SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS

of the Candidate for the Habilitated Doctor Degree

^{17}O and ^{33}S Nuclear Magnetic Resonance of Simple Molecules in the Gas and Liquid Phases

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Faculty of Chemistry
University of Warsaw

Warsaw, February 2016

Contents

1 Personal details

1.1 Name and surname

Makulski Włodzimierz

Date of birth	20.06.1952
Place of birth	Wrocław
Citizenship	Polish
Residential address	Królowej Marysieńki 24 02-954 Warszawa
Place of work	University of Warsaw Faculty of Chemistry Pasteura 1 02-093 Warszawa
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1.2 Diplomas and Academic degrees

I have had a master's degree in chemistry since 11.06.1976

Master's thesis entitled: *Radiolysis and photolysis by vacuum ultraviolet of gaseous butene-1* was realized in the Laboratory of Radiochemistry in the Department of Chemistry UW supervised by Prof. Jerzy Sobkowski.

I was conferred Ph. D. on 23.02.1983

Ph.D. thesis entitled: *Radiolysis of gaseous propylene* I have realized supervised by Prof. Jerzy Sobkowski.

1.3 Employment to date

01.10.1976………..…...……employment as junior assistant in the Department of Chemistry, University of Warsaw

05.07.1976 - 30.09.1977…………………….....……..military service in the School of Reserve Officers

01.10.1977 - 30.09.1981………...................………………Ph. D. studies in the Department of Chemistry, University of Warsaw

01.10.1981…………..…..employment on technical position in the Department of Chemistry, University of Warsaw

01.05.1985…………………………......… employment as a scientific-technical specialist in the Faculty of Chemistry, University of Warsaw

06.09.1985 - 06.09.1986……………………. assistant professor in the Department of Natural Sciences in University of Quebec/Canada

01.10.1994 - 30.09.2005………………….....employment as assistant professor in the Faculty of Chemistry, University of Warsaw

01.10.2005 - at present……...……………………employment as senior lecturer in the Faculty of Chemistry, University of Warsaw.

1.4 Scientific achievements

A total of 51 studies published in chemical literature of international forum.

After Ph.D. degree – 44 publications.

Total IF of all publications: 73.550.

IF of publications used in habilitation process: 20.296 (1.561 per one paper).

Total number of citations: 427, without self-citations: 353 (according to Web of Science) on 04.02.2016.

Number of paper citations used in habilitation process: 176 (13.54 per one paper).

Hirsch Index: 14 (according to Web of Science).

Participation in communications as posters on international conferences: 40.

2 Main scientific achievements

2.1 List of articles published before Ph.D. degree

P.1 J.Niedzielski, W.Makulski, J.Gawłowski
Gas phase photolysis of 1-butene at 147 nm (8.4eV)
J.Photochem., **9** (1978) 519.
My contribution to this publication consisted in planning the investigations, performing of the photolytic experiments, performing of the chromatographic analyses, editing of the results (I estimate my contribution at 33%).

P.2 J.Niedzielski, W.Makulski, H.Zuchmantowicz, J.Gawłowski
Gamma-radiolysis of butene-1 in the gas phase
Nukleonika , **24** (1979) 1169.
My contribution to this publication consisted in: planning of the experiments, their realization and interpretation of the results (I estimate my contribution at 25%).

P.3 J.Gawłowski, W.Makulski, J.Niedzielski
Addition of hot hydrogen atoms to propylene and dissociation of excited n-propyl radicals
Nukleonika , **25** (1980) 1517.
My contribution to this publication consisted in: planning and performing of the experimental part, data collection and interpretation of the results (I estimate my contribution at 33%).

P.4 J.Niedzielski, W.Makulski, J.Gawłowski,
Gas phase photolysis of propylene at 8.4 and 10.0 eV
J.Photochem., **19** (1982) 123.
My contribution to this publication consisted in: planning of the investigations, performing of the experiments and participation in the interpretation of results (I estimate my contribution at 33%).

P.5 W.Makulski, J.Gawłowski, J.Niedzielski
Dissociation of propylene excited by the impact of low-energy electrons in the gas phase
J.Phys.Chem., **85** (1981) 2950.
My contribution to this publication consisted in testing of experimental chamber , performing experimental work along with interpretation of final results (I estimate my contribution at 50%).

P.6 J.Niedzielski, J.Gawłowski, W.Makulski
Reaction of vinyl radicals with propylene in the gas phase

React.Kinet.Catal.Lett.,**18** (1981) 271.

My contribution to this publication consisted in: planning and performing of the experiments (I estimate my contribution at 33%).

2.2 List of articles that form a monothematic series of publications, with estimation of the habilitation candidate's contribution

Q.7 K.Jackowski, M.Jaszuński, W.Makulski
A comparison of the experimental and ab initio values of the ^{17}*O NMR chemical shifts in the carbonyl group*
J.Magn.Reson., **27** (1997) 139.
IF=2.510

My contribution to this publication consisted in: realization of experimental part and its description and correction of the final version of the paper (I estimate my contribution at 33%).

Q.8 K.Jackowski, M.Jaszuński, W.Makulski, J.Vaara
Rovibrationally averaged nuclear shielding constants in COS
J.Magn.Reson., **135** (1998) 444.
IF=2.257

My contribution to this publication consisted in: all experimental data collection and graphical description of results (I estimate my contribution at 20%).

Q.9 M.Wilczek, W.Makulski, K.Jackowski
^{33}*S NMR gas-to-solution shifts for sulfur hexafluoride*
Mol.Phys.Rep., **29** (2000) 180.
IF=0.0

My contribution to this publication consisted in: planning of experiments, preparing of samples, choosing experimental parameters and participating in registration of NMR spectra (I estimate my contribution at 35%).

Q.10 W.Makulski, K.Jackowski
Density-dependent ^{17}*O magnetic shielding in the gas phase*
Chem.Phys.Lett., **341**(2001) 369.
IF=2.364 My contribution to this publication consisted in: collecting of literature, planning of experiments, performing of experiments, realization of graphics and tables, preparing of preliminary version of manuscript (I estimate my contribution at 60%).

Q.11 K.Jackowski, M.Wilczek, W.Makulski, W.Koźmiński
Effects of intermolecular interactions on the ^{33}*S magnetic shielding in gaseous* SF_6
J.Phys.Chem.A, **106** (2002) 2829.
IF=2.630

My contribution to this publication consisted in: collection of literature, performing most of experiments, participation in the interpretation of obtained results (I estimate my contribution at 20%).

Q.12 K.Jackowski, A.Leś, W.Makulski, K.Woźniak
Influence of intermolecular interactions on nuclear magnetic shielding constants of OCS
Pol.J.Chem., **76** (2002) 575.
IF=0.533

My contribution to this publication consisted in: planning of the investigations, performing of the measurements and proof-reading before sending the paper for publication (I estimate my contribution at 45%).

Q.13 K.Jackowski, W.Makulski, W.Koźmiński
An improved ^{33}*S nuclear magnetic shielding scale from the gas phase study of OCS*
Magn.Reson.Chem., **40** (2002) 563.
IF=0.895

My contribution to this publication consisted in: participation in experimental part of work, analysis of experimental errors and graphics summarized results (I estimate my contribution at 35%).

Q.14 W.Makulski, K.Jackowski
The ^{17}*O nuclear magnetic shielding scale from gas phase measurements*
J.Mol.Struct., **651-653** (2003) 265.
IF=0.907

My contribution to this publication consisted in: collecting of literature, performing research samples and NMR measurements, writing the experimental part, analysis of results (I estimate my contribution at 60%).

Q.15 W.Makulski, K.Jackowski
^{17}*O and* ^{33}*S NMR studies of sulfur dioxide and sulfur trioxide*
J.Mol.Struct., **704** (2004) 219.
IF=1.200

My contribution to this publication consisted in: planning of the investigations, performing of all experiments; analysis of experimental results and writing of a preliminary version of the publication. I was involved in the preparation of answers to referees and correspondence with the publisher (I estimate my contribution at 70%).

Q.16 W.Makulski
Multinuclear magnetic resonance studies of gaseous and liquid dimethyl ethers
J.Mol.Struct., **744-747** (2005) 439.
IF=1.440

Q.17 A.Antušek, K.Jackowski, M.Jaszuński, W.Makulski, M.Wilczek
Nuclear magnetic dipole moments from NMR spectra
Chem.Phys.Lett., **411**(2005) 111.
IF=2.438

My contribution to this publication consisted in: performing the main part of experimental research i.e. measurements of ^{17}O and ^{33}S NMR spectra and participation in the interpretation of results (I estimate my contribution at 30%).

Q.18 W.Makulski
^{1}*H,* ^{13}*C and* ^{17}*O nuclear magnetic shieldings of methanol and its deuterated isotopomers from the gas phase measurements*
J.Mol.Struct., **872** (2008) 81.
I.F.=1.594

Q.19 W.Makulski, A.Tulewicz, A.Leś
^{17}*O and* ^{33}*S nuclear magnetic shielding of sulfur trioxides from the experimental measurements and theoretical calculations*
Magn.Res.Chem., **52** (2014) 106-110.
I.F.=1.528

This work was done from my inspiration. My contribution to this publication consisted in: design of the research and experimental data collection. I made the graphics, obtained the preliminary version of the manuscript and its final correction. I exchanged correspondence with the reviewers and the publisher (I estimate my contribution at 40%).

Copies of the above-mentioned publications are collected in Annex 3. Co-authors statements relative to their contributions to particular publications form an enclosure as Annex .

2.3 List of articles published while being a Ph.D. degree holder which are not the subject of the habilitation procedure

R.20 A.Janowski, J.Rzeszotarska, W.Makulski**,** J.Ranachowski,
Investigations of the luminescence of n-alkenylcarbazoles and their charge-transfer complexes with 2,4,7-trinitro-9-fluorenone and 7,7,8,8-tetracyanoquinodimethane
J.Luminescence., **31&32** (1984) 535.
My contribution to this publication (20%) consisted in realization of full experimental part.

R.21 W.Makulski**,** G.J.Collin,
High-pressure photochemistry of alkenes. 4. The 184.9-nm photolysis of cyclopentene
J.Phys.Chem., **91** (1987) 708.
My contribution to this publication (50%) consisted in realization of experimental part and its preliminary description.

R.22 H.Deslauriers, W.Makulski, G.J.Collin,
The α(C-C)/β(C-H) ratio of the primary processes in the 184.9 nm photolysis of gaseous cis- and trans-2-butene
Can.J.Chem., **65** (1987)1631.
My contribution to this publication (33%) consisted in planning of the investigations, participation in experimental work and preparing of the first stage of the manuscript.

R.23 G.J.Collin., H.Deslauriers, W.Makulski
La photochimie des alkenes sous haute pression V: L'irradiation des cyclopentene et cyclohexene au voisinage de leur seuil d'absorption et en presence d'oxygene
J.Photochem., **39** (1987) 1.
My contribution to this publication (33%) consisted in planning of the investigations and their performing.

R.24 A.Chmielewski, J.Żurakowska-Orszagh, W.Makulski
Zastosowanie spektroskopii ^{13}C-NMR z transformacją Fouriera do badania struktury kopolimerów winylowych
Polimery, **39** (1994) 142.
My contribution to this publication (20%) consisted in the planning of NMR experiments and their performing.

R.25 K.Jackowski, W.Makulski, Z.Trenkner-Olejniczak
Effects of intermolecular interactions on the ^{1}H,^{13}C and ^{14}N NMR chemical shifts of N,N-Dimethylformamide dissolved in mono substituted benzenes

Bull.Pol.Acad.Sci.Chem., **48** (2000) 81.

My contribution to this publication (30%) consisted in the planning of the experiments, participation in their realization, analysis of the results and correction of the manuscript before publication.

R.26 J.Jaroszewska-Manaj, J.Oszczapowicz, W.Makulski
Amidynes.Part 41.Effects of substitution at the amidino carbon atom and at the iminonitrogen atom on the preferred configuration at the C=N bond in the ^{13}*C NMR spectra of N1,N1-dimethyl-N2-alkylamidines*
J.Chem.Soc.,Perkin Trans. 2, (2001) 1186.
I.F.=1.837

My contribution to this publication (30%) consisted in the planning of the NMR experiments, their realization and correction of the manuscript before publication.

R.27 W.Makulski,
Isotope effects on the ^{19}*F NMR chemical shifts in sulfur hexafluoride*
Mol.Phys.Rep., **33** (2001) 82.

R.28 K.Jackowski, M.Kubiszewski, W.Makulski
^{13}*C and* ^{19}*F nuclear shielding and spin-spin coupling in gaseous fluoromethane-*d_3,
J.Mol.Structure, **614** (2002) 267.
I.F.=1.122

My contribution to this publication (33%) consisted in the planning of experiments, participation in their realization and correction of the manuscript before publication.

R.29 M.Kubiszewski, W.Makulski, K.Jackowski
Intermolecular effects on spin-spin coupling and magnetic shielding constants in gaseous difluoromethane
J.Mol.Structure, **704** (2004) 211.
I.F.=1.200

My contribution to this publication (33%) consisted in the planning of experiments, participation in their realization and correction of the manuscript before printing.

R.30 E.Wielogórska, W.Makulski, W.Koźmiński, K.Jackowski
^{15}*N,*^{13}*C and* ^{1}*H nuclear magnetic shielding and spin-spin coupling in gaseous* ^{15}*N-enriched methylamine*
J.Mol.Structure, **704** (2004) 305.
I.F.=1.200

My contribution to this publication (25%) consisted in the participation in the work planning, experimental part attainment and correction of the last form of the manuscript.

R.31 M.Kubiszewski, W.Makulski, K.Jackowski
^{1}*H,* ^{13}*C and* ^{19}*F nuclear magnetic shielding and spin-spin coupling in gaseous trifluoromethane*
J.Mol.Structure, **737** (2004) 7.
I.F.=1.200

My contribution to this publication (33%) consisted in choice of the experimental NMR parameters, description of the experiments and final correction of the manuscript.

R.32 W.Makulski, M.Wilczek
Nuclear magnetic shielding and indirect spin-spin coupling constants in cyclopropane. Gaseous and liquid NMR measurements
Pol.J.Chem., **80** (2006) 1055.
I.F.=0.491
My contribution to this publication (60%) consisted in general outline of this research, preparing of the NMR ampoules, writing of the manuscript and correspondence with editorial staff.

R.33 E.Maciąga, W.Makulski, K.Jackowski, B.Blicharska
Multinuclear NMR studies of gaseous and liquid sevoflurane
J.Mol.Struct. **785** (2006) 139.
I.F.=1.495
My contribution to this publication (25%) consisted in choice of the experimental NMR parameters, description of the experimental part and correction of the final form of the manuscript.

