as well as MW[18] studies. Glycidol (GLY) provides two possible sites for hydrogen-bond contact: the ring oxygen atom (acceptor) and the OH group (donor/acceptor). Depending on the orientation of the hydroxy hydrogen with respect to the ring oxygen atom, it can generate two different internally hydrogen-bonded conformers, G1 and G2, whose conformations and energy differences have been determined experimentally by MW spectroscopy.[19] Owing to the small energy difference between the two conformers [$\Delta E_{G2-G1} = 3.6(4)\ kJ\,mol^{-1}$], GLY appears to be a suitable molecule with which to investigate the adducts generated with ammonia by the two species.

Theoretical calculations were performed before the spectroscopic search. Using the program ORIENT 4.6,[20] we optimized the predicted geometries of the molecular adducts at the highest available rank of the multipole expansion, that is, up to the hexadecapole. Within these preliminary calculations, the structures of ammonia and glycidol were frozen and any structural relaxation upon complexation was neglected, while the dissociation energy was corrected for the zero-point energy contribution.

The results obtained with ORIENT are summarized in the Supporting Information. Among twelve energy minima, two

---

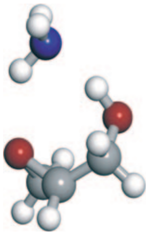
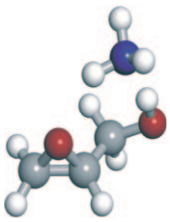
[*] Dr. B. M. Giuliano, Dr. S. Melandri, Dr. A. Maris,
Prof. Dr. W. Caminati
Dipartimento di Chimica "G. Ciamician" dell'Università
Via Selmi 2, 40126 Bologna (Italy)
Fax: (+39) 051-209-9456
E-mail: walther.caminati@unibo.it
Dr. L. B. Favero
Istituto per lo Studio dei Materiali Nanostrutturati (ISMN, Sezione di Bologna), CNR, via Gobetti 101, 40129 Bologna (Italy)

[**] This research was funded by MIUR and the University of Bologna.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200805104.

were significantly more stable than the remaining ones. For these most stable minima, full geometry optimizations of the monomers and dimers were carried out at the MP2(full)/6-311++G** level of theory using the GAUSSIAN 03 suite of programs.[21] All energies were corrected for basis-set superposition error (BSSE) using the counterpoise procedure.[22] The spectroscopic parameters obtained are reported in Table 1. The ab initio structures of monomers and dimers are given as Supporting Information. Upon formation of the complexes, the monomers undergo distortions up to 26° for the H-O-C-C dihedral angles. Similar distortions of the structures of the monomers were found in hydrogen-bonded complexes.[4,16,23]

Table 1: Ab initio[a] values of spectroscopic constants and dissociation energies for glycidol–ammonia.

Parameter	G1–NH_3	G2–NH_3
A [MHz]	4028.4	4100.5
B [MHz]	2547.1	2423.9
C [MHz]	1888.1	1656.2
μ_a [D]	−0.02	1.23
μ_b [D]	1.32	−1.92
μ_c [D]	−1.00	−0.99
χ_{aa}[b] [MHz]	1.22	1.59
χ^-[b,c] [MHz]z	−4.71	−5.45
D_e [kJ mol^{-1}][d]	30.1	32.6
		

[a] MP2(full)/6-311++G**. [b] $Q_N = 1.93 \times 10^{-30}$ m². [c] $\chi^- = \chi_{bb} - \chi_{cc}$. [d] Corrected for BSSE using the counterpoise procedure. C gray, N blue, O red, H white.

We observed the spectra of both conformations, G1–NH_3 and G2–NH_3. Measured rotational transitions were R-type lines involving all three components of the permanent dipole moment, according to the chirality of glycidol, which is preserved in the adducts. All transitions were split in several component lines, corresponding to the A and E species of the NH_3 internal rotation, and to the ^{14}N quadrupole hyperfine structure. An example is given in Figure 1, where the transition 2_{12}–1_{01} is shown for both conformers.

