

es.^{38,39} A phosphine derivative of one of the rhenate monoanions, $\text{Li}[fac-(\text{OC})_3(\text{PPh}_3)(\text{Br})\text{Re}(\text{CH}_3\text{CO})]$, was reported recently.⁴⁰ When $\text{Li}[\text{BEt}_3\text{H}]$ is used in place of CH_3Li , the halorhenate formyl complexes, $\text{Li}[\text{cis}-(\text{OC})_4(\text{X})\text{Re}(\text{HCO})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), are formed.^{36,41,42}

It is interesting that the methyllithium adds to the carbonyl ligands rather than displace the halide ligand under these conditions. Also, the iodo biscarbenoid complex $fac-(\text{OC})_3(\text{I})\text{Re}[\text{C}(\text{CH}_3)(\text{OH})]_2$ decomposes in solution at room temperature with elimination of acetaldehyde.³⁷

Recent Results and Future Directions of Research

When the ferra- β -diketonate complex $[\eta\text{-C}_5\text{H}_5(\text{OC})\text{Fe}(\text{CH}_3\text{CO})(\text{Me}_2\text{HCCO})]\text{BF}_2$ (Figure 2) is treated with a stoichiometric amount of KH , a proton of the acetyl group is removed, affording an anionic complex in essentially quantitative yield.⁴³ This anion has the molecular formula $\{[\eta\text{-C}_5\text{H}_5(\text{OC})\text{Fe}(\text{CH}_2\text{CO})(\text{Me}_2\text{HCCO})]\text{BF}_2\}^-$, although an X-ray structure of the Me_4N^+ salt reveals that C-C bond formation has occurred between the original acyl carbon atoms. These two carbon atoms and the *exo*-methylene carbon atom coordinate to the $\eta\text{-C}_5\text{H}_5(\text{OC})\text{Fe}$ moiety as a substituted η -allyl ligand, as shown in eq 20.

This interligand C-C bond formation represents a transannular coupling across the six-membered metalla- β -diketonate ring and also demonstrates C-C bond formation between adjacent acyl ligands prior to a formal reductive elimination. Cleavage of the Fe and boron moieties may afford glycol or acyloin products. Such interligand coupling reactions are relevant to stoichiometric and catalytic reaction chemistry which occurs at metal atoms.

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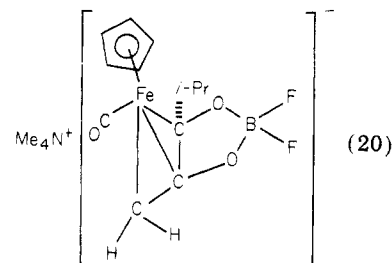
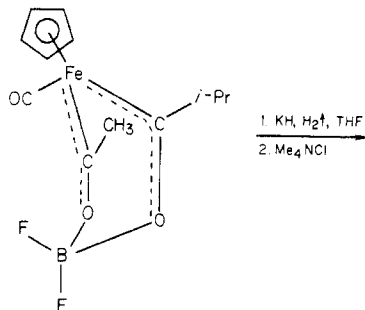
(39) Moss, J. R.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 975.

(40) Parker, D. W.; Marsi, M.; Gladysz, J. A. *J. Organometal. Chem.* **1980**, *194*, C1.

(41) The bromo analog has been prepared by others.⁴²

(42) Gladysz, J. A. *Aldrichim. Acta* **1979**, *12*, 13.

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Future research goals include (1) effecting dicondensation reactions to give unsaturated metalla heterocyclic molecules, (2) preparing metalla derivatives of amino acids, peptides, and other biologically important amines, and (3) investigating the generality and synthetic utility of the transannular C-C bond formation in the α -enolate anions of metalla- β -diketonate molecules. We believe that additional new classes of organometallic compounds will be prepared from designed synthetic methods by utilizing metalla- β -diketone chemistry. The metalla- β -diketones provide an entry into areas of chemistry which are not easily accessible when using more classical transition metal organometallic synthetic methods.

I wish to express my sincere appreciation to my past and present graduate students: Jane Zeile, Paull Torrence, Kevin Darst, Dave Hobbs, Larry Warfield, Lynne Preston, Andy Baskar, K. Srinivasan, and M. Raja, for their efforts in exploring the chemistry outlined in this article. Financial support from the National Science Foundation and the Alfred P. Sloan Foundation as a Research Fellow is gratefully acknowledged.