R.34 W.Makulski, K.Jackowski, A.Antusek, M.Jaszuński
Gas-phase NMR measurements, absolute shielding scales, and magnetic dipole moments of ^{29}Si *and* ^{73}Ge *nuclei*
J.Phys.Chem.A., **110** (2006) 11462.
I.F.=3.047
My contribution to this publication (20%) consisted in performing of all experiments and correction of the manuscript.

R.35 W.Makulski,
An $^{2}H(D)$ *isotope shift in the* ^{1}H *NMR spectra of water in gaseous environment of fluoromethanes*
J.Mol.Struct., **839** (2006) 90.
I.F.=1.495

R.36 W.Makulski**,** M.Kubiszewski
^{1}H *and* ^{13}C *nuclear magnetic shielding in gaseous and liquid propene*
Pol.J.Chem., **82** (2008) 1457.
I.F.=0.518
My contribution to this publication (60%) consisted in the conception of research work, participation in experimental part, writing of the manuscript and correspondence with the editorial staff.

R.37 A. Antušek, D.Kędziera, K.Jackowski, M.Jaszuński, W.Makulski
Indirect spin-spin coupling constants in CH_4*,* SiH_4 *and* GeH_4 *– Gas-phase NMR experiment and ab initio calculations*
Chem, Phys., **352** (2008) 320.
I.F.=1.961
My contribution to this publication (20%) consisted in performing of the NMR measurements, working out of the results and their graphical presentation.

R.38 K.Jackowski, W.Makulski, A.Szyprowska, A.Antušek, M.Jaszuński, J.Jusélius
NMR shielding constants in BF_3 *and magnetic dipole moments of* ^{10}B *and* ^{11}B *nuclei*
J.Chem.Phys., **130** (2009) 044309.

I.F.=3.093

My contribution to this publication (20%) consisted in participation in the work planning, performing of the experimental part, and preparing of the preliminary manuscript.

R.39 K.Jackowski, W.Makulski, A.Szyprowska, A.Antušek, M.Jaszuński

Temperature dependence of the $^{1}J(^{11}B,^{19}F)$ *spin-spin coupling in the* BF_3 *molecule*

Magn.Reson.Chem., **47** (2009) 857.

I.F.=1.612

My contribution to this publication (20%) consisted in planning of the work, participation in NMR measurements, analysis of the results as well as correction of the final manuscript.

R.40 K.Jackowski, W.Makulski

^{13}C *shielding scale for MAS NMR spectroscopy*

Magn.Reson.Chem., **49** (2011) 600.

I.F.=1.437

My contribution to this publication (50%) consisted in performing of the measuring part, analysis of the results and correction of the final manuscript version.

R.41 P.Lantto, K.Jackowski, W.Makulski, M.Olejniczak, M.Jaszuński

NMR shielding constants in PH_3*, absolute shielding scale and the nuclear magnetic moment of* ^{31}P

J.Phys.Chem.A, **115** (2011) 10617.

I.F.=2.946

My contribution to this publication (20%) consisted in realizing of experimental part, analysis of the results and making their graphical presentation.

R.42 W.Makulski, A.Szyprowska, K.Jackowski

Precise determination of the ^{13}C *nuclear magnetic moment from* ^{13}C, ^{3}He *and* ^{1}H *NMR measurements in the gas phase*

Chem.Phys.Lett., **511** (2011) 224.

I.F.=2.337

My contribution to this publication (33%) consisted in the research concept development, choice of the experimental parameters, analysis of the results, writing the first manuscript version and correspondence with editors.

R.43 M.Jaszuński, A.Antušek, P.Garbacz, K.Jackowski, W.Makulski, M.Wilczek

The determination of accurate nuclear magnetic dipole moments and direct measurement of NMR shielding constants

Prog. NMR Spectroscopy, **67** (2012) 49-63.

I.F.=6.022

My contribution to this publication (15%) consisted in the realization of experimental part and participation in the results analysis.

R.44 W.Makulski

Tetramethyltin study by NMR Spectroscopy in the gas and liquid phase

J.Mol.Struct., **1017** (2012) 45.

I.F.=1.404

R.45 W.Makulski
^{19}F and ^{29}Si nuclear magnetic shielding and spin-spin coupling constants in silicon tetrafluoride and hexafluorodisiloxane in the gaseous state
J.Mol.Struct., **1036** (2013) 168.
I.F.=1.599

R.46 P.Garbacz, K.Jackowski, W.Makulski, R.E.Wasylishen
Nuclear magnetic shielding for hydrogen in selected isolated molecules
J.Phys.Chem.A, **116** (2012) 11896.
I.F.=2.771
My contribution to this publication (25%) consisted in performing of the major part of experiments and presentation of results in graphical form.

R.47 M.Jaszuński, M.Repisky, T.B.Demissie, S.Komorovsky, E.Malkin, K.Ruud, P.Garbacz, K.Jackowski, W.Makulski
Spin-rotation and NMR shielding constants in HCl
J.Chem.Phys., **139** (2013) 234302-1-6.
I.F.=3.122
This work was done from my inspiration. My contribution to this publication (15%) consisted in preparation of gaseous ampoules as well as choice of the spectral NMR parameters. I have also performed an final correction of the manuscript.

R.48 R.B.Nazarski, W.Makulski
NMR gas phase studies and precise DFT calculations of indirect $^{1}J(^{13}C,^{1}H\,)$ spin-spin couplings in the methyl group of tetramethyl compounds
Chem.Phys.Phys.Chem., **16** (2014) 15699.
I.F.=4.493
My contribution to this publication (40%) consisted in the research concept development, performing of the measuring part and editing of the first stage of the manuscript.

R.49 W.Makulski
^{83}Kr nuclear magnetic moment in terms of that of ^{3}He
Magn.Reson.Chem., **52** (2014) 430-434.
I.F.=1.179

R.50 P.Garbacz, W.Makulski**,** M.Jaszuński
The NMR spin-spin coupling constant $^{1}J(PH)$ in an isolated PH_3 molecule
Chem.Phys.Phys.Chem., **16** (2014) 21559.
I.F.=4.493
My contribution to this publication (33%) consisted in the research concept development, performing NMR measurements and initial editing of the manuscript.

R.51 W.Makulski
^{129}Xe and ^{131}Xe nuclear magnetic dipole moments from gas phase NMR spectra
Magn.Reson.Chem., **53** (2015) 273-279.
I.F.=1.179

2.4 Conference reports

S.1 M.Skarżyński, W.Makulski
Investigations of the brown coal extracts by ^{1}*H and* ^{13}*C NMR high resolution spectroscopy*
XV Polish Seminar on Nuclear Magnetic Resonance and its applications, Cracow-Poland, 1-2.12.1983.

S.2 W.Makulski, E.Zakrzewski
Estimations of the energetic barrier of the inhibited rotation around C-N bond in N,N-Dimethylformamide dissolved in mono-substituted benzenes
XV Polish Seminar on Nuclear Magnetic Resonance and its applications, Cracow-Poland, 1-2.12.1991.

S.3 A.Chmielewski, J.Żurakowska-Orszagh, W.Makulski
Application of the ^{13}*C NMR spectroscopy to the estimation of the alternate degree in copolymers: S/MA, S/MMA, MS/MA, MS/MMA*
XXVI Polish Seminar on NMR and its Applications, Cracow-Poland 1 - 2.12.1993.
S.4 A.Chmielewski, W.Makulski, J.Żurakowska-Orszagh
Comparative investigations of the vinyl monomers reactivity by NMR spectroscopy
Polish Seminar on NMR and its Applications, Cracow-Poland, 1 - 2.12.1994.

S.5 G.J.Collin, W.Makulski
Photolyse du cyclopentene gazeux a 184.9 nm
54 Congres de l'ACFAS, Montreal- Canada 12 - 16.05.1986.

S.6 G.J.Collin, W.Makulski**,** G.De Mare
The ring contraction of cyclic olefins to yield vinylcycloalkanes
69-Congres Canadien de Chemie, Saskatoon, Saskatchewan, Canada, 1 - 4.06.1986.

S.7 W.Makulski, Z.Trenkner-Olejniczak, M.Kwiecień, K.Jackowski
Molecular association of N,N-dimethylformamide in liquid solvents studied by the ^{13}*C and* ^{14}*N NMR chemical shifts,* 17th Conference Magnetic Resonance and the Structure of Matter, Gosen-Germany, 28 - 30.09.1995.

S.8 J.Jaroszewska-Manaj, J.Oszczapowicz, W.Makulski
^{13}*C NMR spectra of trisubstituted amidines*
Symposium on: Application of Magnetic Resonance in Chemistry and Related Areas, Warsaw-Poland, 9 -11.06.1999.

S.9 W.Makulski
Efekty izotopowe w przesunięciu chemicznym ^{19}*F NMR sześciofluorku siarki*
XXXIII Polish Seminar on NMR and its Applications, Cracow-Poland, 4 - 5.12.2000.

S.10 M.Wilczek, W.Makulski, W.Koźmiński, K.Jackowski

Influence of intermolecular interactionsin the gas phase on the ^{33}*S NMR chemical shifts of sulphur hexafluoride*
XXXIII Polish Seminar on NMR and its Applications, Cracow-Poland, 4 - 5.12.2000.

S.11 W.Makulski, K.Jackowski
^{17}*O nuclear magnetic shielding scale from gas phase studies*
EUCMOS-2002 , Villeneuve d'Ascq-France, 1 - 6.09.2002.

S.12 W.Makulski, K.Jackowski
^{17}*O and* ^{33}*S NMR studies of sulfur dioxide and sulfur trioxide*
VII International Conference on Molecular Spectroscopy, Wrocław-Lądek Zdrój-Poland, September 2003.

S.13 W.Makulski
Multinuclear magnetic resonance studies of gaseous and liquid dimethyl ethers
EUCMOS-2004, Cracow-Poland, 6 -10.09.2004.

S.14 E.Maciąga, W.Makulski, K.Jackowski, B.Blicharska
^{1}*H,*^{13}*C and* ^{19}*F NMR studies of gaseous and liquid sevoflurane*
XXXVII Polish Seminar on NMR and its Applications, Cracow-Poland, 1 - 2.12.2004.

S.15 E.Maciąga, W.Makulski**,** K.Jackowski, B.Blicharska
Multinuclear gas and liquid NMR studies of anesthetics
Ampere XIII NMR School, Zakopane-Poland, 5 - 10.06.2005.

S.16 W.Makulski, M.Wilczek,
Nuclear Magnetic Shielding and Indirect Spin-Spin Coupling Constants in Cyclopropane. Gaseous and Liquid NMR Measurements
NMR in Chemistry, Biology and Medicine, Warsaw-Poland, 8 - 10.09.2005.

S.17 W.Makulski
An ^{2}*H/*^{1}*H isotope shifts in the* ^{1}*H NMR spectra of water in gaseous environment of fluoromethanes*
XXXVIII Polish Seminar on NMR and its Applications, Cracow-Poland, 1 - 2.12.2005.

S.18 M.Jaszuński, K.Jackowski, A.Antušek, W.Makulski, M.Wilczek,
Nuclear magnetic dipole moments from NMR spectra
I Symposium on: NMR in Chemistry, Biology and Medicine, Warsaw-Poland, 8 - 10.09.2005.

S.19 A.Antušek, K.Jackowski, M.Jaszuński, W.Makulski, M.Wilczek
Nuclear magnetic dipole moments from NMR spectra
The 2005 Minerva-Gentner Symposium – A Dive into Magnetic Resonance , Eilat-Izrael, 11 - 15.12.2005.

S.20 A.Antušek, K.Jackowski, M.Jaszuński, W.Makulski, M.Wilczek
Nuclear magnetic dipole moments from NMR spectra – theory and experiment
13th European Seminar on Computational Methods in Quantum Chemistry, Smolenice-Slovak Republic, 21 - 25.09.2005.

S.21 W.Makulski
^{1}H, ^{13}C and ^{17}O Nuclear Magnetic Shieldings of methanol and its deuterated isotopomers from the gas phase measurements
XXVIII European Congress on Molecular Spectroscopy, Istanbul-Turkey, 3 - 8.09.2006.

S.22 K.Jackowski, A.Antušek, M.Jaszuński, W.**M**akulski, M.Wilczek
Nuclear magnetic dipole moments from NMR spectra
XXVIII European Congress on Molecular Spectroscopy, Istanbul-Turkey, 3 - 8.09.2006.

S.23 W.Makulski, M.Wilczek, K.Jackowski
^{17}O and ^{1}H Magnetic Shielding and Spin-Spin Coupling of ^{17}O-Enriched Water in the Gas Phase
II Symposium on: Nuclear Magnetic Resonance in Chemistry, Biology and Medicine, Warsaw-Poland, 11 - 13.09.2006.
S.24 W.Makulski
Tetramethyltin study by NMR Spectroscopy in the gas and liquid phase
XXXIX, Cracow-Poland, 30.11 - 01.12.2006.

S.25 M.Kubiszewski, W.Makulski
^{1}H and ^{13}C Nuclear Magnetic Shielding In Gaseous and Liquid Propene
III Symposium on: Nuclear Magnetic Resonance in Chemistry, Biology and Medicine, Warsaw-Poland, 20 - 22.09.2007.

S.26 W.Makulski**,** M.Wilczek, K.Jackowski
^{17}O and ^{1}H NMR Spectral Parameters of Water in Gaseous Matrices
XL Polish Seminar on NMR and its Applications, Cracow-Poland, 3 - 4.12.2007.

S.27 W.Makulski, A.Wikieł
Nuclear magnetic shielding and spin-spin coupling constants for acetaldehyde from gas-phase NMR spectroscopy
XXIX European Congress on Molecular Spectroscopy , Opatija-Chorvatia, 31.08 - 5.09.2008.

S.28 W.Makulski, A.Tulewicz, A.Leś
Theoretical estimations of ^{17}O and ^{33}S nuclear magnetic shieldings of simple sulfur oxides
XLI Polish Seminar on NMR and its Applications, Cracow-Poland, 1-2.12.2008.

S.29 W.Makulski, A.Szyprowska, K.Jackowski
Stałe ekranowania NMR w BF_3 i dipolowe momenty magnetyczne jąder ^{11}B i ^{10}B
XLI Polish Seminar on NMR and its Applications, Cracow-Poland, 1 - 2.12.2008.

S.30 R.Nazarski, W.Makulski
Stałe sprzężenia $^1J(CH)$ *w grupie metylowej cząsteczek* $X(CH_3)_4$; *badania NMR w fazie gazowej oraz dokładne obliczenia DFT*
XI National Symposium on: Progress in Chemistry of Heteroorganic Compounds, Łódź-Poland, November 2008.

