3. Elementary reactions of FO and FO_2; assessment of ozone depletion caused by CFC's substitutes (with CF_3CH_2F as an example).

L23b МАГНИТНЫЙ РЕЗОНАНС В ХИМИИ АТМОСФЕРЫ

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Создание новых методов магнитного резонанса (МР) во многом обязано непрерывно растущему интересу к процессам, протекающим в атмосфере Земли, и в особенности к антропогенным воздействиям на озоновый слой и на качество воздушной среды.

Цель доклада – осветить методологию исследований в химии атмосферы, рассмотреть новые кинетические методы магнитного резонанса для изучения гомогенных и гетерогенных процессов:

- ЭПР в газах
- Лазерный магнитный резонанс (ЛМР)
- Матричная изоляция/электронный спиновый резонанс

а также комбинации этих методов и вытекающие «синергетические» выигрыши.

Применения методов МР и их комбинаций для решения проблем химии атмосферы обсуждаются на ряде конкретных примеров:

1. Натурные наблюдения HO_2 и лабораторные исследования атмосферных реакций HO_2, выполненные с помощью спектроскопии МР. Сопоставление натурных экспериментов с модельными расчетами.

2. Гетерогенные реакции радикалов OH, HO_2, NO_3 и их воздействие на окислительную способность городской и морской тропосферы. Развитие новых представлений о механизме трансформации поллютантов.

3. Элементарные реакции радикалов FO, FO_2 и оценка разрушающего воздействия альтернативных фторсодержащих хладонов (на примере CF_3CH_2F) на озоновый слой Земли.

L24 NMR INVESTIGATIONS OF HUMIC SUBSTANCES

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Humic substances are polymeric organic materials which are synthesized from animal and plant biomolecules by abiotic and microbial reactions. Their composition reflect the respective eco-system. They are no defined molecules but rather a complex polydisperse mixture of compounds which has not yet been unambiguously characterized.

NMR spectroscopy is typically utilized for the *structural analysis of humic substances* by integrating one dimensional ^1H, ^{13}C, ^{15}N, and ^{31}P NMR spectra. Distinct ranges of chemical shift are then attributed to a specified set of chemical environments such as aliphatic, heteroatom substituted or aromatic positions, or in the case of ^{15}N NMR, to the distribution of nitrogen among amino-, amide- and heterocyclic functions.

It will be demonstrated that *various homo- and heteronuclear two dimensional NMR techniques* allow a more precise characterization of a variety of refractory organic substances.

Polar functional groups are relevant constituents of humic substances and account for their physicochemical behavior as well as their ecological efficacy. *Chemical derivatization of humic substances* substitutes acidic protons by rather unpolar substituents and, consequently, disaggregates these polymers to materials of intermediate molecular weight which are soluble in organic solvents. The introduction of *NMR active labels* provides additional analytical tools for the structural analysis of humic substances. Single resonances in heteroatom NMR spectra provide direct information indicating whole functional groups. This may lead to a quantification of many different groups of *exchangeable protons* in humic substances. Favourable relaxation characteristics enable the acquisition of highly resolved one- and two dimensional NMR spectra.

Multinuclear NMR spectroscopy is also a useful tool for the investigation of *interactions of small molecules and ions with refractory organic substances.* We will show various examples of our current work, including ^{1}H, ^{11}B, ^{13}C, ^{29}Si and ^{113}Cd NMR spectroscopy.

L25a THE 2.03 SIGNAL AS A FINGER PRINT OF DINITROSYL IRON COMPLEXES WITH THIOL-CONTAINING LIGANDS

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The parameters of EPR signal from dinitrosyl iron complexes (DNIC) with bovine serum albumin (BSA), equine hemoglobin (Hb) and apo-metallothionein (apo-Mt) of horse kidney incorporating one (BSA, Hb) or two thiol-containing ligands (apo-Mt) were compared. The EPR signal from DNIC-BSA was characterized by the rhombic symmetry of g tensor at room temperature (ambient temperature) or at 77K in the solution frozen in the presence of glycerin. In freezing of the solution in the absence of glycerin, under the exposure of DNIC-BSA to negatively charged sodium dodecyl sulfate (SDS) ions, or in the incorporation of DNIC-BSA into the reversed micelles formed by negatively charged ions of surfactant AOT, the symmetry of the g tensor of DNIC-BSA EPR signal increased to axial. A similarly high symmetry of g tensor was observed for the DNIC-Hb EPR signal in the absence of any influence on this protein complex. The shape of EPR signals from these preparations recorded at 77K was identical to that of EPR signal from DNIC with cysteine in frozen solution. In this connection it was concluded that the EPR signal from this low-molecular DNIC with the $(RS-)_2Fe^{+}(NO^{+})_2$ structure cannot be considered as a peculiar «fingerprint» of DNIC with the same structure in biosystems. In such systems the same signal can originate from protein DNIC incorporating only one thiol-containing ligand along with a non-thiol ligand. The EPR signal displayed by DNIC with apo-Mt with a high content of cysteine residues at room temperature of registration was identical to the EPR signal from frozen solution of DNIC with cysteine. This protein DNIC is apparently characterized by the same structure as DNIC with cysteine.