Laser Magnetic Resonance Spectroscopy and Its Application to Atmospheric Chemistry

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The paramagnetism of free radicals has always provided an attractive method for detecting them in the presence of molecules which lack unpaired electronic

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angular momentum. Historically, electron paramagnetic resonance (EPR) has been the favored technique, and for a simple free radical trapped in a solid, a steady magnetic field of strength H causes a level with net electron spin S to split into $(2S + 1)$ components with energy $g\beta M_s H$, where $g = 2.00232$ and β is the Bohr magneton ($=0.04669 \text{ cm}^{-1}/\text{kG}$). Transitions between these components with $\Delta M_s = \pm 1$ are induced by the interaction between the magnetic dipole of the electron and the magnetic vector of the microwave radiation

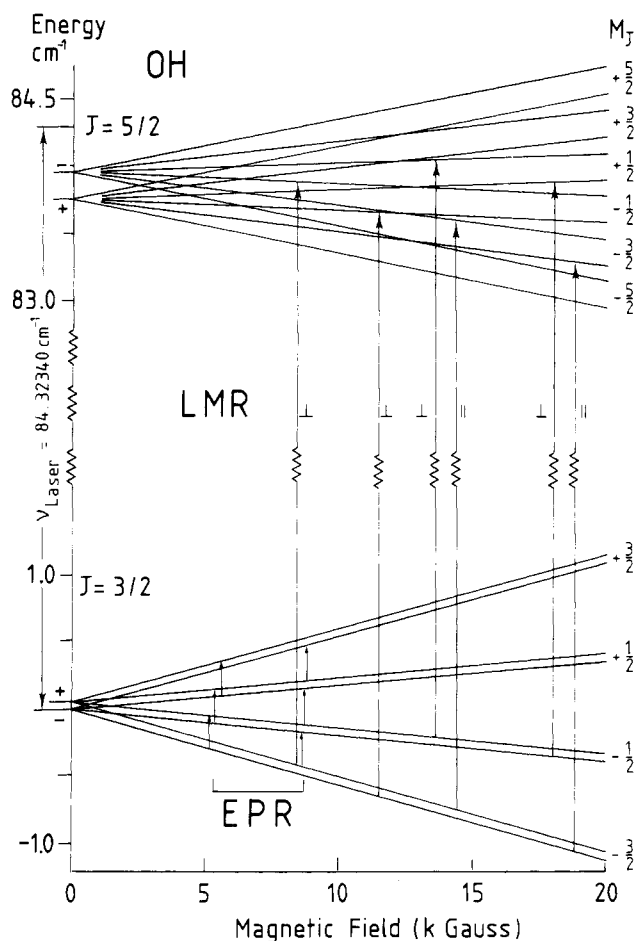


Figure 1. Comparison of the EPR spectrum of the ground state of HO ($^2\Pi_{3/2}$) with the LMR spectrum observed with the 118.6- μm line of the H_2O laser. Parallel transitions have $\Delta M_J = 0$; perpendicular transitions have $\Delta M_J = \pm 1$.

used; this is some 10^4 times weaker than for electric dipole transitions in the rotational spectra of polar molecules. For enhancement of its sensitivity, EPR is normally studied at a fixed frequency in a resonant cavity and the magnetic field is varied to obtain resonance as is done in laser magnetic resonance spectroscopy (LMR).

When one goes from a condensed phase into the gas phase the much smaller total density of particles and the high reactivities of many interesting free radicals limit the concentrations which can be achieved. Furthermore, the gas-phase EPR spectrum is observed as a transition between the Zeeman components of a low rotational level for the radical whose fractional population may be as low as 1% or 0.1% at room temperature. However, many linear free radicals have electronic angular momentum about the molecular axis which interacts with the nuclear rotation to give pairs of levels of opposite parity (Λ doubling); their presence gives rise to much stronger electric dipole allowed transitions in the EPR spectrum. This is illustrated for the lowest ($J = 3/2$) level of a $^2\Pi_{3/2}$ state in Figure 1. OH, SH, ClO, BrO, CF, and NCO are examples of radicals with $^2\Pi$ ground states which have been detected by gas-phase EPR.¹

This diagram applies in Hund's coupling case (a), which includes the paramagnetic $^1\Delta$ states of PH, SO,

O_2 , and NF. Figure 1 also shows how the LMR spectrum arises as a transition between low-lying rotational levels. Here the Zeeman energies are approximately $g_J\beta M_J H$, with $g_J \approx 0.80$ and 0.34 for $J = 3/2$ and $J = 5/2$ levels of a $^2\Pi_{3/2}$ state.² Tuning ranges approaching 1 cm^{-1} can be achieved with a conventional 20-kG electromagnet.

For many interesting free radicals, such rotational transitions lie in the far-infrared between 20 and 200 cm^{-1} (500–50 μm). There the larger values of the absorption coefficient and the greater difference between the Boltzmann populations of the levels give a 100-fold increase in sensitivity as compared with gas-phase EPR or conventional microwave spectroscopy.³ In this region, there are many molecular gas lasers which provide convenient monochromatic sources of a precisely known frequency. For LMR spectroscopy, the laser is chosen to have a frequency close to a rotational transition of a free radical, and individual Zeeman components of the transition are brought into resonance with the laser by applying a strong magnetic field.