S.31 K.Jackowski, W.Makulski, A.Szyprowska, A.Antušek, M.Jaszuński
Temperature dependence of the $^1J(^{11}B^{19}F)$ *spin-spin coupling in* BF_3 *molecule*
V Symposium on: Nuclear Magnetic Resonance in Chemistry, Biology and Medicine, Warsaw-Poland, 22-24.09.2009.

S.32 M.Wilczek, A.Szyprowska, W.Makulski
Wyznaczanie jądrowego momentu magnetycznego węgla wyznaczony na podstawie pomiarów ^{13}C *i* ^3He *w gazowych matrycach*
XLII Polish Seminar on NMR and its Applications, Kraków-Poland, 1 - 2.12.2009.

S.33 W.Makulski, K.Jackowski
^{13}C *shielding scale for MAS NMR spectra*
EUROMAR 2010 and ISMAR 17th Conference, Florence-Italy, 4-9.07.2010.

S.34 W.Makulski
Reconsideration of the ^{13}C *Absolute nuclear magnetic shielding scale from NMR measurements of CO/He and* CH_4*/He gas phase mixtures*
XXIX European Congress on Molecular Spectroscopy, Florence-Italy, 29.08 - 3.09.2010.

S.35 W.Makulski, K.Jackowski
Absolute nuclear magnetic shieldings in TMS (tetramethylsilane) from NMR measurements in the gas phase
VI Symposium on: Nuclear Magnetic Resonance in Chemistry, Biology and Medicine, Warsaw-Poland, 22 - 24.09.2010.

S.36 K.Jackowski, P.Garbacz, W.Makulski, E.R.Wasylishen
Accurate gas-phase ^1H *NMR frequency measurements of hydrogen molecules and the absolute magnetic shielding of protons in several model compounds*
52-nd ENC Conference, Asilomar-USA, 10 - 15.04.2011.

S.37 K.Jackowski, M.Jaszuński, W.Makulski, M.Wilczek, P.Garbacz, A.Antušek
Absolute shielding scale for multinuclear magnetic resonance spectra
53-rd ENC Conference, Miami-USA, 15 - 20.04.2012.

S.38 W.Makulski
Absolute NMR shielding scale and nuclear magnetic moment of ^{83}*Kr*
VII Symposium on: Nuclear Magnetic Resonance in Chemistry, Biology and Medicine, Warsaw-Poland, 26 - 28.09.2012.

S.39 R.B.Nazarski, W.Makulski
How two electronegativiesties values related to germanium were improved using J-coupling data?
VIII Symposium on: Nuclear Magnetic Resonance in Chemistry, Biology and Medicine, Warsaw-Poland, 24 - 26.09.2014.

S.40 P.Garbacz, W.Makulski, M.Jaszuński
Gas-phase studies of the spin-spin coupling constant J(P,H) in PH_3 *molecule*
VIII Symposium on: Nuclear Magnetic Resonance in Chemistry, Biology and Medicine, Warsaw-Poland, 24 - 26.09.2014.

3 Course of scientific work

3.1 Research problems before obtaining the Ph.D. degree

My M.Sc. and Ph.D. thesis were realized in Laboratory of Radiochemistry, Department of Chemistry at the University of Warsaw in the area of the effect of high energy radiation on the matter: photolysis by vacuum ultraviolet and radiolysis of gaseous hydrocarbons in the presence of scavengers - radicals and ions. The result of this research were 6 published works. The most valuable of them is: W.Makulski, J.Gawłowski, J.Niedzielski, D*issociation of propylene excited by the impact of low energy electrons in the gas phase*. J.Phys.Chem. **18** (1981) 2950. For the reason that in the science took place the back ward trend of the classical radiation chemistry - stationary methods, I have decided to use my experience in operating of gaseous substances in NMR spectroscopy research.

3.2 Subject of research after obtaining the Ph.D. degree

Just after obtaining the Ph.D. degree I have continued my research projects in the field of photolysis in the Laboratory of Prof. Guy J.Collin at Quebec University (Canada), whose result were 3 publications in this topic (R. 21-23). After returning home I dealt with spectroscopy problems in inorganic and organic chemistry. In the beginning I realized

UV/VIS spectroscopy subjects and fluorescence of organic substances (R. 20) and afterwards the research of high resolution NMR of liquid carbon (R. 24) and materials in the gas phase (R. 25-50). In the works mentioned above I measured NMR spectra of ^{1}H, ^{2}H, ^{3}He, ^{10}B, ^{11}B, ^{13}C, ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{29}Si, ^{31}P, ^{33}S, $^{35/37}$Cl, ^{73}Ge, ^{83}Kr, $^{115/117/119}$Sn, $^{129/131}$Xe. The greatest part of this research were publications related to ^{17}O and ^{33}S resonances, which were selected as a monothematic series of works in the habilitation proceedings.

Hereby I report to habilitation proceedings the monothematic series of publications, which consists of 13 studies, as a scientific achievement according to Art.16 (2) of the Act of 14 March 2003 on scientific and artistic titles (Journal of Laws no.65, item 595 as amended) which I am sole or co-author. The title of this study is: *^{17}O and ^{33}S Nuclear Magnetic Resonance of Simple Molecules in the Gas and Liquid Phases.*

The discussion of this achievement and several papers of this subject is presented in the second part of this document.

3.3 Presentation of a monothematic cycle of scientific studies included in the scope of postdoctoral thesis

Title of scientific achievement:

Nuclear magnetic resonance ^{17}O and ^{33}S for simple molecules in gaseous and liquid phases

3.3.1 Introduction

The great success of nuclear magnetic resonance spectroscopy with high resolution in liquids overshadowed the achievements of this spectroscopy in other phases: in the solid state and in gases. Previously, it was observed that the spectrum image depends to a great extent from the type of the medium in which the measurement of nuclear magnetic resonance spectrum is taken. A significant broadening of resonance lines in solid bodies and in gases often eliminates or darkens the subtle structure of the signals registered. In solid state, this extending is the result of dipole interactions that are trapped in the crystalline grid of atomic nuclei, and in gases, from an effective spin-rotation relaxation being the consequence of the free rotation of molecules. The low density of the medium examined constitutes an obvious impediment to research. On the other hand, the advantages of this research are invaluable: the possibility to use temperature and pressure as variables in specific cases. An analysis of the courses of temperature and pressure dependences allows one to define the influence of intermolecular interactions on the image of nuclear magnetic resonance spectrums. Today, laboratory work in the field of compressed gases, that are often explosive or strongly poisonous, is not attractive to many junior chemistry researchers. Because of all of this, 70 years after the first spectrum was registered of a gaseous sample (1946, H_2 with the pressure of 10 atmospheres), the number of studies based on experiments in gas is still limited. At present, the group of Prof. K. Jackowski from the Faculty of Chemistry at the University of Warsaw is the only one laboratory in the world where experimental studies in this field are regularly performed. Studies in a gaseous phase provide spectroscopic data of an unique significance for understanding the basic magnetic nuclear resonance phenomena that occur in the matter. The nature of the gaseous phase being a set of relatively isolated and weakly interacting gas molecules is undoubtedly their most important feature. No information of this type can be obtained from observations in condensed phases. Investigations of the gaseous phase involve several fundamentally separate spectroscopic phenomena: (1) research into dynamic processes: in chemical reactions and conformational processes within molecules[1],

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[1] S. Suarez, Chemical Educator, **3** (1998) 1.

(2) research into the relaxation processes of individual nuclei in the aspect of the determination of various parameters, *e.g*. relaxation times T1 and T2, spin-spin coupling constants and other[2], (3) determination of the constant values of shielding and spin-spin coupling through extrapolation to “zero” pressure, as well as virial coefficients that describe intermolecular forces in gaseous systems. The latter experiments allow one to obtain the values of the absolute shielding of individual nuclei, *i.e*. towards an exposed nucleus deprived of electrons that surround it. Obviously enough, its shielding is zero. In relation to the constants of nuclear coupling, data can be collected for single molecules which are not burdened by interactions with the environment. The spectroscopic data of this type usually forms the basis for the verification of the theoretical calculations of magnetic nuclear resonance parameters with quantum-chemical methods. The presented review of studies is in principle dedicated to problems included in Point (3), and it does not involve the whole of issues in the area of magnetic nuclear resonance in gases. However, a number of the aspects of spectroscopy in condensed phases were taken into consideration. This was essential in order to emphasize the essence of physicochemical phenomena that occur in various media. Before I took up the issues referred to in the title, significant experimental material had been collected for nuclei that are characterized by a high detection sensitivity: ^{1}H, ^{19}F, ^{31}P and ^{13}C. The resonance of quadrupolar nuclei such as ^{17}O and ^{33}S with little occurrence in nature and small magnetogyric ratios was researched to a considerably smaller extent[4]. A substantial improvement of magnetic nuclear resonance apparatus which has been observed over the past fifteenth years, *i.e*. the common use of high-field superconducting magnets (up to 18.8 and 21.1 Tesla), cryogenic probes, new correlation techniques of magnetic nuclear resonance (at present, *ca*. 500 impulse sequences) allowed one at least in part to overcome problems connected with the time sensitivity and stability of the magnetic nuclear resonance experiment. This contributed to a great extent to a new impulse for experiments in the gaseous phase.

Measuring conditions of ^{17}O and ^{33}S nuclear magnetic resonance

^{17}O is one of very difficult measuring nuclei in magnetic nuclear resonance spectroscopy for two reasons at least. Firstly, the only one magnetically active nucleus ^{17}O with 5/2 spin is

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2. C.B. LeMaster, J.Progress NMR Spectrosc., **31** (1997) 119.
3.C.J. Jameson, Chem.Rev., **91** (1991) 1375.
4. K. Jackowski, J. Mol. Struct., **563-4** (2001) 159.

0.0037%, other sources: 0.048%); secondly, it is characterized by a substantial electric quadrupolar moment.

That is why in spite of the absolute detection sensitivity of 6.11×10^{-2} in relation to the ^{13}C nucleus, the sensitivity in relation to proton resonance is as little as 1.11×10^{-5}.

Liquid water ($H_2{}^{17}O$) used in the form of an external standard is a commonly accepted standard of a chemical shift in the case of oxygen-17. This is not a perfect standard because of a substantial width of the resonance signal, yet it is generally accepted due to its easy availability and a great spectral range of oxygen-17 which compensates for the inaccuracy of the location of the standard.

Table 1.
Physical properties of ^{17}O and ^{33}S nuclei.

Parameter	Type of nucleus	
	^{17}O	^{33}S
Nucleus spin, I	(5/2)	(3/2)
Nuclear magnetic moment, μ_N	-1.8935426(104)	0.6432507(155)
Magnetogyric ratio, γ_x [rad $T^{-1}s^{-1}$]	-3.62759521	2.053864832
Occurrence in nature, %	0.038	0.76
Frequency@ 2.3488 T [MHz]	13.556457	7.676000
Quadrupolar moment, Q [mb]	-0.02578	-0.678
Spectral range, ppm	1160	964
Standard	H_2O or D_2O	$(NH_4)_2SO_4$ in D_2O
Full width at half max. of standard, $\Delta_{1/2}$ [Hz]	44 or 68	10
Sensitivity towards ^1H	1.11×10^{-5}	1.72×10^{-5}
Sensitivity towards ^{13}C	0.065	0.101

Recently, the International Union of Pure and Applied Chemistry has been recommending the use of pure heavy water $D_2{}^{17}O$. The difference in the shielding of both nuclei in these compounds is ~ 3ppm. However, this standard has all the advantages and disadvantages of the previous one.

Sulphur, due the low abundance of its only one magnetically active nucleus ^{33}S (0.76%), is characterized by even worse analytical conditions than oxygen, just because of a great quadrupolar moment and a low resonance frequency. The latter quantity is certainly the consequence of the small magnetic moment of this nucleus (*i.e.* 1/13 of the value of the proton moment). It is not without significance that sulphur atoms occur in molecules in

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5. R.K. Harris, E.D. Becker, S.M. Cabral de Menezes, P. Granger, R.E. Hoffman, K.W. Zilm, *Pure Appl. Chem.* **80** (2008) 59.

positions with a small symmetry around the sulphur atom. Less than 200 studies in this field had been prepared by the year 2003[6] and not many more till this day because of the reasons mentioned above. In resonance with high resolution analyses, a saturated water solution of ammonium sulphate remains a standard that is recommended by the International Union of Pure and Applied Chemistry. An alternative is sulfate solutions of metals from the first periodic table group of known concentration.

In nature, three different oxygen isotopes occur; as two of them: ^{16}O and ^{18}O have the spin number I = 0, ^{17}O is practically the only one active nucleus in magnetic nuclear resonance. A low abundance of this isotope can be overcome through an isotopic enrichment of the chemical substances under examination. Unfortunately, there are few commercially available compounds at present: water, carbon dioxide, molecular oxygen and methyl alcohol. The prices of enriched products remain high. Therefore, individually conducted chemical syntheses may be the source of this type compounds. A wide review of these methods can be found in the book by Boykin[7]. Every reaction with the participation of oxygen-16 can be used to build oxygen-17 or oxygen-18 into the given molecule. For example, in my study (Q.16), I carried out a synthesis of partially deuterated dimethyl ether (CH_3OCD_3) with the aid of the Williamson's method from an adequately enriched alcohol and methyl iodide. In contrast to oxygen-17, distribution companies do not currently offer any chemical reagents enriched with sulphur-33, apart from atomic sulphur.

Theory of the experiment

The general features of magnetic nuclear resonance spectrums with a high resolution in gases are analogical as for liquids and fluid solutions. However, the values of the chemical shifts of gaseous and liquid samples of the same objects vary because of differences in the local environment of nuclei. As a rule, a gaseous sample possesses a smaller and sometimes completely negligible volume magnetic susceptibility, and it is characterized by a small participation of intermolecular interactions. Due to the differences in the magnetic susceptibilities of liquid and gaseous samples, the whole spectrum measured in gas is shifted by several ppm in relation to the liquid spectrum. The direction and the size of this shift depends from the substance examined, the measuring magnetic field induction, the shape of

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[6] T.A. Wagler, W.A. Daunch, P.L. Rinaldi, A.P.R. Palmer, J.Magn.Reson., **161** (2003) 191.

[7] D.W. Boykin (ed.), *^{17}O NMR Spectroscopy in Organic Chemistry*, CRC Press, Boca Raton, 1991.