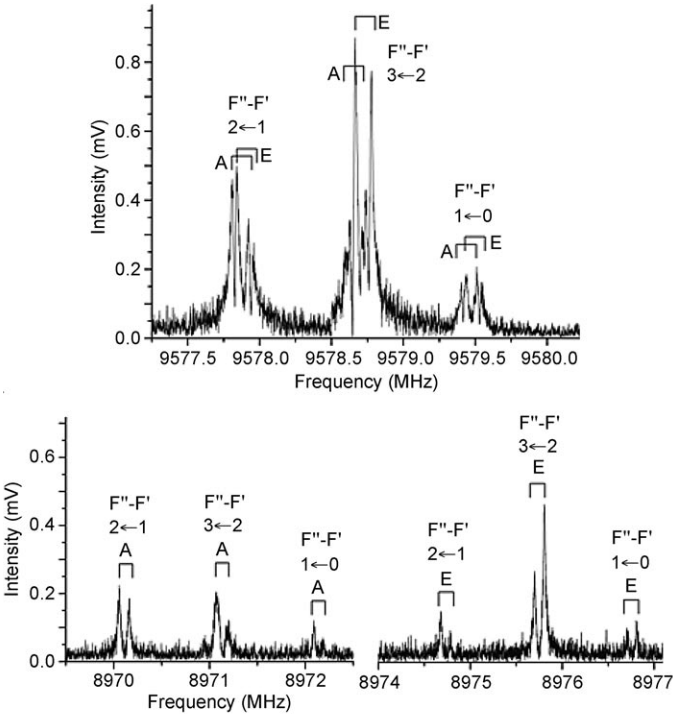


Figure 1. FTMW spectra of the transition 2_{12}–1_{01} for G1–NH_3 (top) and G2–NH_3 (bottom) conformers.

The spectra of the $^{15}NH_3$ isotopologues were simpler, with each transition split only into two A and E component lines.

All line frequencies (given as Supporting Information) were fitted with computer program XIAM,[24] and the parameters obtained are shown in Table 2. A "rigid" limit set of rotational constants has been determined, common to A and E sublevels, together with quartic centrifugal distortion constants (S-reduction and I^r-representation),[25] and the

Table 2: Experimental spectroscopic parameters for the detected conformers of glycidol–NH_3.

Parameter	G1–NH_3	G1–$^{15}NH_3$	G2–NH_3	G2–$^{15}NH_3$
A [MHz]	4006.550(2)[a]	3992.850(1)	4079.158(1)	4035.447(2)
B [MHz]	2502.7685(8)	2431.3359(4)	2382.1668(6)	2326.6815(4)
C [MHz]	1857.2265(4)	1814.7855(5)	1630.5642(3)	1597.6225(4)
D_J [kHz]	2.11(3)	2.04(2)	1.52(2)	1.52(1)
D_{JK} [kHz]	−0.3(1)	[−0.3][b]	−0.16(6)	[−0.16][b]
D_K [kHz]	2.9(2)	[2.9][b]	3.8(3)	[3.9][b]
d_1 [kHz]	−0.66(2)	[−0.66][b]	−0.57(1)	[−0.57][b]
d_2 [kHz]	[0][c]	[0][c]	0.09(1)	[0.09][b]
D_{c3J} [MHz]	1.95(4)	[1.95][b]	−1.57(1)	[−1.57][b]
D_{pi2K} [MHz]	−0.336(4)	[−0.336][b]	0.299(2)	[0.299][b]
χ_{aa} [MHz]	1.092(4)		1.535(3)	
χ^-[d] [MHz]	−4.200(3)		−5.056(5)	
V_3 [kJ mol^{-1}]	3.517(2)	3.522(2)	2.4382(3)	2.4369(4)
I_α [uÅ^2]	2.620(1)	2.620(1)	2.7849(3)	2.7885(5)
∢ai [°]	69.287(7)	68.11(1)	83.7341(7)	82.076(8)
∢bi [°]	24.55(1)	25.57(1)	7.1555(9)	8.623(8)
∢ci [°]	77.402(7)	77.45(1)	86.5584(7)	86.621(3)
σ [kHz]	3	3	3	3
N[e]	66	16	90	26

[a] Error in parentheses in units of the last digit. [b] Fixed to the value of the parent species. [c] Fixed to zero, [d] $\chi^- = \chi_{bb} - \chi_{cc}$. [e] Number of lines in the fit.

nuclear quadrupole coupling constants. For the internal rotation motion, we determined the V_3 barrier, the I_α moment of inertia of NH_3, and the angles ($\sphericalangle ai$, $\sphericalangle bi$, and $\sphericalangle ci$) that the axis of rotation of NH_3 forms with the principal axes of inertia. The V_3 values for the two complexes differ considerably from each other, being 3.52 and 2.44 kJ mol^{-1} for G1–NH_3 and G2–NH_3, respectively. These values correspond, in a first approximation, to the energy of the N−H···O bonds, since the bottom of the threefold potential surface can be associated with the presence of a hydrogen bond which is removed at the top of the potential surface. The conformational arrangement of G1–NH_3 makes this interaction more favorable than in G2–NH_3.