Figure 2 shows a typical apparatus based on a water vapor discharge laser.⁴ Free radicals are produced in a discharge flow system, commonly by using fluorine atoms to abstract hydrogen from the parent molecule. This system is isolated from the discharge laser by a thin polyethylene Brewster angle window, rotation of which aligns the electric vector of the laser radiation parallel or perpendicular to the magnetic field giving different selection rules for the observed transitions ($\Delta M_J = 0$ or ± 1 , respectively). As in EPR, sinusoidal modulation is applied to the magnetic field which is slowly swept through the resonances, and the spectra are displayed in differential form. Detection within the cavity gives a 100-fold increase in sensitivity compared with conventional spectroscopy. When a germanium bolometer at 1.5 K is used to detect the dip in laser power at resonance, detection sensitivities better than 10^7 cm^{-3} for HO and 10^9 cm^{-3} for HO_2 can be achieved, their difference stemming largely from the very different rotational partition functions. The discharge laser illustrated in Figure 2 only provides about 10 lines, which provide coverage of only a fraction of the rotational spectrum. This difficulty can be overcome by replacing the discharge section by a far-infrared molecular laser containing, for instance CH_3OH , CH_3NH_2 , HCOOH , or CH_2F_2 at a pressure of about 50 mtorr. This is made to lase on a rotational transition by pumping a vibration-rotation line with an external CW CO_2 laser.⁵ Such lasers provide over 500 lines between 10 and 200 cm^{-1} whose frequency can be determined⁶ to about 1 part in 10^7 .

LMR Spectroscopy of Free Radicals

A molecule with electronic orbital angular momentum was chosen to compare LMR with gas-phase EPR because such species show strong spectra in both regions.

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(5) Radford, H. E.; Litvak, M. M. *Chem. Phys. Lett.* **1975**, *34*, 561.

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(1) Carrington, A. "Microwave Spectroscopy of Free Radicals"; Academic Press: New York, 1974.

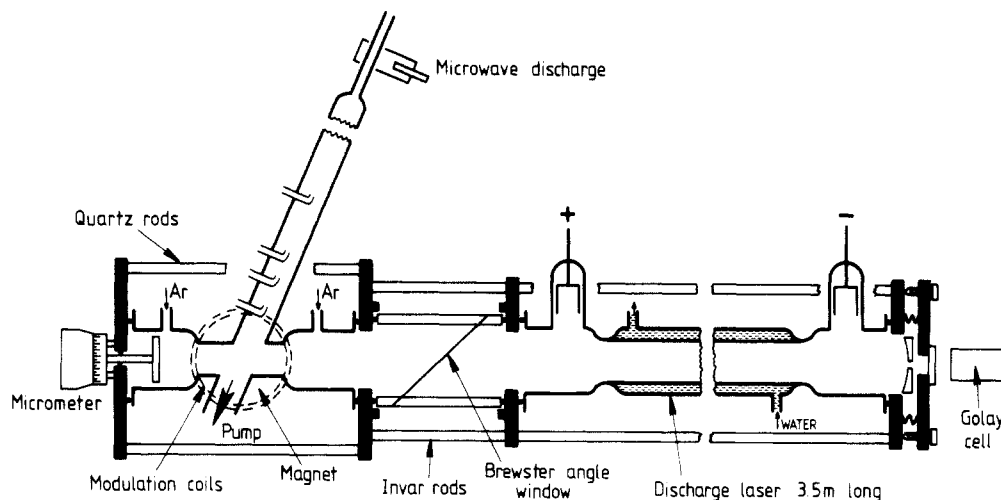


Figure 2. Laser magnetic resonance spectrometer based on far-infrared discharge laser.²

However, the majority of gaseous free radicals, including almost all the nonlinear polyatomics, have no electronic orbital angular momentum. For such species, the Zeeman effect is comparatively simple if the molecule has only a single unpaired electron.⁷ In the absence of an applied field, the spin-rotation interaction splits each level with quantum number N for nuclear rotation into two components, $J = N \pm 1/2$, their splitting being $\gamma(N + 1/2)$, where γ is the spin-rotation interaction constant. The applied field splits each level into $(2J + 1)$ components which are best described in terms of the quantum number $M_J = M_N + M_s$. Eventually, at high fields the electron spin becomes largely uncoupled from the molecular rotation and aligned with or against the applied field (Paschen-Back effect), giving lines of slope $\delta E/\delta H = g\beta M_s$, where $M_s = \pm 1/2$, as in Figure 3. When the selection rules $\Delta M_J = 0, \pm 1$ are applied to a transition between two such rotational levels whose spacing is close to a laser line, it can be seen from this figure that the LMR spectrum consists of regular branches (Figure 4) from the spacing and intensity of which it is often possible to establish individual values of M_J and hence identify the rotational transition.

For molecules like NH_2 which have strong spin-rotation interaction, tuning ranges approaching 1 cm^{-1} can be achieved, but, if the spin-rotation coupling is weak, the Paschen-Back effect takes over at low fields and the rapidly tuning transitions between Zeeman components with opposite slope are forbidden by electric-dipole radiation by the selection rule $\Delta M_s = 0$. Under these conditions, the tuning range is narrow, LMR spectra are observed only at low magnetic fields, and many laser lines are needed to detect enough rotational transitions.