[8] W.T. Raynes, A.D. Buckingham, H.J. Bernstein, J. Chem. Phys., **36** (1961) 3481.

the measuring ampoule and the orientation of the whole sample in relation to the magnetic field force lines. In the samples of pure gases, magnetic shielding can be defined in gas as virial expansion in relation to molar volume (V_m)[8]:

$$\sigma = \sigma_o + \sigma_1/V_m + \sigma_2/V_m^2 + \ldots \qquad (1)$$

or concentration (ρ):

$$\sigma = \sigma_o + \sigma_1\rho + \sigma_2\rho^2 + \ldots \qquad (2)$$

where the σ_0 coefficient represents shielding in an isolated molecule, and further it represents bi-, trimolecular interactions etc. Of course, bimolecular collisions dominate in diluted gas, and that is why the second virial coefficient of the shielding of nucleus σ_1 can be defined in any temperature available in the experiment[3]:

$$\sigma_1(T) = -(1/\nu_o) \lim_{\rho\to o} (\partial\nu/\partial\rho)_T \qquad (3)$$

The individual inputs to σ_1 involve interactions of the van der Waals type, electric interactions, interactions from the molecular anisotropy of neighbouring molecules and also from the magnetic susceptibility of the system. The coefficient of volume magnetic susceptibility can be principally calculated accurately and removed from the value of σ_1 so that it is only the input from intermolecular interactions that is taken into consideration. This coefficient depends from the geometry of the sample and its composition. For a perfectly spherical sample, this parameter is zeroed out; in the case of a sufficiently long magnetic nuclear resonance cylindrical test tube in a magnetic field oriented perpendicular to the axis of the sample, it is $\sigma_{1b} = +(2\pi\chi_V/3)$, and in the field oriented in parallel, it is $\sigma_{1b} = -(4\pi\chi_V/3)$. It is accepted that if the relation of the length of the cylindrical test tube to its diameter exceeds the value of 5, the error caused by a deviation from the ideal infinite cylinder is *ca*. 5%. This correction is identical for all the nuclei in the measuring sample. The values for the volume susceptibility of diamagnetic substances are calculated taking into consideration the density of the medium in a given temperature and the molar coefficient of magnetic susceptibility. Many basic chemical substances possess well defined values of molar susceptibility; however, as a rule, literature data is characterized by considerable divergences between individual results. This has a significant influence on errors in the determination of the shielding of liquids and solutions. Similarly, the determination of the density of a liquid substance in a temperature which is close to the room temperature is very problematic when it is gas in normal conditions. Each parameter σ_1 is described by a complicated function of the distance between molecules and the mutual orientation (surfaces of intermolecular shielding). These functions can be calculated with the use of *ab initio* methods, yet an appropriate procedure requires extremely advanced computer calculations, and currently they are performed strictly only for the simplest molecular systems.

In two-component gaseous mixtures, for molecule A including nucleus X, whose shielding σ(X) is the subject of our interest, and gas B as a solvent, we may write an analogical equation[3]:

$$\sigma(X) = \sigma_o(X) + \sigma_{AA}(X)\rho_A + \sigma_{AB}(X)\rho_B + \dots \qquad (4)$$

where ρ_A and ρ_B are densities A and B, and $\sigma_o(X)$ is the shielding of nucleus X in an isolated molecule. Coefficients $\sigma_{AA}(X)$ and $\sigma_{AB}(X)$ include adjustments for magnetic susceptibility and inputs from intermolecular interactions during the collisions of molecules A-A and A-B. Obviously enough, the parameters of shielding in Equation (4) depend from temperature, and that is why many experiments are performed in a constant and closely inspected temperature (often in 300K). If only the density of component A is sufficiently low, Equation (4) is simplified to the following formula:

$$\sigma(X) = \sigma_o(X) + \sigma_{AB}(X)\rho_B \qquad (5)$$

Similarly as for the shielding of nuclei, the constants of spin-spin scalar coupling are modified in the gaseous phase by intermolecular interactions; an appropriate equation for the constants of coupling takes on the form which is similar to Function (2):

$$J(T) = J_o(T) + J_1(T)\rho + J_2(T)\rho^2 + \dots \qquad (6)$$

where $J_o(T)$ is the spin-spin coupling constant for the isolated molecule, and terms $J_1(T)\,\rho$, $J_2(T)\,\rho^2$, … are caused by the effects of the intermolecular interactions of colliding molecules. In the recent years, research in this field has involved considerably more frequently theoretical calculations rather than experimental calculations. The quantum-chemical calculations of the shielding of individual nuclei have been very popular since the early 1990s. An inclusion of the effects of electronic correlation (the perturbation method and the method of coupled clusters), solving the selection problem of the beginning of the reference frame for the vector potential (GIAO, IGLO) and the costs of the efficiency of calculations (the DFT theory) allowed one to collect many results and to compare them with the experimental results in the gaseous phase [9,10,11].

Experimental aspects

In the Laboratory of NMR Spectroscopy, a method was developed of an analysis of gases and

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[9] M. Kaupp, M. Bühl, V.G. Malkin (eds.), *Calculation of NMR and EPR Parameters. Theory and Applications*, Wiley-VCH, Weinheim, 2004.

[10] J. Vaara, *Phys. Chem. Chem. Phys.*, **9** (2007) 5399.

[11] M.A. Teale, O.B. Lutnaes, T. Helgaker, D.J. Tozer, J. Gauss, J.Chem.Phys., **138** (2013) 024111.

low-boiling liquids in gaseous mixtures with “real” buffer gases of the type of Xe, Kr, CO_2, CH_3F, CHF_3, SF_6 or N_2O, which are gases in room temperatures, up to the pressures of *ca*. 30-40 atm. The substance examined is found in a mixture in the concentration of $10^{-2} – 10^{-3}$ mol/L. An increase of the pressure in the mixture results in a substantial increase of spin-rotation relaxation times and, in consequence, a significant narrowing of the resonance lines measured. This allows one to determine with a greater precision the position of resonance lines, and thus to determine the values of chemical shifts and spin-spin couplings. The mutual miscibility of the components can be a limitation of the method. In general, non-polar substances require the use of analogical non-polar compounds, and polar substances require the use of polar solvents. Before an appropriate gaseous solvent is selected, it is usually advisable to carry out a number of initial tests.

As mentioned previously, the experiments ^{17}O and ^{33}S of nuclear magnetic resonance have their obvious limitations, *i.e*. the compressibility of the substance examined, the detection sensitivity and a natural width of the resonance line, all of which limit the range of the pressures and temperatures available. The time of spin-network relaxation T1, as the function of concentration, is long at very low gas densities, where the frequencies of collisions are low, they pass through the characteristic minimum that corresponds to a balance between collisions and the frequency of spin precession, only to pass to the area where it grows together with an increase of the density of the medium, which is known as the “extreme narrowing” range [12]. In experimental conditions used in the experiments discussed, this last requirement is always fulfilled. ^{17}O and ^{33}S nuclei in dispersed molecules in the gaseous phase relax through effective spin-rotation and quadrupolar mechanisms. The relaxation mechanisms in gases are so quick that many intramolecular and intermolecular polarization transfer sequences, which can be successfully used routinely in condensed phases, cannot be used here. Unfortunately, the number of these studies that take into consideration these difficulties is marginal as regards the interests of the present-day magnetic nuclear resonance spectroscopy. The phenomenon of “acoustic ringing”, which is connected with the emission and absorption of acoustic frequencies that occur in the spectrometer probe, constitutes an additional measuring complication in the research into the nuclei under discussion. This is a common phenomenon in the registration of nuclei with low Larmor frequencies, and it depends from the size of B_0 field where we take a measurement. Wherever it is possible, the INEPT impulse sequence

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[12] D. Neuhaus, M. Williamson, *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, VCH, New York,1989.

turns out to be an extremely useful measuring method. In the sequence with decoupling, we obtain a smoothing effect of the base line of the spectrum and enhancing of the resonance signal intensity. This method is effective only if the neighbouring nucleus is subject to quick relaxation[13]. On the other hand, if there are no interfering nuclei with ½ spin in the environment of the quadrupolar nucleus, the use of one of the methods to remove the base line ringing of the RIDE type[14] seems to be the only solution to this situation. Let us take the spectrum ^{33}S of magnetic nuclear resonance of liquid sulphur trioxide as an example; the resonance signal of the full with at half maximum of *ca*. 1000 Hz can be successfully registered (Fig. 1a). The INEPT spectrum of a liquid sample of sulphur hexafluoride is presented next to it as comparison (Fig. 1b); the full width at half maximum of the peak is *ca*. 3 Hz, and the base line distortion phenomenon does not occur at all.

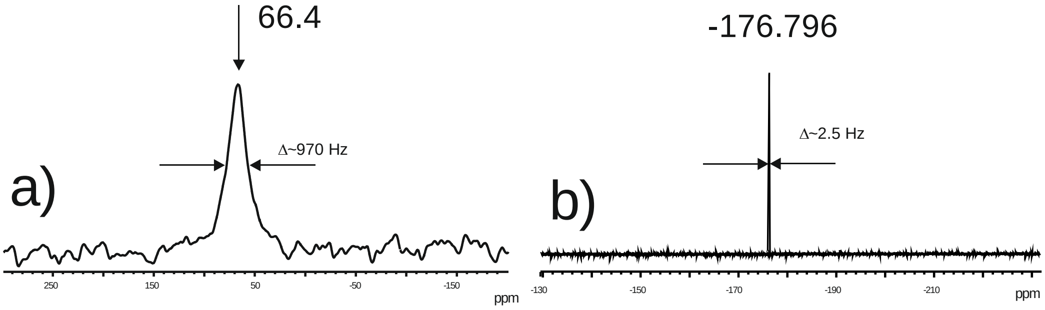

Figure 1.
^{33}S NMR spectra of liquid samples: (a) SO_3 - RIDE method and (b) SF_6 – INEPT method.

In the acquisition of 2D spectrums in SF_6, a modified PFG-HSQC sequence of impulses was used, which is required in the measurements of the passive coupling constants (Q 11). The use of popular standard HSQC techniques with the gradient selection with echo-antiecho coherence does not offer any good results due to weakening which is caused by a very effective spin-rotation relaxation. Instead of this, a selection of longitudinal two-spin coherence $2I_zS_z$ was used through the two gradient pulses with opposite signs in the time of both stages of the INEPT sequence. This technique allows one to remove all the unwanted transverse magnetizations, and it is little sensitive to the effects of diffusion and convection in gases. The use of this measuring technique effectively shortens the time required for the spectrum acquisition. It is worth noting that a similar correlation was later used in the analyses of SF_6 dissolved in thermotropic liquid crystals[15].

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[13] M. H. Levitt, *Spin Dynamics*, John Wiley & Sons Ltd., Chichester, 2001.

[14] W.Koźmiński, K.Jackowski, Magn. Reson. Chem., **38** (2000) 459.

[15] H.Tervonen, J.Saunavaara, L.P. Ingman, J.Jokisaari, J.Phys.Chem.B, **110** (2006) 16232.

3.3.2 Chemistry of small sulphur and oxygen molecules

The habilitation dissertation presented herein is related to those chemical compounds that include oxygen and sulphur atoms in their structures. Both elements are found in group VIa in the periodic table, which means a similarity of their electronic configurations, *i.e*. $[He]2s^22p^4$ for oxygen and $[Ne]3s^23p^4$ for sulphur. Due to this fact, these elements form many analogical chemical structures. Apart from the obvious structural analogies, both classes of these chemical compounds differ considerably as regards their physiochemical properties. This is the result of numerous causes: a considerably smaller electronegativity of sulphur (EN=2.58) as compared to oxygen (EN=3.44), a considerably greater covalent radius of sulphur (0.104 nm) than that of oxygen (0.066 nm), and the fact that only sulphur can expand its shell up to over 8 electrons (up to 10 and even 12). The number of sulphur oxidation degrees is substantially richer (from -2 to +6) than in the case of oxygen (from -2 to +2). It becomes evident that double bonds O=O are considerably stronger than S=S in contrast to single bonds. The series of the compounds of oxygen and sulphur which are similar to each other including their boiling temperatures (T_w)[16] are provided in Table 2.

Table 2
Chemical compounds that include oxygen and its sulphur analogs.

Oxygen compounds	$T_{w.}$(°C)	Sulphur compounds	$T_{w.}$(°C)
H_2O (water)()	100	H_2S (hydrogen sulphide)	-60.7
O_3 (ozone)	-111.9	SO_2 (sulphur dioxide)	-10
SO_3 (sulphur trioxide)	44.8	SO_3 (sulphur trioxide)	44.8
COS (carbon oxysulphite)	-50	COS (carbon oxysulphite)	-50
Cl_2O (dichlorine monoxide)	3.8	SCl_2(sulphur dichloride)	59
$COCl_2$ (phosgene)	8.3	$CSCl_2$ (thiophosgene)	73.5
HOCN (cyanic acid)	23.5	HSCN (thiocyanoacetic amid)*	
$OC(NH_2)_2$ (urea)*		$SC(NH_2)_2$ (thiourea)	150-160
CO_2 (carbon dioxide)	$-78.6^{sub.}$	CS_2 (carbon disulphide)	46.3
H_2O_2 (hydrogen peroxide)	150.2	H_2S_2 (hydrogen disulphide)	70.7
CH_3OH (methanol)	65.15	CH_3SH (methanethiol)	6.2
$(CH_3)_2O$ (dimethyl ether)	-24.8	$(CH_3)_2S$ (metyl sulphide)	37.34
CH_3CHO (acetaldehyde)	20.8	CH_3CHS (methyl thioaldehyde) **	
$(CH_3)_2CO$ (acetone)	56.2	$(CH_3)_2SH$ (thioacetone)*	
CH_3COOH (acetic acid)	117.9	CH_3COSH (thioacetic acid)	93
CF_3COOH (trifluoroacetic acid)	72.4	CF_3COSH (trifluorothioacetic acid)**	

* unstable,
** unknown compound

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[16] D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, CRC Press, **81**, Boca Raton, 2000-2001.

A number of sulphuric analogs are unstable in normal conditions and cannot be used. Many of the chemical compounds included in the table are gases or low-boiling liquids in standard conditions. They were taken into consideration as the objects of MRJ studies in the gaseous phase.