The inertia values ($I_\alpha(NH_3)$) are slightly different for the two conformers, underlying different tilt angles and structural relaxations of the hydrogen-bond parameters upon NH_3 internal rotation. They are relatively close, however, to the value calculated from the structure of isolated ammonia, 2.70 uÅ^2.[26]

The structural parameters defining the position and orientation of NH_3 with respect to GLY can be obtained, for each conformer, from the six rotational constants, from the set of quadrupole coupling constants, and, in principle, from the angles $\sphericalangle ai$, $\sphericalangle bi$, and $\sphericalangle ci$. Actually these last three values are not fully reliable, because the internal rotation is not the pure rotation of ammonia around its symmetry axis, but it contains the effects of the structural relaxations which accompany the motion, and for this reason we did not use these data in determining structural parameters.

In Table 3 we report the r_s-coordinates[27] of the nitrogen atom in the principal axis systems of Gi–$^{14}NH_3$ obtained from the rotational constants of the Gi–$^{14}NH_3$/Gi–$^{15}NH_3$ pairs.

Table 3: The r_s coordinates of the N atom compared to the r_e and to the r_0 values.

Parameter	G1–NH_3			G2–NH_3		
	$\lvert r_s \rvert$	r_e[a]	r_0[b]	$\lvert r_s \rvert$	r_e[a]	r_0[b]
a [Å]	2.446(1)[c]	−2.399	2.450	2.247(1)	−2.194	−2.259
b [Å]	0.687(2)	0.724	−0.691	1.197(1)	−1.223	−1.191
c [Å]	0.03(5)	−0.069	−0.068	0.08(2)	−0.103	0.091

[a] r_e(ab initio) MP2(full)/6-311++G** values. [b] From the experimental r_0 structure of Table 4. [c] Error in parentheses in units of the last digit.

The r_0 coordinates in Table 3 have been calculated with partial r_0-structures, obtained from the ab initio geometries by fitting five parameters to reduce the discrepancies between calculated and experimental values to less than 1 MHz and 0.2 MHz for the rotational and for the quadrupole coupling constants, respectively. These fitted parameters are indicated in Table 4, where they are given along with the ab initio values for comparison.

Table 4: Partial r_0 geometry.

	G1–NH_3		G2–NH_3	
	r_e[a]	r_0	r_e[a]	r_0
Fitted parameters				
N-O_{OH} [Å]	2.840	2.880(1)[b]	2.857	2.888(1)
$NO_{OH}C$ [°]	101.3	102.4(1)	100.1	101.4(1)
NO_{OH}-CC [°]	71.8	71.4(1)	−66.0	−65.1(1)
HN···H_{OH} [°]	92.5	94.(1)	99.2	99.5(1)
HN···HO [°]	−5.7	−11.(5)	6.099	−4.(3)
Derived hydrogen-bond distances				
N···H_{OH} [Å]	1.897	1.916	1.889	1.917
H_N···O_{Ether} [Å]	2.194	2.267	2.204	2.271

[a] MP2(full)/6-311++G** values. [b] Error in parentheses in units of the last digit.

From the above geometries, the quadrupole coupling constants χ_{zz} in the principal quadrupole tensor of the ^{14}N nucleus have been obtained. The values are $\chi_{zz} = 3.63$ and 3.61 MHz for the G1–NH_3 and G2–NH_3 conformers, respectively, with a reduction of approximately 10% with respect to the free NH_3 value, $\chi_0(^{14}N) = 4.090$ MHz.[28] A similar decrease of $\chi_{zz}(^{14}N)$ with respect to $\chi_0(^{14}N)$ was observed by Legon in the H_3N···HX (X = F, Cl, Br, I) series.[29] This behavior was attributed to a weak perturbation of the electric field gradient at ^{14}N in NH_3 upon formation of the complex. In some molecular complexes in which ammonia is involved with a single O−H···N,[6,8] or N−H···N,[7] C−H···N[5] hydrogen bond, the reduction ($\Delta\chi = \chi_0(^{14}N) - \chi_{zz}(^{14}N)$) from 4.090 MHz of the $\chi_0(^{14}N)$ value to the effective χ_{zz} values has been explained in terms of zero-point angular oscillations of the NH_3 moiety relative to the a-axis of the complex. In the case of GLY–NH_3, the secondary N−H···O hydrogen bond quenches such an oscillation, because, as indicated by the relatively high V_3 barriers, it should break the corresponding intermolecular interaction. It seems therefore, that $\Delta\chi$ can be attributed to a small charge transfer, induced by a "cooperative" effect of the two (O−H···N and N−H···O) hydrogen bonds.