For light free radicals it is therefore possible to observe sufficient rotational transitions to determine the rotation, distortion, and spin-rotation constants to high precision as well as the nuclear hyperfine interaction parameters. The last are of particular interest because both isotropic and anisotropic constants are obtained free from matrix effects. Figure 5 shows the hyperfine structure for two rotational transitions of NH_2 which contains two equivalent protons. The transition between ortho levels shows proton hyperfine splitting which is absent for the para levels. From these and particularly from the ^{14}N splittings, it can be shown that the unpaired electron is almost exclusively in a 2p or-

bital on the nitrogen atom with its axis perpendicular to the molecular plane. A total of 17 rotational transitions have been observed for NH_2 using 15 different laser lines.⁸ The parameters derived from these measurements compare in range and accuracy with those obtained from electronic absorption spectroscopy and microwave optical double resonance. However, the optical spectra of such important species as CH_3O and HO_2 have not been or cannot be fully resolved, and for these species the geometrical parameters have to be derived from LMR spectra.^{9,10}

LMR spectroscopy can also be carried out in the infrared by using the many lines of the various isotopic CO_2 lasers between 9 and $11 \mu\text{m}$ or CO lasers around $5 \mu\text{m}$. Vibration-rotation spectra of a number of free radicals have been detected in this way, notably by groups at N.R.C., Ottawa, Institute of Molecular Sciences, Okazaki, and Southampton University. However such spectra are difficult to analyze without information from other regions of the spectrum.

Kinetic Studies by LMR

In addition to the structural information which it provides about free radicals, its high sensitivity makes LMR spectroscopy a powerful method for studying free-radical reactions in the gas phase. The technique is at its most sensitive for total pressures below 1 torr where the line width is governed by Doppler broadening; direct measurements are effectively limited to total pressures below 10 torr by collisional line broadening.¹¹ This pressure range and the experimental arrangement lend themselves to the use of discharge-flow systems in which reactants are added to fast flowing gases at different distances (reaction times) from a fixed observation region although pyrolytic and photochemical sources of free radicals could also be used. In LMR spectroscopy there is an accurately linear relation over two or three orders of magnitude between the concentration of a species and the peak height of its spectrum (which is normally displayed in first or second derivative form). Although it is not difficult to calculate ab-

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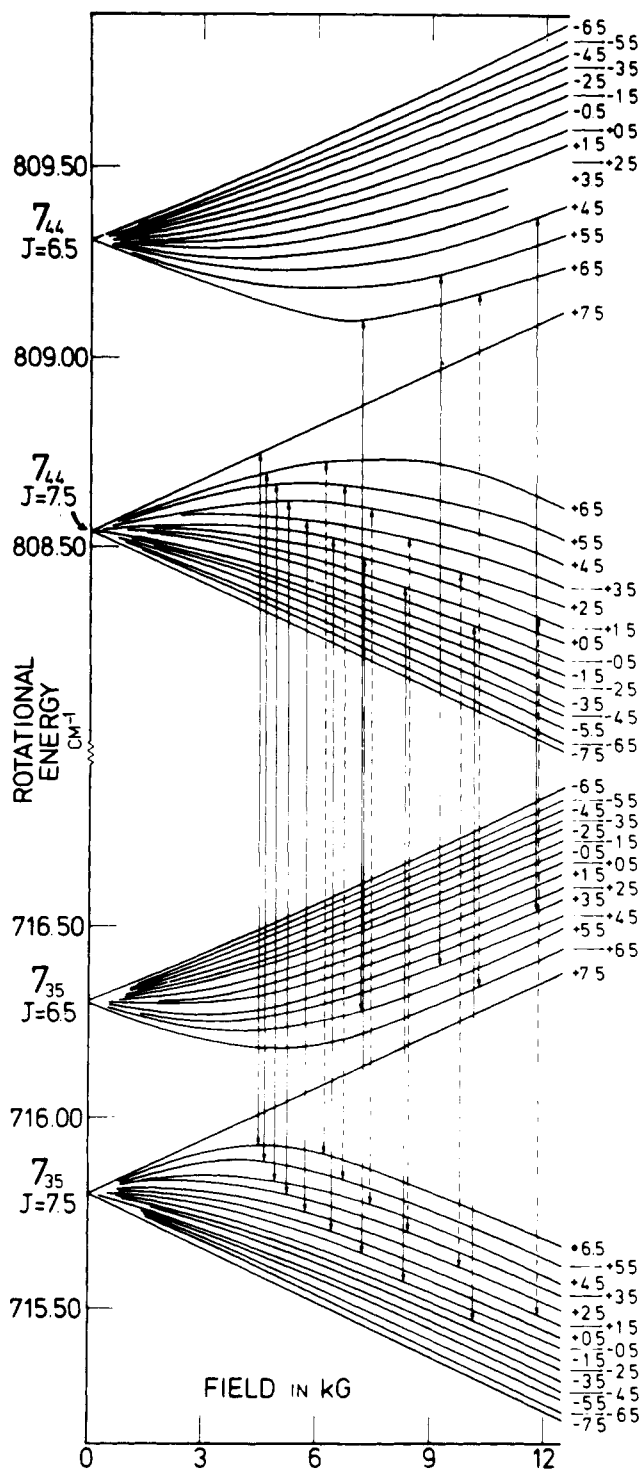
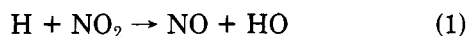