3.3.3. Results described in the publications that form the basis of habilitation project

Absolute ^{17}O nuclei shielding scales

The first systematic studies of ^{17}O nuclei shielding were undertaken both as experimental and theoretical studies in relation to the simplest molecules that include oxygen atoms in the carbonyl group (Q.7). The results presented serve to demonstrate that solvent effects in the pure liquids of carbonyl compounds play an essential role. The data available to date on shielding concerns mainly those liquid substances where strong intermolecular interactions occur connected with the presence of electron pairs located on the oxygen atom from the carbonyl group. In order be experimentally closer to the gaseous phase, we used the solutions of selected substances in cyclohexane. This project proved to be correct because the results received agreed well with the theoretical results obtained for the isolated molecules. Comparisons were made in the domain of the values of chemical shifts (δ). This allowed us to eliminate a number of systematic errors in quantum calculations. All the results were intentionally related to the carbon monoxide molecule (CO). Carbon monoxide, as a simple two-atomic molecule, was selected to determine the absolute scale of shielding in the resonance of ^{13}C and ^{17}O nuclei. Appropriate calculations were performed based on spin-rotation constants C_I measured in the molecules of $^{13}C^{16}O$ and $^{12}C^{17}O$ isotopomers. While the carbon spin-rotation constant $C_I(^{13}C)$ is known with a good accuracy, the appropriate value $C_I(^{17}O)$ has not been well defined so far. The first fully “experimental” scale of the absolute shielding of oxygen[17] was introduced on the basis of $C_I(^{17}O) = -30.4(12)$ kHz[18]. The spin-rotation constant was measured from rotation transition J = 1←0 in $^{12}C^{17}O$ from an analysis of infrared radiation emitted by a interstellar clouds (in the Bok globule B335). Taking into consideration the equations of dia- and paramagnetic parts for the isotropic term of the magnetic tensor of ^{17}O shielding, the value $\sigma_{v=0}(^{12}C^{17}O) = -42.3(172)$ ppm corresponding to the basic oscillating state of the molecule was calculated.

This result turned out to be rather insufficient since the chemical shielding of nuclei, which

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[17] R.E. Wasylishen, S. Mooibroek, J.B. Macdonald, J. Chem. Phys., **81**(1984) 1057.

[18] M.A. Frerking, W.D. Langer, J.Chem.Phys., **74** (1981) 6990.

are estimated based on this value, were defined with an accuracy to a dozen or so of ppm. Soon the same constant of shielding was happily determined on the basis of quantum-chemical calculation in the temperature of 300K as equal -59.34(200) ppm. The value of -62.3(15) ppm was given on the basis of MCSCF calculations for water -59.5(120) ppm[19]. Taking into consideration the difference between the so-called experimental and wholly theoretical quantity of ^{17}O shielding, the error of around ±2 ppm seems credible in the case of theoretical data.

A precise registration of the spin-rotation constant for the molecule $^{12}C^{17}O$ equals to -31.609(41)[20] kHz allowed us to determine a new and corrected experimental oxygen scale of magnetic shielding[21]. By taking into consideration the oscillation and rotation adjustments to the equilibrium value σ_e, it was possible to establish a new scale of absolute shielding for oxygen in the temperature of 300K (-62.7(6) ppm), which means the constant of shielding $\sigma_{300K}(H_2O_{liquid}) = 287.5(6)$ ppm. Our precise magnetic nuclear resonance measurements in the isolated CO molecule performed in the year 2001 allowed us to accurately measure the distance from the signal of the standard liquid H_2O sample and to slightly improve the above mentioned value: $\sigma_{300K}(H_2O_{liquid}) = 287.4(6)$ ppm (Q. 14). This last value became a secondary standard in the recalculations of all the experimental results of the shielding of oxygen nuclei in small molecules in the gaseous phase (*cf*. Table 3).

The first step in obtaining the results of the shielding for ^{17}O nuclei in the gaseous phase constituted analyses of a series of small molecules, which in room temperatures remain gases in a wide range of pressures, *i.e.*: CO_2 (carbon dioxide), N_2O (nitrous oxide), COS (carbonyl sulphide) and CO (carbon monoxide) (Q10). The results are presented in Fig. 2. In each of these cases, an increase of the concentration of the sample causes a decrease of the shielding of the nuclei examined, just as is the case in many other situations. The concentration-shielding functions are always linear. This means that $\sigma_2(T)$ and higher coefficients in Equation (1) can be neglected. We obtain $\sigma_o(T)$ from extrapolation to the zero pressure. The measurements of the second virial coefficient $\sigma_1(300K)$ prove that intermolecular interactions can effectively modify the shielding constants of oxygen nuclei in the gaseous phase. The quantity of this coefficient also depends on the spectral range of a given nucleus.

In the case of absolute values for oxygen, it is considerably greater than for ^1H and ^{13}C nuclei.

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[19] J. Vaara, J. Lounila, K. Ruud, T. Helgaker, J.Chem.Phys., **109** (1998) 8388.

[20] G. Cazzoli, L. Dore, C. Puzzarini, S. Beninati, Phys. Chem. Chem. Phys., **4** (2002) 3575.

[21] R.E. Wasylishen, D.L. Bryce, J. Chem. Phys., **117** (2002) 10061.

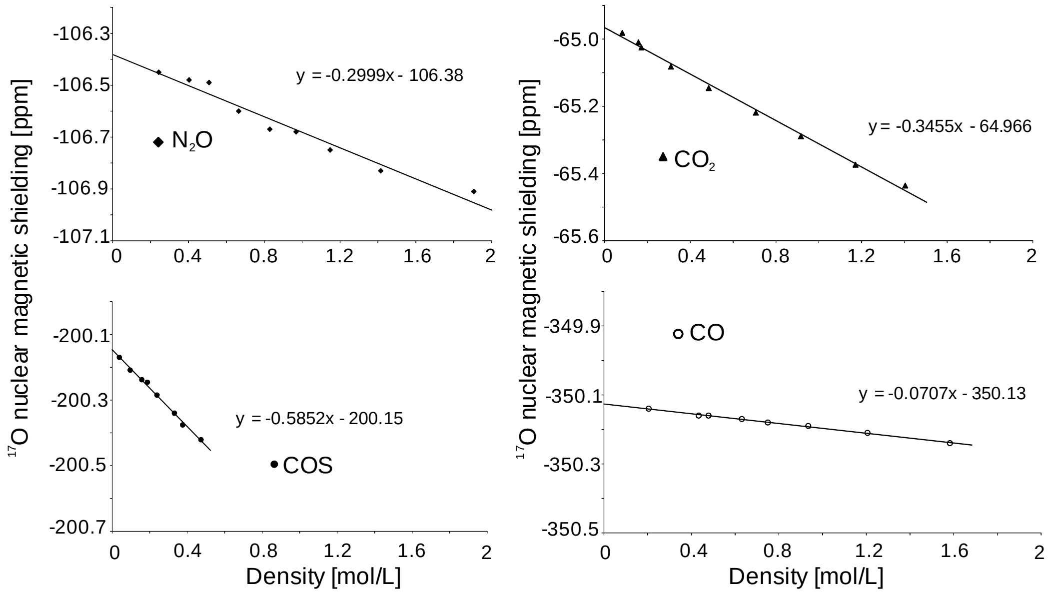

Figure 2.
Dependences of the ^{17}O shielding of in N_2O, CO_2, COS and CO molecules on the density of the medium examined.

If one is to take into account an adjustment in relation to the susceptibility of the substance σ_{1b} examined, the impact of interactions on the shielding of ^{17}O nuclei can be compared. We can see that interactions in pure CO are the weakest, and in pure COS they are the strongest (*cf.* Table 2). This does not come as a surprising fact because the molecular collisions of molecules with permanent electric dipole moments (COS- 0.715 D, N_2O- 0.166 D, CO- 0.112 D) are the most effective ones. It is evident that inductive interactions are equally important, where the values of molecular polarizability become essential. Hence, there are stronger interactions in CO_2 than these in pure CO.

Shortly afterwards, valuable results were obtained for other small molecules, *i.e.* SO_2, SO_3 (Q15) and a series of methyl ethers: $(CH_3)_2O$, CH_3OCD_3, $(CD_3)_2O$ (Q16) in spite of the fact that their vapour pressures are small in these temperatures which are close to room temperatures. This manner of the experimental conduct, where pure gases are examined under significant pressures, cannot be used in relation to oxygen compounds of a low volatility. In such cases, it is necessary to use measurements in gaseous solvents. As the concentration of the substance examined is then small, the use of compounds enriched with the ^{17}O isotope becomes a necessity. Few experimental studies have been performed before to determine NMR parameters for the molecules of alcohols in the gaseous phase[22].

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[22] J.P. Chauvel, N.S. True, Chem. Phys. **95** (1985) 435.

The observation of ^{1}H and ^{17}O resonance lines in alcohols is limited to those systems where a fast exchange of protons connected with the presence of hydrogen bonds can effectively be stopped. Conditions of this type were created in experiments with gaseous solutions of water (S.26) and methyl alcohol $CH_3{}^{17}OH$ (Q18). Fluor containing hydrocarbons CH_3F and CHF_3 were used here, ones which possess permanent dipole moments and that are capable of strong directional interactions with water molecules, even in the gaseous phase in a temperature

Table 3.

^{17}O parameters of magnetic nuclear resonance for molecules in the gaseous phase.

Molecule	Nucleus	σ_0 ppm	Solvent	$\sigma_1 - \sigma_{1b}$ ppm×ml×mol^{-1}	Ref.
Water (gaseous phase)	$H_2\underline{O}$	325.3(9)			
			Xe	-1148(40)	S.23
			Kr	-592(40)	
			CH_3F	-818(20)	
			CHF_3	-1305(40)	
Water (liquid)	$H_2\underline{O}$	287.4(6)			Q.14
Deuterium oxide (liquid)	$D_2\underline{O}$	290.2(7)			
Carbon oxide	$C\underline{O}$	-63.05(60)	CO	-119(12)	Q.10
Carbon dioxide	$C\underline{O}_2$	222.08(70)	CO_2	-432(12)	
Carbonyl sulphide	$C\underline{O}S$	86.93(70)	COS	-720(12)	
Nitrous oxide	$N_2\underline{O}$	180.64(80)	N_2O	-335(25)	
Sulphur dioxide	$S\underline{O}_2$	-231.3	SO_2	+869(50)	Q.15
	$S\underline{O}_2$(333K)	-231.4		+709(50)	
Sulphur trioxide	$S\underline{O}_3$(333K)	55.0(6)	SO_3	-948(150)	
Methyl ether	$(CH_3)_2\underline{O}$	336.06(60)	$(CH_3)_2O$	-1400(120)	Q.16
	$(CH_3)_2\underline{O}$(333K)	336.73(60)		-1575(50)	
	$(CD_3)_2\underline{O}$	338.62(60)		-1394(120)	
	$(CD_3)_2\underline{O}$(333K)	339.16(60)		-1550(50)	
Methanol	$CH_3\underline{O}H$	329.61	CH_3F	-106.5(20)	Q.18
			CHF_3	-980.1(300)	
	$CH_3\underline{O}D$	331.46	CH_3F	-152.4(30)	
			CHF_3	-1023.0(400)	

which is close to the room temperature (*e.g.* 300K).

The experimental results for the shielding of oxygen nuclei in $CH_3{}^{17}OH$ (Q18) are presented in Tab. (3). The course of concentration dependences is analogical as for the other molecules from Fig. (2). The first list of the whole group of experimental results performed in the gaseous phase in the absolute shielding scale is presented in Table 3.

One of the main features of experiments in the gaseous phase is the possibility of their direct comparison with the results of quantum calculations for individual molecules. The condition is to take into account both the shielding of nuclei in molecules for equilibrium geometry and rotation-oscillatory effects as well as temperature effects.

This type calculations were performed by Auer in the year 2009[23]. The results of the correlation of experimental and theoretical results are provided in Fig. 3. A good consistency of the results was obtained, yet the absolute term of the parameter of linear regression 5.28 ppm points to a systematic redefinition of theoretical results.

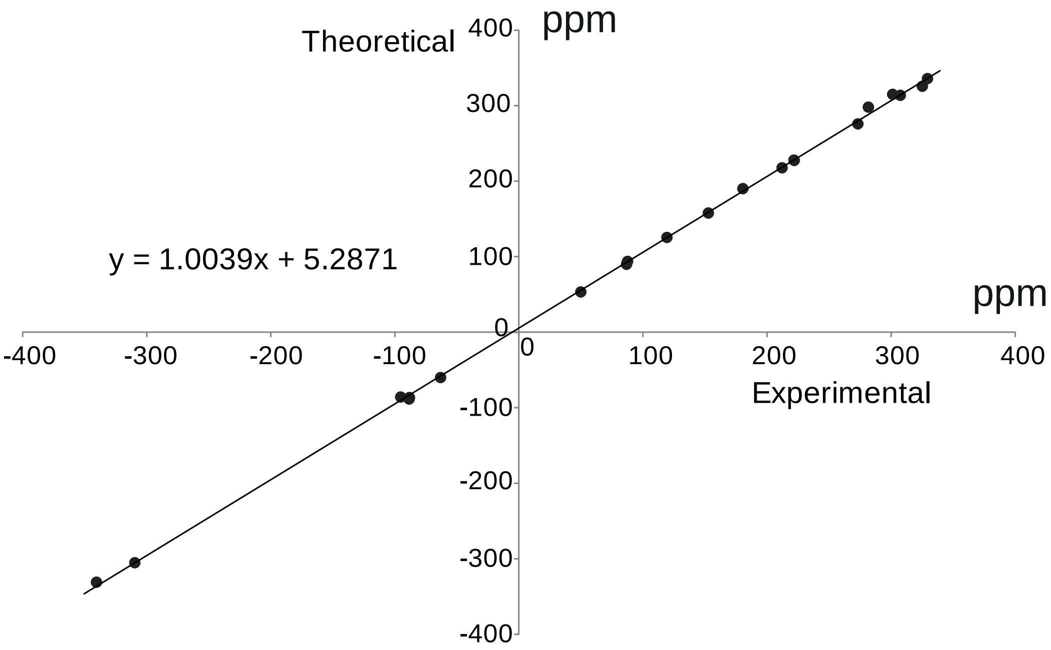

Figure 3.
${}^{17}O$ NMR shielding dependence of the experimental and theoretical values in a series of 20 simple chemical compounds for isolated molecules in the gaseous phase.

In the case of the SO_3, it was possible to measure the ${}^{17}O$ chemical shift in the liquid phase only. The spectrum of this substance sample (Q. 19) is extremely interesting. An explanation

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[23] A.A. Auer, *J. Chem. Phys.*, **131** (2009) 024116.

of the presence of as many as three resonance signals became possible only on the basis of quantum-chemical calculations. It became evident that SO_3 molecules in pure liquid tend to create six-membered trimers that remain in a dynamic balance with monomers. The participations of the individual forms change depending on the temperature.

It is worth noting that similar attempts of observations of many signals in the ^{17}O spectrum of the liquid sample SO_2 up to its freezing temperature gave no positive result.