This small charge transfer and the corresponding increase of the strength of the O−H···N bond is confirmed by the comparison of the ab initio minimum value of the electronic density at the O−H···N hydrogen bond in GLY–NH_3, (0.034 for both conformers) with that in *tert*-butanol···NH_3 (0.027; Figure 2).

We also performed a set of intensity measurements aimed at the determination of the relative populations of the two conformational arrangements of GLY–NH_3. Taking into account the linear dependence of the amplitude spectra intensities on the value of the dipole moment component

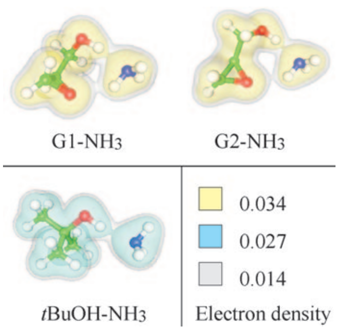


Figure 2. The electron density at the O-H···N hydrogen bond in GLY–NH_3 is higher than in *tert*-butanol···NH_3.

involved, the line strength, and the frequency of each transition, the ratio between the G2–NH_3 on G1–NH_3 in the jet expansion is 0.8 with an accuracy of 30%. This ratio is more or less in agreement with the predicted similarity of the conformational energies of G1–NH_3 and G2–NH_3, because the higher conformational energy of G2 in the monomer is compensated by the higher association energy of G2 with ammonia.

Although IR experiments on jet-cooled complexes of 2-naphthol have indicated complexation of the two *cis* and *trans* isomers of 2-naphthol with ammonia,[30] and the behavior of ammonia as a protic wire (both a hydrogen-bond donor and acceptor) has been found in 7-hydroxyquinoline–ammonia complexes,[31] our study outlines these aspects for the first time by rotational spectroscopy. From the rotational measurements, we could derive a variety of precise chemical data which is difficult, if not impossible, to obtain with other techniques: 1) in both complexes, NH_3 is linked to the alcohol molecule through an O−H···N (stronger) and an N−H···O (weaker) hydrogen bond; 2) the energies of the N−H···O interactions, determined from the V_3 barriers for the internal rotation of the ammonia moiety, are 3.522(2) and 2.270(1) kJ mol^{-1} for the G1–NH_3, and G2–NH_3, respectively; 3) the conformational energy difference between the two G2–NH_3 and G1–NH_3 species is almost zero; 4) an incipient charge transfer takes place at the O−H···N bonds; 5) precise hydrogen-bond structural parameters are obtained.

Finally, the experimental detection of the complexes of ammonia with both conformers of glycidol can be interpreted in terms of "molecular recognition", where two locks (G1 and G2) accept the same master-key (NH_3).

Experimental Section

The rotational spectra in the 6–18.5 GHz frequency region was measured using a COBRA-type[32] pulsed supersonic-jet Fourier-transform microwave (FTMW) spectrometer[33] described elsewhere,[34] recently updated with the FTMW++ set of programs.[35] A gas mixture of approximately 1% of NH_3 in He at a total pressure of 3 bar was passed over (*R*)-(+)-glycidol (Aldrich, 97%) and expanded through a solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry–Pérot cavity. Each rotational transition displays a Doppler splitting, originating from the expansion of the supersonic jet coaxially along the resonator axes. The rest frequency is calculated as the arithmetic mean of the frequencies of the two Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz. Lines separated by more than 7 kHz are resolvable.

Received: October 17, 2008

Keywords: ammonia · conformation analysis · hydrogen bonds · rotational spectroscopy

---

[1] S. Melandri, A. Maris, P. G. Favero, W. Caminati, *Chem. Phys.* **2002**, *283*, 185, and references therein.

[2] S. Blanco, J. C. López, J. L. Alonso, P. Ottaviani, W. Caminati, *J. Chem. Phys.* **2003**, *119*, 880.

[3] W. Caminati, A. Dell'Erba, G. Maccaferri, P. G. Favero, *J. Am. Chem. Soc.* **1998**, *120*, 2616.

[4] S. Blanco, J. C. López, A. Lesarri, J. L. Alonso, *J. Am. Chem. Soc.* **2006**, *128*, 12111.

[5] G. T. Fraser, F. J. Lovas, R. D. Suenram, D. D. Nelson, Jr., W. Klemperer, *J. Chem. Phys.* **1986**, *84*, 5983.