Figure 3. Zeeman splitting of two rotational levels of NH_2 . The vertical lines show LMR transitions observed with the $108\text{-}\mu\text{m}$ D_2O laser line (Figure 4). Parallel transitions ($\Delta M_J = 0$) are shown as broken lines; perpendicular transitions ($\Delta M_J = \pm 1$) as solid lines.

solute line strengths which depend on the square of the electric dipole moment of the species, the use of these to convert observed peak heights into radical concentrations involves so many instrumental parameters that calibrations are normally made by chemical methods using stoichiometric reactions such as



The first application of LMR to chemical kinetics was studies of the reactions of HO radicals by Howard and

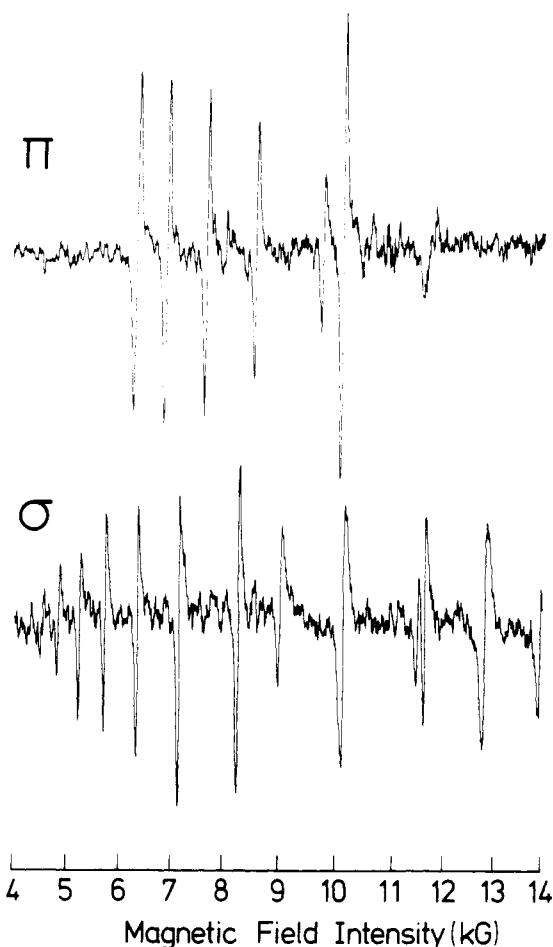


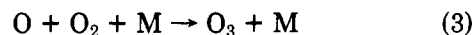
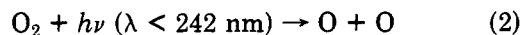
Figure 4. Laser magnetic resonance spectrum of NH_2 with $108\text{-}\mu\text{m}$ D_2O laser line. Note the clear formation of branches in both the parallel (\parallel) and perpendicular (\perp) spectra.

Evenson.¹² Subsequently their work and ours have concentrated on reactions of HO_2 which are important in atmospheric chemistry. Because of the weakness and inaccessibility of its near-infrared spectrum, the only other spectroscopic method commonly used to study reactions of HO_2 involves its featureless UV absorption between 200 and 230 nm which it shares with other peroxy compounds.

Applications to Atmospheric Chemistry

Recently, interest in laboratory studies of the reactions of several free atoms and free radicals has been stimulated by the need to make accurate predictions of the effect on ozone of nitrogen oxides (NO , NO_2) released directly into the stratosphere by high-flying aircraft and of chlorine species (Cl , ClO) formed there by the decomposition primarily of the chlorofluoromethanes [CFCl_3 (F-11); CF_2Cl_2 (F-12)] used as aerosol propellants, refrigerants, and foam-blowing agents.¹³

In the stratosphere, ozone is generated by the photolysis of oxygen (eq 2 and 3). Ozone itself is rapidly



photolyzed by visible and ultraviolet light, but this

(12) Howard, C. J.; Evenson, K. M. *J. Chem. Phys.* 1974, 61, 1943.

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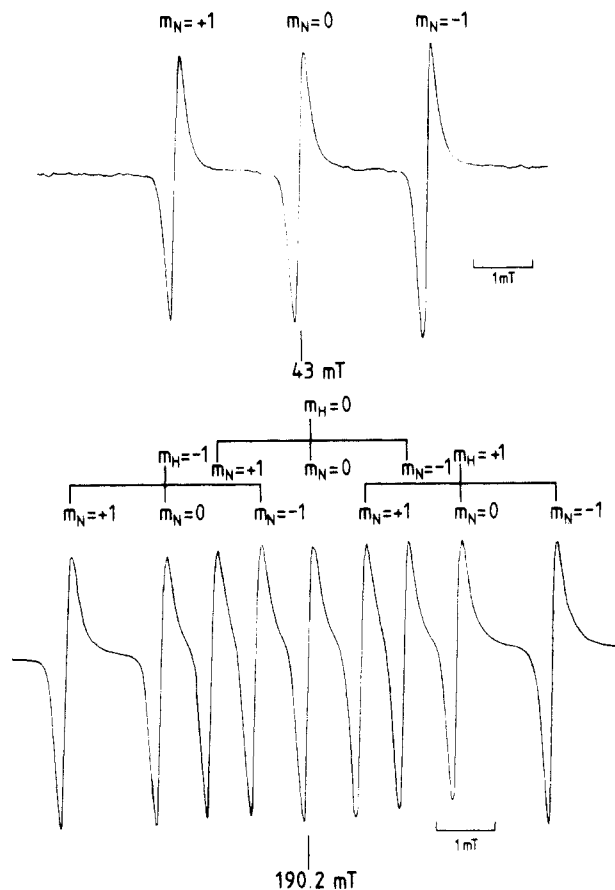
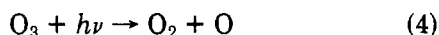
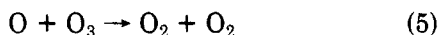