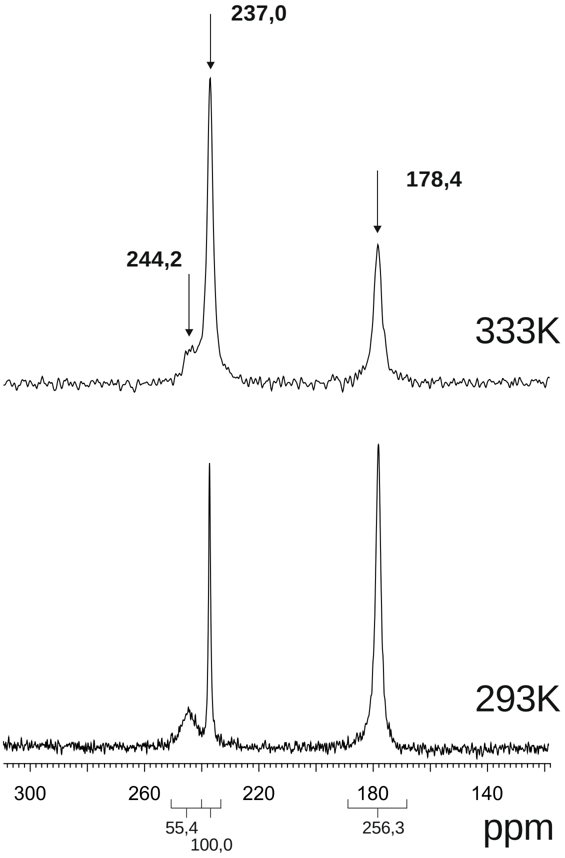

Figure 4.

^{17}O NMR spectra of liquid SO_3 at different temperatures.

Absolute shielding scales of ^{33}*S nuclei*

The original standard of the shielding of ^{33}S nuclei is an isolated molecule of carbonyl sulphide [24]. Wasylishen was first to propose the use of the value of 843(12) ppm as the shielding of ^{33}S in an isolated molecule of carbonyl sulphide (COS). This result was obtained with the use of the spin-rotation constant for COS measured in an experiment of molecular

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[24] R.E. Wasylishen, C. Connor, J.O. Friedrich, Can.J.Chem., **62** (1984) 981.

beams according to the Flygare's procedure[25] and the CHF calculations of diamagnetic shielding of a free sulphur atom. A more precise value was obtained when the diamagnetic term was calculated with the aid of the CCSD(T) method, *i.e.* σ_0= +817(2) ppm (Q. 8).

The sulphur atom in a COS molecule receives an extreme position, and the electric field gradient on the ^{33}S nucleus is quite significant (0.1877). This causes a generation of a wide signal ^{33}S NMR in the COS molecule even in a neat liquid ($\Delta\nu_{1/2}$ ~ 440Hz) and rather unfavourable registering conditions in the gaseous phase. In spite of this, the use of a modified RIDE sequence allowed the researchers to obtain good results: the ^{33}S NMR signal was observed in the range of the densities of samples from 0.499 up to 0.965 mol/ L in the temperature of 323K (Q. 13).

Correct defining of the shielding of nuclei in the COS molecule requires a determination of the so-called rotation and vibration adjustments (ZPV, zero-point vibrations) and temperature effects. The evaluations of these effects are often performed on the basis of theoretical calculations. The temperature dependences of shielding constants in molecules substituted isotopically: $^{12}C^{17}O^{32}S$, $^{13}C^{16}O^{32}S$ and $^{12}C^{16}O^{33}S$ were calculated with the GIAO method and several correlation wave functions (Q. 8). In the range of 170 – 420 K temperatures, the input from ZPV effects is considerably more significant as compared to the part from oscillatory excitations. Various terms from vibrations that stretch bonds and deform angles in the molecule were discussed in detail. In the range of the temperatures examined (278 – 373K), shielding in COS changes by *ca*. -0.25, -2.75 and -3.1 ppm, respectively for ^{13}C, ^{17}O and ^{33}S nuclei. In the study discussed, equilibrium and rotation-vibrationally averaged quadrupole constant couplings: ^{17}O and ^{33}S were also calculated. They were $\chi(^{17}O) = -1.084$ MHz and $\chi(^{33}S) = -31.46$ MHz. Both of these values demonstrate good compliance with similar theoretical and experimental data.

While extending the experiments of gaseous objects, some properties of the COS molecule were also examined in condensed phases (Q.12). The COS crystallizes in a specific trigonal position of the spatial group with 3 molecules in a spatial unit. It is evident that there are 6 symmetrically oriented COS molecules in the first coordinating sphere, which is distant by 4.063 Å from the first central molecule, 6 in the second one and 2 in the third molecular sphere. Such clusters may serve as a good model to examine the impact of intermolecular interactions on the shielding of ^{13}C, ^{17}O and ^{33}S nuclei.

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[25] W.H. Flygare, Chem.Rev., **74** (1974) 653.

Calculations based on CHF approximation do not promise exceptionally accurate results of the constants of nuclei shielding, yet the results obtained agree well with the best experimental data and *ab initio* calculations for ^{13}C nuclei. Approximate results for ^{17}O and ^{33}S nuclei show a tendency with which their change of shielding occurs in the course of carbonyl sulphide condensation. The data presented showed a strong dependence of the shielding of ^{33}S from intermolecular interactions; these may reach even ~ 30 ppm.

Out of the whole variety of chemical compounds that include sulphur, hexafluoride SF_6 possesses a unique electronic structure. This high symmetric octahedral structure (O_h) is characterized by an equilibrium length of the S-F bond equal to r_e = 1.5560(1) Å[26]. A chemical inertness and a high stability of this compound in relation to the majority of materials up to the temperature of ca. ~ 200 °C is a consequence of its electronic structure. From the perspective of NMR spectroscopy, the high symmetry of the molecule reduces the electric field gradient on the sulphur nucleus to zero, and the resonance line ^{33}S achieves the full width at half maximum ~1Hz. This permits precise observations of the resonance line in SF_6 both in the liquid and in the gaseous phases.

We used this fact in the observations of the pressure dependence of the ^{33}S nucleus shielding in the gaseous SF_6 (Q.11). These were the first in the world pressure measurements of sulphur nuclei in the gaseous phase, moreover carried out with a natural content of the isotope examined in samples. The shielding of sulphur was registered with a great accuracy (σ_0=379.90 ppm). This value can be compared to the latest calculations with non-relativistic CC (σ_0=392.6 ppm) methods and relativistic methods DFT (σ_0=350.0 ppm)[27]. We can observe a divergence of around 10-30 ppm in each of these cases, which confirms the rule that the quantum calculations of sulphur nuclei are considerably more demanding than those concerning oxygen. Lack of calculations of rotation and vibration terms constitutes an additional complication in this comparison.

In the subsequent years, I undertook experiments with sulphur oxides. Sulphur can form various oxides: SO, SO_2, SO_3, SO_4, S_2O, S_2O_2 and a whole series of cyclic oxides: S_5O, S_6O, S_7O, S_7O_2 and S_8O. Only two of them are thermodynamically stable in normal conditions, namely SO_2 and SO_3. Only in the case of SO_2, the measurements of ^{33}S shielding were possible in the function of concentration (Q.15) and the determination of the value $\sigma_0(^{33}S)$ = -152.5(20) ppm in the temperature of 333K was completed.

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[26] V. Boudon, J.L. Doménech, D. Bermejo, H.Willner, J. Mol. Spectrosc., **228** (2004) 392.

[27] K. Ruud, T.B. Demissie, M. Jaszuński, J. Chem. Phys., **140** (2014) 194308.

Additionally, I performed the measurements of a number of the samples of liquid substances regarding the standard frequency of solution $(NH_4)_2$ SO_4 in D_2O, and I determined their absolute constants of shielding: $\sigma(CO\underline{S})$=798 ppm $\sigma(H_2\underline{S})$=707.1 ppm, $\sigma(C\underline{S}_2)$=536.1 ppm, $\sigma(\underline{S}F_6)$=380.7 ppm, $\sigma(\underline{S}O_2)$=-178.5 ppm, $\sigma(\underline{S}O_3)$=270.4 ppm. Nevertheless, these results cannot fully replace the results for the isolated molecules obtained in the gaseous phase.

Scalar spin-spin coupling constants involving of ^{17}O and ^{33}S nuclei

An observation of the scalar constants of the spin-spin coupling in the spectrums of ^{17}O and ^{33}S NMR is clearly made difficult as a result of a significant broadening of resonance lines. Hence, there is a small number of this type data. In order to register and determine the coupling constants, an observation can be selected of any coupled nucleus. Additionally, for the registration sensitivity factor, which can be corrected by isotope enriching, quadrupole decoupling must be taken into account. This takes place if the relaxation of ^{17}O or ^{33}S is too fast. To have an opportunity to observe the coupling constants $^1J(^{17}O,^1H)$ in the conditions of a proton exchange, the speed of the process needs to be minimized. In solutions, this is achieved through a selection of the appropriate pH and temperature or an addition of electrolytes. Unfortunately, even in optimal cases, the quadrupole broadening of ^{17}O may exceed the values of coupling constants. Such constants can sometimes be extracted from an analysis of the shape of resonance bandwidth.

The coupling constants of J (also in the form of the reduced constant K) that have been measured so far from investigations in liquids and gaseous substances for simple molecules are collected in Table 4. The results come from an extrapolation in the gaseous phase (S.23, Q.18), single observations in a gas or a liquid performed by the author or information from the literature [29]. The constants observed involve couplings with one bond ^{17}O-^{1}H, ^{14}N-^{17}O, ^{15}N-^{17}O, ^{13}C-^{17}O and ^{33}S-^{19}F. We can see that the values for the liquid samples clearly differ from these registered in gases, especially in the case of water and alcohols. It needs to be remembered that the reduced constants K are a better measure of the effectiveness of interactions between nuclei than the constants J. The knowledge of the coupling constants with the participation of nucleus ^{33}S is considerably smaller than of these with the participation of oxygen. It was possible to obtain experimentally only several certain values of these constants.

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[28] W.Makulski, author's own information

[29] J.P. Gerothanasis, Prog. NMR Spectrosc., **57** (2010) 1.

Table 4.
Spin-spin coupling constants (J and K)from measurements in gaseous and liquid phases.

Substance	Measuring conditions	$^nJ(^{17}O,X)$ Hz	$^nK(^{17}O,X)$ $\times10^{19}J^{-1}T^{-1}$	Ref.
$H\underline{OH}$	liquid-steam balance, 488K	-79		29
	Gaseous phase, extrapolation	-78.22	48.02	
	0.1% in cyclohexane-d_{12},293K	-78.7		
	0.5mol% in nitromethane-d_3	-80.6		
	1.6mol% in nitromethane-d_3,300K	-81.07		
	343K	-80.36		
	liquid	-89.8	55.1	
$CH_3\underline{OH}$	gaseous phase, extrapolation	-79.45	48.77	Q.18
	liquid	-85.5	52.5	
$C_2H_5\underline{OH}$	gaseous phase, extrapolation	-78.48	48.18	28
	liquid	-83.6	51.3	
$(CH_3)_2\underline{CO}$	liquid	22	54	28
$^{13}\underline{CO}$	in chloroform-d	16.4	40	29
	in cyclohexane	16.44		
	gaseous phase, 35atm	11.95		28
$O^{13}\underline{CO}$	in chloroform-d	16.1	39.3	
$^{13}CH_3{}^{13}\underline{C}H\underline{O}$	liquid	28.9	70.5	28
$^{15}N^{15}\underline{NO}$	gaseous phase, 50atm.	51.47	311.6	29
$^{14}N^{14}\underline{NO}$	supercritical phase	37	314	29
	in acetonitrile-d_3	35.5		
$^{33}\underline{SF}_6$	gaseous phase, extrapolation	-250.95	288.8	Q.11
	liquid	-251.6		
	supercritical phase	-251.4		
	in acetonitrile	-253.38		
	nematic phase ZLI 3125	-253.9[15]		

* $J_{KL} = h\frac{\gamma_K}{2\pi}\cdot\frac{\gamma_L}{2\pi}\cdot K_{KL}$

The constant of coupling $^1J(^{33}S,^{19}F)$ in the molecule of sulphur hexafluoride SF_6 is the only one that is well defined in various experimental conditions. Owing to the favourable attributes of this molecule, ones that have been previously described, we know $^1J(^{33}S,^{19}F)$ both in the pure liquid, different solutions, the supercritical state and in the gas (Q.11), as well as in nematic phases[15]. The value of the constant changes little, no more than by 2%. In consequence, this allows one to conclude that the structure of the molecule SF_6, in the length of bond S-F in particular, is independent from the state of aggregation in which it occurs. Quantum calculations with the DFT method do not yield any good results and, in spite of the application of a number of different functionals, they are overestimated by *ca*. 20%[30].

3.3.4 Other effects observed in NMR spectra

Change of the nucleus shielding with transition from gas to liquid

The so-called difference of shielding $\Delta\sigma_{gl}$ with a transition from a gas to a liquid or a fluid solution is easy to determine by comparing the appropriate values in a gas and in a pure liquid or in a solution. The numerical value of this parameter is defined as:

$$\Delta\sigma_{gl} = \delta_{liq} - \delta_{gas} - (4\pi/3)\chi_v \qquad (7)$$

where χ_v is the volume susceptibility of a liquid substance. If possible, it is best to use δ_{gas} in the above formula as a quantity extrapolated to zero pressure. Then, this parameter is a good measure of intermolecular interactions in the liquid phase. Parameters of this type can be verified in quantum and chemical calculations, especially if they concern all the nuclei in the molecule examined. Table 5 presents a series of the results for the shielding difference with a change of the state of aggregation ($\Delta\sigma_{GL}$) of small molecules that include an ^{17}O atom.

The parameter calculated as the shielding difference of the nucleus determined in a gas and a liquid illustrates the impact of intermolecular interactions with a transition from a gas to a pure liquid, and so it allows one to determine how strong an association in a liquid is and with the interaction of which of nuclei it is connected. In the case of oxygen chemical compounds, which are usually strongly polar (as alcohols or acids), these effects are significant, *e.g.*: -38.22 ppm for water, +24.3 ppm for acetaldehyde, *etc*. What is more, the effects of intermolecular interaction may change shielding in the opposite directions. This parameter constitutes a very strict criterion of the correctness of the theoretical calculations performed because it requires not only the performance of complicated calculations for the shielding in the isolated molecule but also taking into consideration intermolecular interactions in the liquid phase. The latter ones are definitely more difficult, especially with reference to

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[30] W. Deng, J.R. Cheeseman, M.J. Frisch, J.Chem. Theory Comput., **4** (2006) 1028.

liquids associated with strong electrostatic or directional interactions, such as typical hydrogen bonds.

Table 5.
Experimental gas-to-liquid shifts $\Delta\sigma_{GL}(^{17}O)$ in the series of small compounds at 300K (in ppm).