[6] G. T. Fraser, R. D. Suenram, F. J. Lovas, W. J. Stevens, *Chem. Phys.* **1988**, *125*, 31.

[7] C. Rensing, H. Mäder, F. Temps, *J. Mol. Spectrosc.* **2008**, *251*, 224.

[8] B. M. Giuliano, M. C. Castrovilli, A. Maris, S. Melandri, W. Caminati, E. A. Cohen, *Chem. Phys. Lett.* **2008**, *463*, 330.

[9] S. J. Humphrey, D. W. Pratt, *J. Chem. Phys.* **1996**, *104*, 8332.

[10] S. J. Humphrey, D. W. Pratt, *J. Chem. Phys.* **1997**, *106*, 908.

[11] J. A. Fernandez, E. R. Bernstein, *J. Chem. Phys.* **1997**, *106*, 3029.

[12] C. Laurence, M. Bethelot, *Perspect. Drug Discovery Des.* **2000**, *18*, 39.

[13] S. Antolínez, J. C. López, J. L. Alonso, *Angew. Chem.* **1999**, *111*, 1889; *Angew. Chem. Int. Ed.* **1999**, *38*, 1772.

[14] S. Antolínez, J. C. López, J. L. Alonso, *ChemPhysChem* **2001**, *2*, 114.

[15] M. E. Sanz, J. C. López, J. L. Alonso, *Chem. Eur. J.* **1999**, *5*, 3293.

[16] Z. Su, N. Borho, Y. Xu, *J. Am. Chem. Soc.* **2006**, *128*, 17126.

[17] N. Borho, M. A. Suhm, *Phys. Chem. Chem. Phys.* **2002**, *4*, 2721.

[18] A. Maris, B. M. Giuliano, D. Bonazzi, W. Caminati, *J. Am. Chem. Soc.* **2008**, *130*, 13860.

[19] K. M. Marstokk, H. Møllendal, Y. Stenstrøm, *Acta Chem. Scand.* **1992**, *46*, 432.

[20] A. J. Stone, A. Dullweber, O. Engkvist, E. Fraschini, M. P. Hodges, A. W. Meredith, D. R. Nutt, P. L. A. Popelier, D. J. Wales, *Orient*, version 4.6, University of Cambridge **2006**.

[21] M. J. Frisch et al., Gaussian 03, Revision B.01, Gaussian, Inc., Pittsburgh PA, **2003**, see Supporting Information.

[22] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553.

[23] J. R. Aviles-Moreno, J. Demaison, T. R. Huet, *J. Am. Chem. Soc.* **2006**, *128*, 10467.

[24] H. Hartwig, H. Dreizler, *Z. Naturforsch.* **1996**, *51*, 923.

[25] J. K. G. Watson in *Vibrational Spectra and Structure*, *Vol. 6* (Ed.: J. R. Durig), Elsevier, New York, **1977**, pp. 1–89.

[26] P. Helminger, F. C. De Lucia, W. Gordy, *J. Mol. Spectrosc.* **1971**, *39*, 94.

[27] a) J. Kraitchman, *Am. J. Phys.* **1953**, *21*, 17; b) B. P. Van Eijck, *J. Mol. Spectrosc.* **1982**, *91*, 348.

[28] M. D. Marshall, J. S. Muenter, *J. Mol. Spectrosc.* **1981**, *85*, 322.

[29] A. C. Legon, *Chem. Soc. Rev.* **1993**, *22*, 153.

[30] Y. Matsumoto, T. Ebata, N. Mikami, *J. Mol. Struct.* **2000**, *552*, 257.

[31] C. Tanner, C. Manca, S. Leutwyler, *Science* **2003**, *302*, 1736.

[32] J.-U. Grabow, W. Stahl, *Z. Naturforsch A* **1990**, *45*, 1043; J.-U.Grabow, doctoral thesis, Christian-Albrechts-Universität, Kiel, **1992**; J.-U. Grabow, W. Stahl, H. Dreizler, *Rev. Sci. Instrum.* **1996**, *67*, 4072.

[33] T. J. Balle, W. H. Flygare, *Rev. Sci. Instrum.* **1981**, *52*, 33.

[34] W. Caminati, A. Millemaggi, J. L. Alonso, A. Lesarri, J. C. López, S. Mata, *Chem. Phys. Lett.* **2004**, *1*, 392.

[35] J.-U. Grabow, Habilitationsschrift, Universität Hannover, **2004**; http://www.pci.uni-hannover.de/~lgpca/spectroscopy/ftmw.