Figure 5. Hyperfine structure in the rotational transitions of NH_2 observed at $312 \mu\text{m}$. Both spectra show ^{14}N hyperfine splitting. The lower spectrum involving the "ortho" levels $0_{00} \rightarrow 1_{11}$ shows proton hyperfine structure, but the upper spectrum involving the "para" levels $3_{03} \rightarrow 3_{12}$ does not.⁸

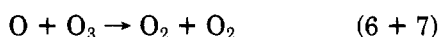
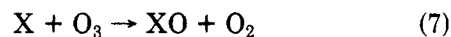
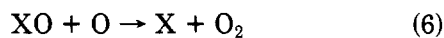
merely regenerates the atomic oxygen from which ozone is formed (eq 4), and reactions 3 and 4 set up a steady



state between the two forms of "odd oxygen", O and O_3 . In a pure oxygen atmosphere, odd oxygen would be removed only by the relatively slow reaction



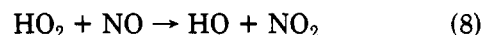
In the stratosphere, reaction 5 only accounts for about 20% of the odd oxygen removal. The overall chemistry of the stratosphere is extremely complex, but the remainder of the odd oxygen (ozone) destruction can be regarded as arising from catalytic cycles of the form



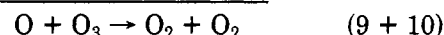
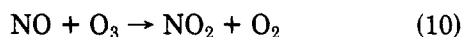
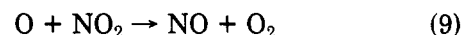
in which reaction 6 can be regarded as the rate-determining process in forming the new O-O bond¹⁴. Such cycles have been recognized for $\text{X} = \text{NO}$, Cl, H, and HO, and Figures 6 and 7 illustrate the main processes involved for $\text{X} = \text{NO}$ derived from natural sources and for $\text{X} = \text{Cl}$ from chlorofluoromethanes. In both cases the HO radical plays a vital role, in one case converting catalytically active NO and NO_2 to inactive HNO_3 and in the other converting inactive HCl into active Cl and

ClO.¹³ Thus HO plays an important role in all the odd oxygen destruction cycles except reaction 5, but it has not yet proved possible to measure its concentration in the stratosphere at altitudes between 20 and 30 km where ozone is densest.

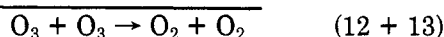
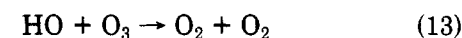
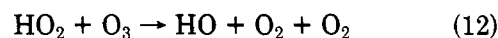
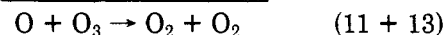
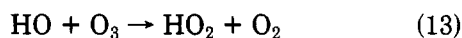
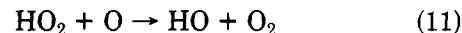
Figure 8 shows the atmospheric behavior of the "odd hydrogen" radicals H, HO, and HO_2 which are rapidly interconverted, but only slowly removed by radical-radical reactions. Knowledge of reaction rates for HO_2 radicals is clearly essential to understanding the balance between HO and HO_2 in the stratosphere and the rate of removal of these species and hence the importance of the various catalytic cycles which destroy ozone. This is well illustrated by Figure 9, which shows the various revisions of the estimates ozone depletion by nitrogen oxides from the exhausts of large fleets of supersonic aircraft.¹⁵ The large decreases in this estimate since the end of the Climatic Impact Assessment Program in 1974 are associated with new measurements of reaction rates involving HO_2 . The measurement by LMR of a high rate coefficient ($8.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reaction^{16,17}



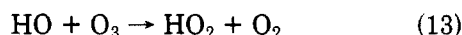
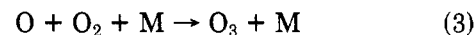
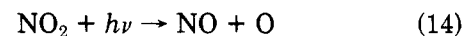
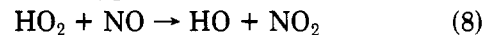
led to the surprising conclusion that additional nitrogen oxides in the lower stratosphere might enhance stratospheric ozone, notwithstanding the efficient catalytic cycle.



This arises because reaction 8 bypasses the odd oxygen destruction cycles



and replaces them with a "null cycle" which does not itself destroy odd oxygen.



As Figures 6 and 7 show, HO radicals regenerate Cl and ClO but remove NO and NO_2 . For this reason, the corresponding estimates of eventual ozone depletion due to continued release of F-11 and F-12 vary in the opposite sense to the lines of Figure 9 but less strikingly so. They rise from 10% to about 15% and then fall to around 12%.