Molecule/nucleus	$\Delta\sigma_{GL}$	Molecule/nucleus	$\Delta\sigma_{GL}$
Water, $H_2\underline{O}$	-36.2[31] -38.22	Trimethylene oxide, $(CH_2)_3\underline{O}$	0.9
Fluorine monoxide, $F_2\underline{O}$	-18[17]	Trifluoroacetic anhydride, $(CF_3C\underline{O})_2CO$	3.3
Methyl acetate, $CH_3CO\underline{O}CH_3$	-8.6	Methyl acetate, $CH_3C(\underline{O})OCH_3$	5.4
Methyl formate, $HCO\underline{O}CH_3$	-8.6	Methyl trifluoroacetate, $CF_3C(\underline{O})OCH_3$	6.3
Methanol, $CH_3\underline{O}H$	-8.3	Vinyl formate, $HC(\underline{O})OC_2H_5$	8.0
Ethanol, $C_2H_5\underline{O}H$	-8.7	Ethyl formate, $HC(\underline{O})OC_2H_5$	8.1
Methyl ether, $(CH_3)_2\underline{O}$	-5.19	Methyl formate, $HC(\underline{O})OCH_3$	9.2
(333K)	-4.86		
$(CD_3)_2\underline{O}$	-4.96	Acetyl chloride, $CH_3C\underline{O}Cl$	11.0
(333K)	-4.67	Propionaldehyde, $C_2H_5CH\underline{O}$	16.1
Ethyl ether, $(C_2H_5)_2\underline{O}$	-2.5	Acetone, $(CH_3)_2C\underline{O}$	19.7
Furan, $C_4H_4\underline{O}$	-2.4	$(CD_3)_2C\underline{O}$	20.1
1,3-Dichlorotetrafluoroacetone, $(CF_2Cl)_2C\underline{O}$	2.1	Acetaldehyde, $CH_3CH\underline{O}$	24.3

Based on the results presented in the table above, it is evident that oxygen nuclei in alcohols and, to a smaller extent, in ethers undergo deshielding, while ^{17}O nuclei in carbonyl groups substitutes undergo a greater screening with electrons during a transition from a gaseous phase to a pure liquid. However, it is the value $\Delta\sigma_{GL}$ for the water molecule that attracted the most attention both in theory and in practice. The new data obtained in the strictly determined temperature of 300K from a liquid and a gas (Q. 10) has a significant advantage over the values which have been widely quoted until now, and whose result was obtained in difficult measuring conditions in a high temperature of 110 °C and a pressure of 1-2 atm in a diphase system[31]. Both signals ^{17}O are very wide (~3ppm) in these conditions, which drastically increases the denotation error. The strong negative effect means an shielding increase in the molecule placed in the gas as compared to a molecule associated in a liquid. A similar yet a weaker effect occurs in alcohols, and it is connected with the presence of hydrogen bonds.

In the case of the changes of the state of aggregation of the substances examined, there are few observations of changes to the shielding of nuclei ^{33}S. The case of hexafluoride SF_6 dissolved in a number of organic and non-organic solvents (Q. 9) was more widely examined. The influence of the solvent proves to be slight in this case. The parameters of shielding presented in Table 5 constitute a measure of the association processes of pure liquids, and they constitute a good point of departure for the simulation with various quantum chemistry methods (methods of clusters, continuous medium, molecular dynamics) of the structures of liquid solvents. This type simulations are currently very rare and they are known for selected objects only[32].

Isotopic effects in the chemical shift and in spin-spin coupling constants

Isotopic effects, which are so popular in various branches of atomic and molecular spectroscopy, can be divided into intermolecular (solvent) and intramolecular one. The latter ones are considerably more important, and they are more frequently examined in NMR. When there is an isotopic substitution in chemical molecule, each neighbouring nucleus undergoes a slight modification of its spectral parameters. If isotopic enrichment is lower than 100%, resonance lines are observed both in the substituted and non-substituted chemical compound in proportions which are related to their statistical quantitative distribution. The anharmonic oscillations and inertial distortions of the molecule make the lengths of bonds and angles between bonds dependent from the masses of those atoms that form the molecule. The accompanying changes to the shielding of nuclei are the cause of the effects observed of isotopic NMR parameters. Isotopic phenomena, in spite of their small values, are common in the majority of spectral techniques.

Isotopic effects in a chemical shift can be defined based on the scale of the chemical shift (δ) or of shielding constants (σ):

$$^{n}\Delta X(^{m/M}Y) = \delta_x(^{M}Y) - \delta_x(^{m}Y) = \sigma_x(^{m}Y) - \sigma_x(^{M}Y) \qquad (8)$$

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[31] A.E. Florin, M. Alei, J.Chem.Phys., **47** (1967) 4268.

[32] M. Cossi, O. Crescenzi, J.Chem.Phys., **118** (2003) 8863.

where n means the number of bonds between nuclei and, m and M of the mass of isotopomers. Isotopic effects defined in this way were in the past widely examined both from the perspective of practice and theory. A lot of data of this type was collected for nuclei with ½ spins. There is considerably less knowledge about these effects in resonance ^{17}O and ^{33}S. As it has already been mentioned on several occasions, effective relaxations of both nuclei under discussion do not allow one in a majority of cases to precisely observe resonance lines and, what follows from that, subtle isotopic effects. Substitutions in the type of deuterium/proton in various groups of substitutes are an exception. Various molecules of dimethyl ethers: $(CH_3)_2O$, CH_3OCD_3 and $(CD_3)_2O$ can serve as an example. The calculated values of isotopic effects with a triple substitution are as follows: $^{2}\Delta^{17}O(^{2/1}H)$ =-1.30(2) ppm and -1.29(2) ppm, and they are additive within the limits of the measuring error (Q.16). Therefore, a substitution with a single deuterium atom provides *ca*. 0.43 ppm of an increase of the ^{17}O shielding as nucleus observed.

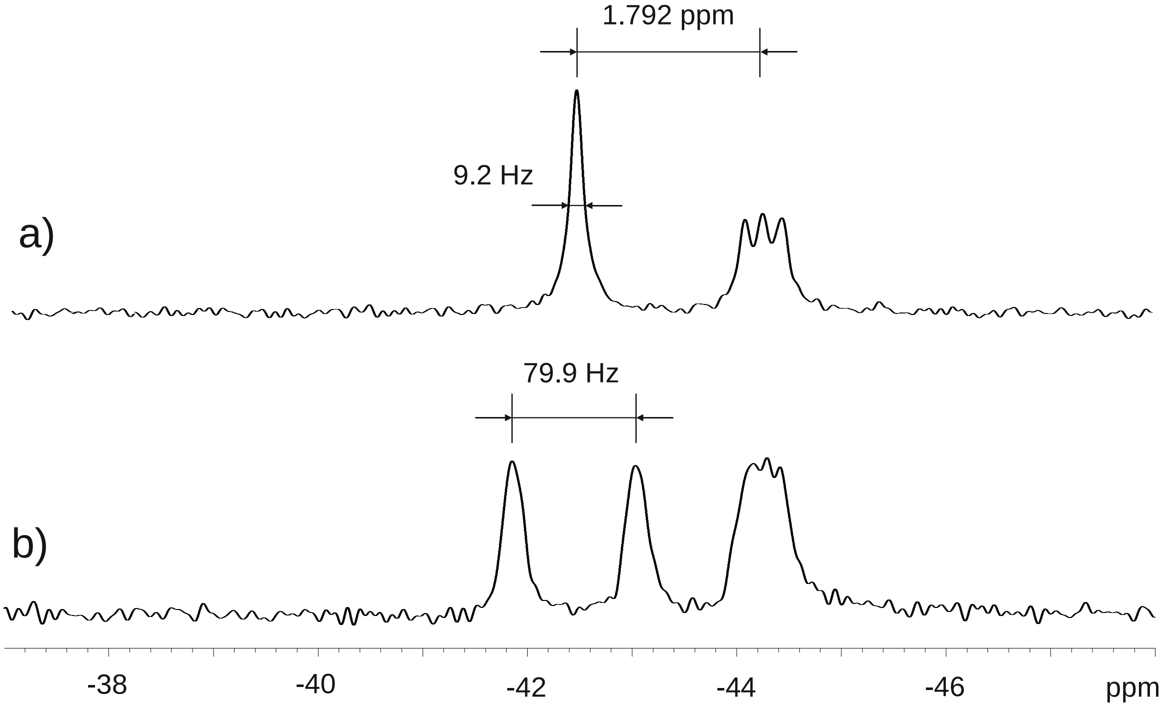

Figure 5.
Isotope effect observed in the spectrum of ^{17}O NMR 67.861 MHz connected with the substitution of H/D in the hydroxyl group of methanol in gaseous phase: a) secondary isotope effect, b) visible splitted signal of nucleus ^{17}O coupled with hydroxyl proton.

The methanol molecule constitutes a more spectacular example of the measurement of isotropic effects (Q.18). In the case of the isotopic substitution of H/D in the hydroxyl group of methanol, we observe $^{1}\Delta^{17}O(^{2/1}HO)$= -1.60 ppm in the liquid, whereas in the gaseous phase there is even a more clear effect: $^{1}\Delta^{17}O(^{2/1}HO)$= -1.85 ppm. The study under discussion provides many precise results of isotopic effects that are measured in ^{1}H, ^{13}C and ^{17}O resonances; it was quickly noticed and it became an inspiration to advanced calculations of the shielding of individual nuclei taking into consideration rotational and vibration effects and the use of large computational databases[33]. The consistence of the results is impressive, and it is within the hundredths of ppm. Both studies referred to above constitute are a good example of the spectroscopic theory and practice being complementary to one another in the area of nuclear magnetic resonance.

An interesting issue is the observation of the presence of various isotopes of oxygen (^{16}O,^{17}O and ^{18}O) and sulphur (^{32}S,^{33}S,^{34}S and ^{36}S) by nuclei of other types that are present in molecules, *e.g.* ^{1}H or ^{19}F, and the so-called secondary isotope effects of NMR. In particular, fluorine nuclei are particularly predestined for the measurements of subtle differences in frequencies owing to their wide spectrum range (1000 ppm), a high sensitivity and a half value of the nuclear spin. Exceptionally spectacular measurements of this type were successfully performed for molecule SF_6 in a liquid phase, where a very weak signal ^{19}F NMR was observed from isotopomer $^{36}SF_6$ of a very rare natural abundance: 0.02% (R.27). All the values of shielding systematically grow starting from $^{32}SF_6$ going through $^{33}SF_6$, $^{34}SF_6$ up to $^{36}SF_6$. The results for the gas are completely analogical, which serves to prove that the condensation process has little influence on the isotope effects measured. These results were confirmed for the issue discussed previously, namely the influence of the thermotropic medium LC on the structure of the molecule in question.

Nuclear magnetic moments from NMR spectra

Elementary particles are characterized through providing their basic physical properties, *i.e.* the mass (m), the electric charge (q) and the magnetic moment (μ). The same quantities characterize such molecules as the proton and neutron and atomic nuclei. The magnetic moment of nucleus X is expressed in the following form:

$$\mu_X = g_X \mu_N I_X/\hbar \qquad (9)$$

where I_X is the so-called spin, g_X is the nuclear factor g of nucleus X and constant $\mu_N = e\hbar/2m_p$ (where m_p is the proton mass) known as the nuclear magneton $\mu_N = 5.05078353(13)\times10^{-27}$ J/T. In an external magnetic field that is oriented along axis z, a nucleus with spin I may receive $2I+1$ orientations from $I_Z = m_I\hbar$ where $-I \le m_I \le I$.

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[33] A.A. Auer, Chem.Phys.Lett., **467** (2009) 230.

In an NMR experiment, only μ_X can be determined, the maximum projection of the magnetic moment on the axis of the external field connected with I_X:

$$\mu_X = h\,\gamma_X\, I_X = \mu_N\, g_X\, I_X \tag{10}$$

where γ_X and g_X is the magnetogyric ratio and the nuclear factor g of the nucleus itself. The resonance frequency ν_X of nucleus X in an isotropic sample is:

$$h\,\nu_X = \Delta\,\mu_X^z\,(1-\sigma_X)\,B_z \tag{11}$$

where B_z is the external magnetic field, σ_X is the shielding constant. In the NMR experiment, transitions are observed between spin states, which differ by unit ($\Delta I_X^z = 1$), and the frequency is proportional to $\Delta\mu^z{}_X = \mu_X\,\Delta I_X^z / I_X$. The absolute shielding constant (σ_X) determines the shielding of the nucleus in the molecule in relation to the nucleus itself. Absolute constant shielding may come from experimental investigations or from increasingly accurate calculations of the *ab initio* type. Equation (11) can be used in an analysis of the relation of the NMR frequency for a pair of different nuclei (Q.17). We used two forms of equations[34], the first one:

$$\Delta\mu_Y^z = \frac{\nu_X}{\nu_Y}\cdot\frac{(1-\sigma_X)}{(1-\sigma_Y)}\cdot\Delta\mu_X^z \tag{12}$$

which makes it possible to calculate the magnetic moment μ_Y when all the other quantities are known. Or, we may use the other equation in order to verify the conformity of the new nuclear values of the moments and the shielding of magnetic nuclei in the molecules, and a different form of Equation (12) can be used:

$$\sigma_X = 1-\frac{\nu_X}{\nu_Y}\cdot\frac{\mu_X}{\mu_Y}\cdot(1-\sigma_Y) \tag{13}$$

We utilize Formulae (12) and (13) for each pair of nuclei in the molecule under investigation. Calculations (Q.17) take into account the relations of the frequency and chemical shifts that were measured in this study from the spectra of appropriate gases. Next, the appropriate shielding constants were calculated. The magnetic moments of nuclei ^{17}O and ^{33}S were determined with a high accuracy in this way. Molecules H_2O, D_2O and CS_2, SF_6 were selected for the examinations. The new values of magnetic moments of the nuclei under inspection are provided in Table 1.

Equation (13) can be used in order to calculate the shielding of NMR signals directly in the

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[34] K. Jackowski, M. Jaszuński, Concepts Magn. Reson.A, **30** (2007) 246.

spectrum that is being recorded. It is enough to accept the signal ^{2}H(D) of the solvent as the base nucleus, which is used to stabilize the value of the field in the "lock" system of the NMR spectrometer. Then, the resonance frequency ^{2}H(D) can be treated as a secondary reference[35]. The formulae that were obtained in this manner for the scaling of oxygen and sulphurous spectrums are presented below:

$$\sigma_O = 1 - 1.1320528(1 - \sigma_D^*) \tag{14}$$

$$\sigma_S = 1 - 1.9994642(1 - \sigma_D^*) \tag{15}$$

The shielding of most of deuterated solvents were precisely measured, and they are generally available[35]. However, the use of the above mentioned relations does not solve the problem of the magnetic susceptibility of the sample, and these can be strictly used in the case of spherical test tubes.