Partly because atmospheric modellers require precise data on reactions which are not readily studied in the laboratory and partly because the data are required over the range of temperatures encountered in the strato-

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(17) Burrows, J. P.; Cliff, D. I.; Harris, G. W.; Thrush, B. A.; Wilkinson, J. P. T. *Proc. R. Soc. London, Ser. A* 1978, 368, 463.

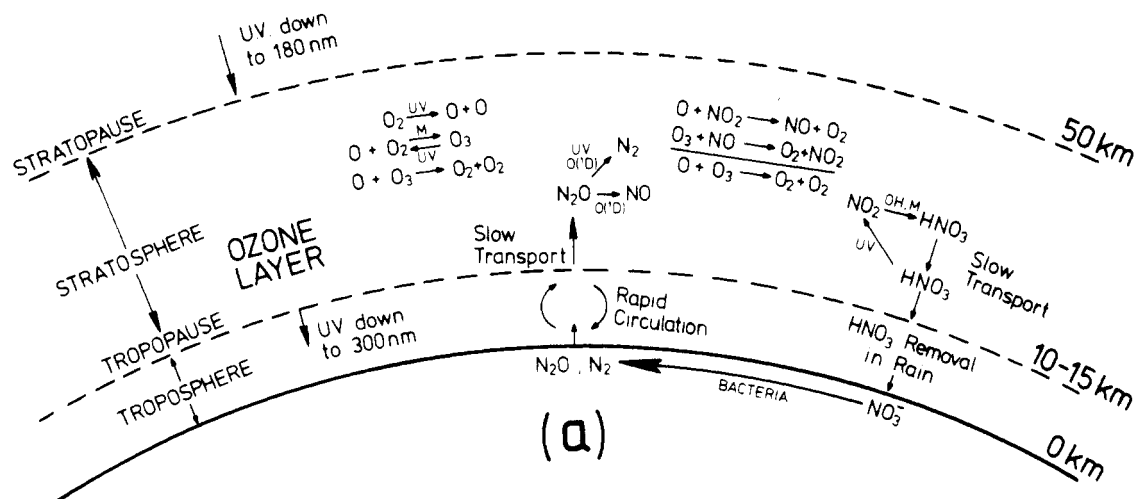


Figure 6. Simplified diagram illustrating ozone formation in the stratosphere and the role of the nitrogen oxides (NO and NO₂). Note that hydroxyl radicals are important for their conversion to nitric acid.¹³

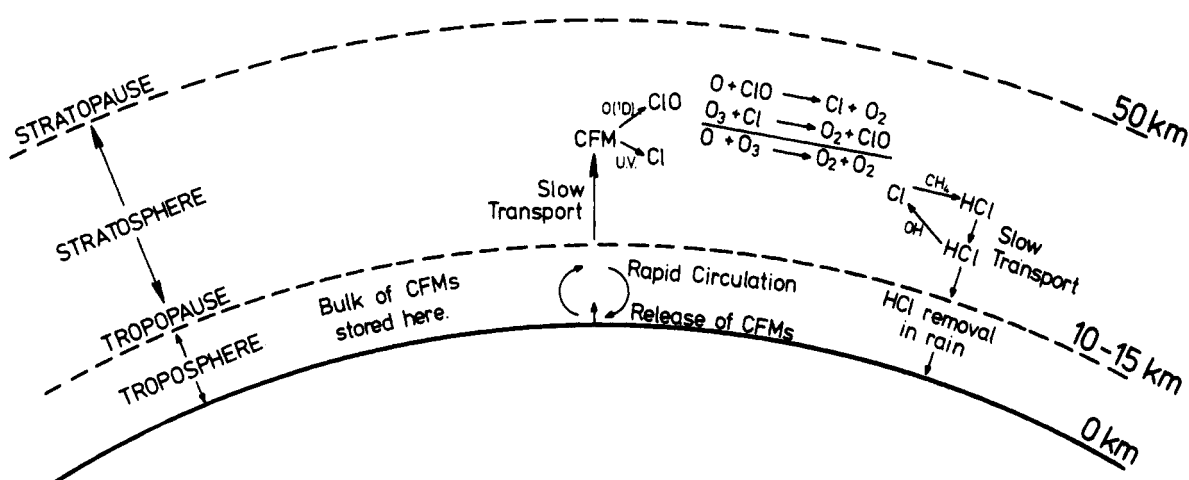


Figure 7. Basic processes in the atmospheric degradation of CFMs (chlorofluoromethanes). Note that here hydroxyl radicals convert hydrogen chloride into atomic chlorine which can catalytically destroy ozone.¹³

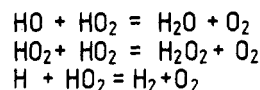
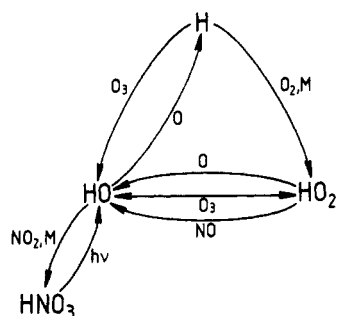
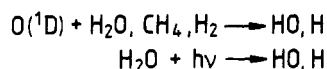
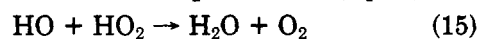