3.3.5 Conclusions and prospects

It is difficult to find in the periodic table nuclei that are so troublesome in NMR measurements as oxygen-17 and sulphur-33, and that are at the same time so important from the point of view of the present-day chemistry. This is due to their rare natural abundance (0.038 and 0.76%) as well as the significant electric values of quadrupole moments (-0.026 and -0.064 barn). Before I had undertaken research in this area, our knowledge of the role of NMR spectra ^{17}O and ^{33}S in an interpretation of chemical problems was limited to qualitative conclusions and it was only single measurements that were performed in the gaseous phase. It was merely 15 years ago that the first systematic measurements were performed of the resonance of these nuclei in the gaseous phase. Most of these were initiated and carry out in the Laboratory of NMR Spectroscopy in the Faculty of Chemistry at University of Warsaw. The diagrams of the dependences of chemical shifts (δ) and magnetic screening of nuclei ^{17}O and ^{33}S in the absolute scale (σ) for molecules in the gaseous phase are presented in Figures 6 and 7. Only those substances are taken into account in the diagram results for which were obtained for isolated molecules. We can observe that resonance ^{17}O covers a substantially greater group of chemical compounds than resonance ^{33}S. This involves some consequences, hence the ^{17}O scale is much better documented both in experimental and theoretical aspects.

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[35] K. Jackowski, M. Jaszuński, M. Wilczek, J.Phys.Chem.A, **114** (2010) 2471.

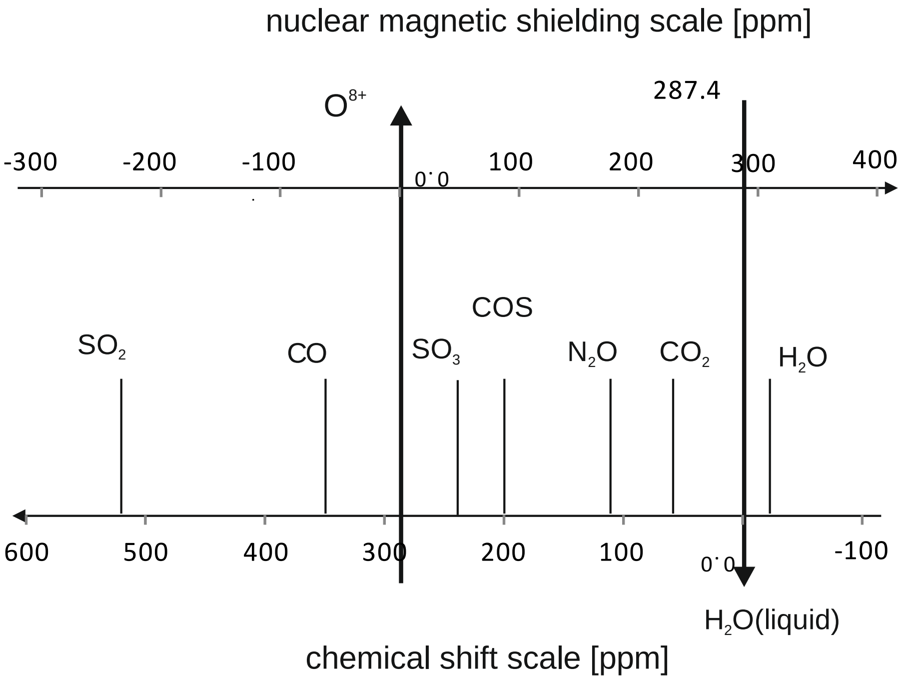

Figure 6.
^{17}O NMR chemical shifts and shielding of a number of simple molecules in the gaseous phase in relation to the signal of liquid H_2O.

It is worth to note that the spectral range of nuclei ^{17}O is significantly broader than the one provided in the figure above. The most strongly shielded nuclei include these in the ozone molecule O_3 (1598, 1032 ppm), and those that are exposed the most include the oxygen nucleus in F_2O (-493.6 ppm). All in all, this gives an impressive spectral range of over 2000 ppm. It seems that the scale of absolute shielding for this nucleus is known with an error being smaller than 5 ppm. There is constant interest in the final determination of this scale. Even while this review was being prepared, a study by Komorovsky[36] came out, who performed revised calculations of screening based on a new value of the rotational constant that is observed in the fine structure of microwave spectrums for the water molecule $H_2{}^{17}O$[37]. The shielding value presented is substantially different from those previously accepted (325.7 ppm, which gives -60.6 ppm for CO), and it requires further critical verification. For this reason, I have planned and partly realized works that consisted in the use of atoms ^3He in a mixture with $C^{17}O$ for a verification of the shielding of nuclei ^{17}O in accordance with the analytical procedure presented above.

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[36] S. Komorovsky, M. Repisky, E. Malkin, K. Ruud, J. Gauss, J.Chem.Phys., **142** (2015) 091102.
[37] C. Puzzarini, G. Cazzoli, M. Harding, J. Vázquez, J. Gauss, J.Chem.Phys., **131** (2009) 234304.

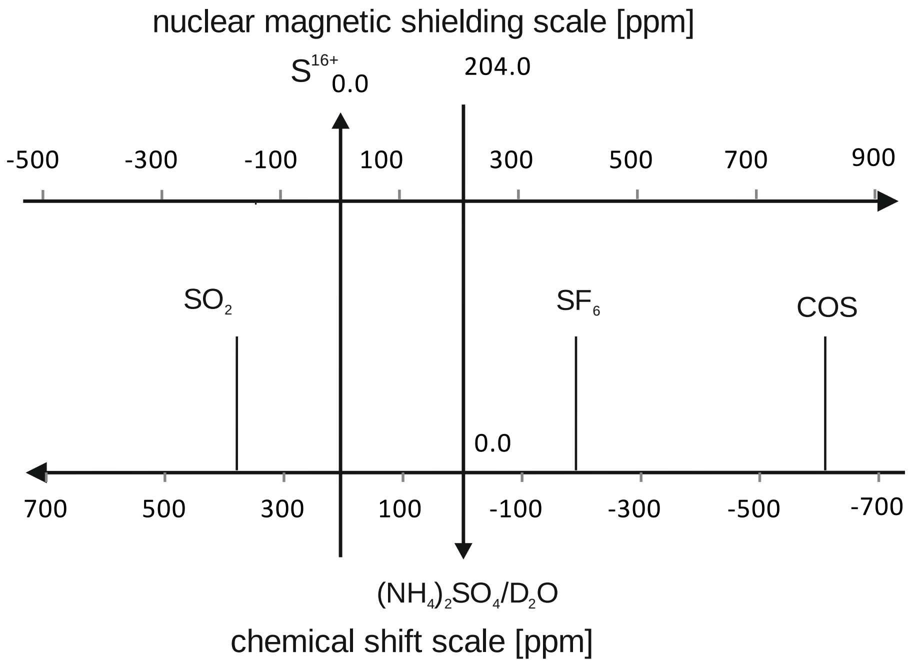

Figure 7.
^{33}S NMR chemical shifts and shielding of a number of simple molecules in the gaseous phase in relation to the signal $(NH_4)_2SO_4$ in liquid D_2O.

The scale of the absolute screening of nuclei ^{33}S has been empirically investigated into to a much smaller extent in the gaseous phase. An error in its determination may reach a dozen or so ppm or more. It seems that a key step in the determination of the absolute shielding scale could be experiments with the use of hydrogen sulphide (H_2S), all the more that advanced calculations for this molecule have already been completed[36]. It is particularly important to extend investigations related to the resonance of ^{33}S in the gaseous phase. It seems to be possible in the case of molecules CS_2 and H_2S on condition that they are enhanced with the nuclei of sulphur-33.

At present, our knowledge in the scientific field of the spectroscopy of ^{17}O and ^{33}S NMR is much broader and deeper than ever before. There is a need for an extension of the set of the compounds under examination to include such an important molecule as O_3 (ozone), whose shielding being record large in both positions, has been measured only in low temperatures and a solid state. It is certainly worth to return to the measurements of the coupling constant in the F_2O molecule, which has been determined with an exceptionally high experimental error. Both gases mentioned here are considered by theoreticians as being very problematic for quantum calculations.

The development of the methodology of work with gaseous mixtures for binary and ternary systems in the application for NMR measurements was of a key importance in the development of the research topic discussed in the present outline. It covers both vacuum apparatus and the preparation of ampoules from borosilicate glass that are safe to operate in laboratory conditions. I used this methodology in the measurements of the resonance of ^{17}O and ^{33}S nuclei. The further development of experimental NMR measuring techniques will consequently pace up the development of quantum-mechanical calculations of NMR parameters including relativistic ones (the majority of theoretical results referred to herein are related to calculations in non-relativistic approximation). There are broad prospects for further research and these are connected with a modernization of NMR measuring techniques.

I consider the determination of the magnetic moments of nuclei ^{17}O and ^{33}S with the measurement uncertainty of 0.01 % to be the most important achievement of my research work. Results of this type are one of the most accurately determined physicochemical values. The results collected with the aid of NMR for many other nuclei, too, can be found under the following address: http://ww2.icho.edu.pl/ZXXII/node1.html.

4. Rewards, internships in foreign and national academic centers, grants, courses

I have received the following awards:

- Awards of the Dean of the Chemistry Faculty in the years 1982, 1984, 1987, 1988 and 1991 in recognition for personal commitment and distinguishing treatment of duties,

- Warsaw University Vice-Chancellor Scientific scholarships for the leading achievements in the research work in the years 2003, 2005 and 2007,

- Jubilee Awards of the Warsaw University Vice-Chancellor on the occasion of the 20th, 25th, 30th and 35th years of professional activity,

- scientific grant of the II grade for "study on the method of measurements of NMR shielding constants as a gas density functions" awarded by the Chemistry Faculty Council in 2012.

- on 11.06.2014 I was awarded the Gold Medal for the Long-standing Duty (I stage).

After the completion of my Ph.D. studies I have carried out my post-doc research on Natural Sciences Faculty of Quebec University/Canada in photochemistry lab supervised by Prof. Guy J. Collin, 06.09.1985 – 06.09.1986 (Appendix 7.).

I have participated in the following trainings:

- Course in Application Laboratory of Varian-Co. in Darmstadt-Germany, 14-23 March 1994,

- NMR Course of Interacademy NMR Laboratory in the Chemical Department of Technical University in Gdańsk-Poland, 19-21 June 1996.

5. Participation in the research projects

Subjects realized at the Warsaw University Faculty of Chemistry with my participation:

1. KBN 2 P303 007 07 Grant
Investigations on the influence intermolecular interactions on ^{1}H, ^{13}C *and* ^{19}F *nuclear magnetic shielding in gases, liquids and solid states by high resolution NMR measurements and quantum-chemistry ab initio calculations*
(realized in the years1994 - 1997, supervisor: Prof. K.Jackowski);

2. KBN 2 T09A 008 16 Grant
Analysis of intermolecular effects on chemical shifts and spin-spin coupling constants of multinuclear magnetic resonance
(realized in the years1999 - 2001, supervisor: Prof. K.Jackowski);

3. KBN 4 T09A 035 23 Grant
Investigations of influence intermolecular interactions and temperature on nuclear magnetic shielding and spin-spin couplings NMR in the gas phase

(realized in the years 2002 -2005, supervisor: Prof. K.Jackowski);

4. Research grant for NESTEC LTD (Suisse)
Storage test study by ^{33}S NMR technique on coffee aroma distillate model
(realized 2005 -2006, supervisor: Prof. K.Jackowski);

5. MN i SW N N204 244134 Grant
Magnetic shielding of ^{3}He and of other nuclei in gaseous solutions: experimental investigations on a scale of NMR spectroscopy and modeling by theoretical and quantum statistical physics
(realized 2008 - 2011, supervisor: Prof. K. Jackowski)

6. Grant NCN: DEC-2011/01/B/ST4/06588, GR-4002
Universal standardization of NMR spectra on the basis of direct measurements and quantum-chemical computations of nuclear magnetic shielding in molecules
(realized 2011 - 2014, supervisor: Prof. K. Jackowski);

7. BST-132616/2008
Investigations of intermolecular interactions by multinuclear NMR spectroscopy and ab initio calculations
(supervisor: Prof. K. Jackowski);

8. 120-501/68/BW-1522/21/2001
NMR of heavy metals as investigation tool of substrate-acceptor interactions
(carried out as an individual project);

9. 120-501/68/BW-1562/21/2002
Supercritical phase C_2F_6 as a new medium in the investigation of NMR spectroscopic parameters
(carried out as an individual project);

10. 120-501/68-BW-1681/9/05
Isotope effects of heavy atoms in NMR spectra
(realized in 2002 - 5, as an individual project).

6. Didactic and organization activity

1976 - 1981 Laboratory of Radiochemistry and Radiation Chemistry.

1982 - 1984 Laboratory of Analytical and Inorganic Chemistry. Chemistry laboratory in the scope of electronic and vibrational spectra.

1996 - 1999 Laboratory of Physical Chemistry. Chemistry lab in the area of chemical kinetics, UV/VIS spectroscopy and physical chemistry.

1999 - 2015 Laboratory of Analytical and Inorganic Chemistry. Laboratories in the area of complex compounds composition, investigations of the element isotope abundances, quantitative analyses by NMR method.

Laboratory of Analytical and Inorganic Chemistry for Biology Majors. Organization work.

Instrumental Analysis for Macrofaculty: Enginering of Nanostructure and Energetics and Nuclear Chemistry. Chemistry laboratory in the area of isotope exchange measured by NMR spectroscopy.

2008 - 2009 Participation in the Individual Laboratories on: *NMR spin-spin couplings in small molecules from gas phase measurements*.

Supervisor’s care of three M.Sc. theses:

- Marcin Wilczek (2000) *Influence of intermolecular interactions on* ^{33}*S NMR chemical shifts of sulfur hexafluoride;*
- Anna Szyprowska (2009) ^{11}*B,*^{10}*B and* ^{19}*F NMR chemical shifts studies of* BF_3 *molecule in the gas phase;*
- Magdalena Donten (2010) *Determination of perfluorinated organic compounds and total organic fluorine using chromatographic methods and NMR.*

The scientific supervison of two M.Sc. thesis curricula:

- Agata Wikieł (2009) *Chemical shifts and spin-spin coupling constants of gaseous* $^{13}CH_3{}^{13}CHO$*;*
- Mateusz Godlewski (2014, in progress) ^{1}*H,* ^{13}*C,* ^{17}*O NMR study of etanol isotopomers in the liquid and gas phase.*

7. The public activity

Since 01.09.1981 I am a member of the Independent Self-governing Trade Union „Solidarity”.

During tenure 2006 - 2010 and 2011 - 2015 chairman of the Department’s Commission in the Faculty of Chemistry. During 2006 - 2010 tenure, a vice-chairman of the Works Committee of „Solidarity” in the Warsaw University.

Member of the Polish Chemical Society since 2002.

Member of Polish Nucleonic Society since 2015.

President of the *Foundation for the Construction of the Monument of the King John III Sobieski in Wilanow* in Warsaw in the years 1999 - 2002.