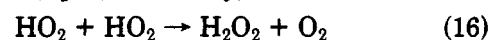
Figure 8. Summary of the main processes forming, interconverting and removing the hydrogen radicals, H, HO, and HO₂, in the stratosphere.¹⁷

sphere (200–270 K), recent studies have yielded some interesting points in chemical kinetics. The disproportionation of HO and HO₂ radicals¹⁸ (eq 15) is a

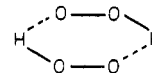


$$k_{15} = (5.1 \pm 1.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

hundred times faster than the corresponding reaction of HO₂ radicals (eq 16). Recently, we have shown¹⁹ that



this reaction becomes third order at low pressures due to the intermediate formation of a short-lived H₂O₄ species which probably has the structure



since pulse radiolysis studies²⁰ have shown that the proton of HO₂ forms a strong hydrogen bond to H₂O and to NH₃. Reaction 16 shows a negative temperature coefficient, in contrast to the rate constant of the related reaction (eq 17) which passes through a minimum near



ambient temperature, suggesting that it has two paths, an associative one, which predominates at low temperatures, and a hydrogen abstraction, which becomes important at elevated temperatures.²¹

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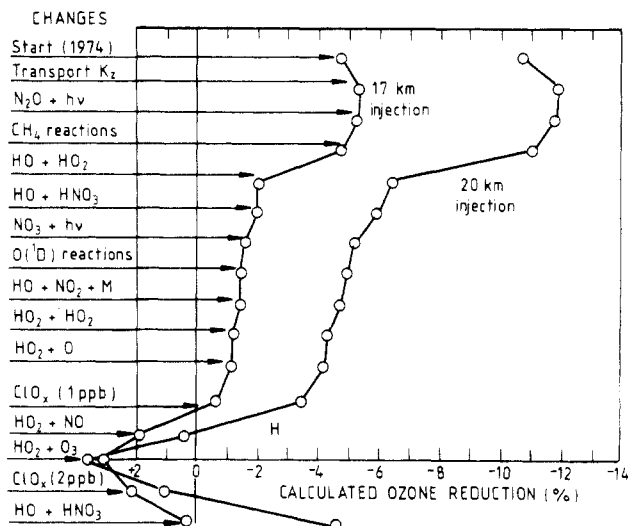


Figure 9. Predicted ozone depletions for large fleets of Concorde or proposed U.S. SST aircraft, corresponding to 17- and 20-km altitude injection of nitrogen oxides, respectively. Top point corresponds to the termination of the Climatic Impact Assessment Program in 1974; successive lower points correspond to increased understanding of atmospheric chemistry or new laboratory determination of the rate coefficient for an atmospheric reaction; lowest point corresponds to the situation in 1980.

HO_2 also undergoes a third-order combination reaction with NO_2 to form pernitric acid (HO_2NO_2),²² a species which may have some importance in atmospheric chemistry. In contrast, $\text{HO}_2 + \text{NO}$ undergo the bimolecular transfer reaction 8 which has a negative temperature coefficient,²³ presumably because it proceeds via the intermediary of a vibrationally excited

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pernitric acid molecule (HO_2NO). Interestingly, ClO shows exactly analogous behavior to HO_2 in these reactions, bringing to mind the similarities between the reactions of Cl and HO which were noted by kineticists many years ago.

The recent observation by Radford²⁴ that the $\text{F} + \text{CH}_3\text{OH}$ reaction yields both CH_3O and CH_2OH and that the latter, which is thermodynamically the more stable, reacts rapidly with O_2 to yield $\text{CH}_2\text{O} + \text{HO}_2$ whereas CH_3O does not shows that we may expect many interesting new applications of LMR spectroscopy in chemical kinetics.

Conclusion

Because far fewer gaseous species have identifiable UV spectra than have characteristic far-infrared or infrared spectra, the potential of these spectral regions for both kinetic and structural studies is considerable. The very narrow line widths of lasers and the possibility of intracavity detection give LMR spectroscopy a much higher sensitivity for free radicals than Fourier transform infrared spectroscopy. This is particularly important for the application to the atmospheric reactions discussed in this Account. Although tunable infrared lasers have considerable potential for studies of this sort, the problems of frequency measurements and stability need to be solved for infrared lasers to become as useful for gaseous species as laser magnetic resonance spectroscopy.

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Conformational Studies of Poly(oxyethylene)-Bound Peptides and Protein Sequences

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A thorough knowledge of the conformation of proteins and biologically active peptides is necessary for the understanding of their structure-activity relationships and physicochemical properties.^{1,2} The confor-

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mation of a peptide or a protein is determined by the balance of the intramolecular noncovalent interactions between the various groups in the amino acid sequence as well as of interactions between these groups and the surrounding solvent medium.³ The biological activity and functions of proteins depend mainly on the way the molecule is folded, and in many cases conformational changes appear to be the prerequisites for effective biological action.^{4,5}

Experimental and theoretical investigations on model peptides have been extremely useful in the interpreta-

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