



The impact of these reactions on the global cycle of tropospheric ozone is substantial. Recent studies suggest that this *in situ* photochemical production of ozone may be the largest source of ozone in this region of the atmosphere [5] and that the total ozone column in the atmosphere may have increased by as much as 10% because of anthropogenic activity [6].

Thus it is clear that the atmospheric budgets of carbon monoxide, ozone, nitrogen oxides and odd hydrogen radicals are quite interdependent. Furthermore, our understanding of these interactions has changed considerably in the past year because of the new chemical kinetics data which have appeared recently in the literature.

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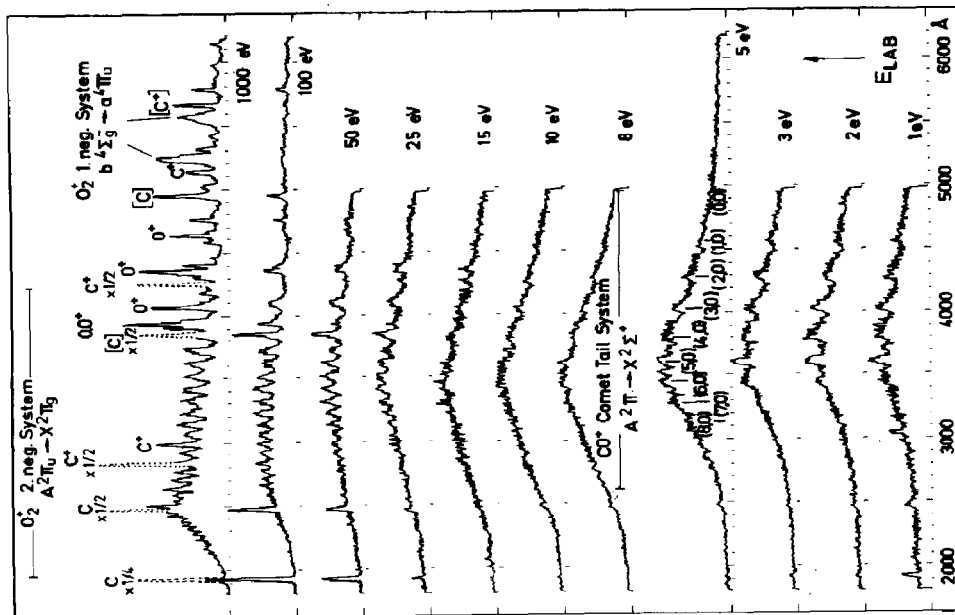
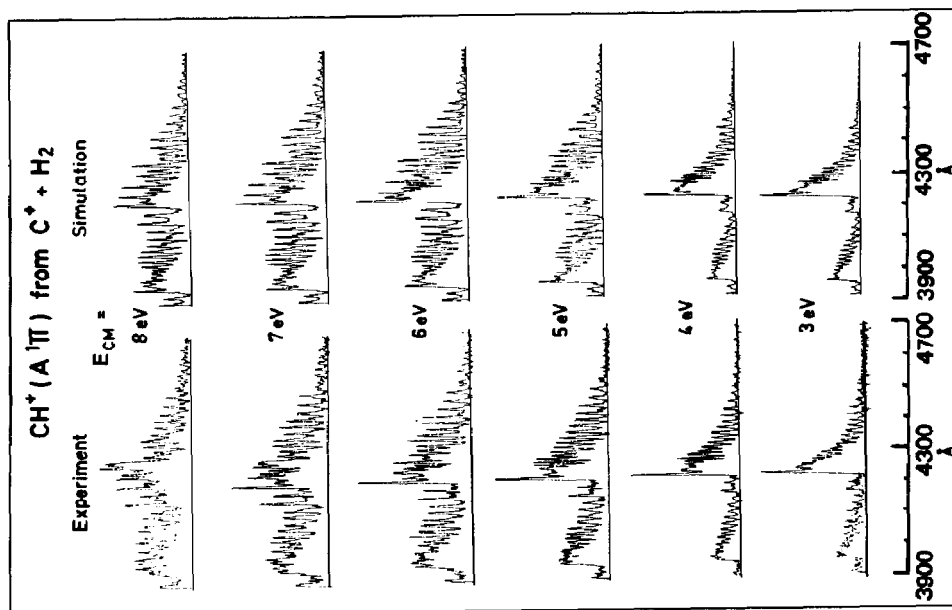
CHEMILUMINESCENT ION-MOLECULE REACTIONS

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Chemical reactions with charged reactants, traditionally called "ion-molecule reactions", have been studied for a long time using mass spectrometers. Recently optical detection of the reaction products has been introduced to this field. One studies the emission spectrum for electronically excited products, thereby exploiting the high energy resolution inherent in optical spectroscopy to obtain detailed information on the reaction mechanism. Luminescence from simple charge transfer, e.g. $\text{A}^+ + \text{BC} \rightarrow \text{A} + \text{BC}^{\dagger*}$ or $\text{A}^* + \text{BC}^+$, has been investigated quite extensively, while the optical study of "true" ion-molecule reactions, which proceed by exchange of an atom (rather than just an electron), is a new development. In this report reactions of the type $\text{A}^+ + \text{BC} \rightarrow \text{AB}^{\dagger*} + \text{C}$ or $\text{AB}^* + \text{C}^+$ will be dealt with, which one might call Chemi-Luminescent Ion-Molecule Atom-EXchange (CLIMAX) reactions.

Systems studied so far include reactions of C^+ , O^+ and N^+ ions with hydrogen and hydrocarbons [1 - 5], the reaction $\text{C}^+ + \text{O}_2 \rightarrow \text{CO}^{\dagger*} + \text{O}$ [6] and the reaction $\text{N}^+ + \text{NO} \rightarrow \text{N}_2^{\dagger*} + \text{O}$ [7]. (The last example is a case where the $\text{N}_2^{\dagger*}$ product was first identified optically, and later mass spectrometrically.) The experiments were done using the

Fig. 2. Spectra from the $C^+ + O_2$ reaction.Fig. 1. Spectra from the $C^+ + H_2$ reaction.

“beam-gas” arrangement whereby a mass-selected ion beam traverses a collision chamber containing the target gas. Typical operating parameters of the Göttingen apparatus are: ion energy variable from 1 to 1000 eV (spread about 1 eV FWHM), ion current through collision chamber 10^{-7} - 10^{-10} A, target gas pressure 10 mTorr. With an optical resolution of 2 - 20 Å FWHM photon count rates of 1 - 50 pps are recorded.

Figure 1 shows as an example spectra obtained from the $C^+ + H_2$ reaction. The (0, 0) band (at 4215 Å) and the (1, 0) band (at 3940 Å) of the well-known $CH^+(A^1\Pi \rightarrow X^1\Sigma^+)$ transition are prominent [8]. Although the rotational structure is well resolved, an exact determination of the rotational-vibrational level population requires a computer simulation of the spectra with adjustable distributions. Figure 1 shows on the right synthetic spectra produced in this way. As is qualitatively apparent from Fig. 1, both the mean rotational and vibrational excitation of $CH^+(A)$ increase with increasing collision energy. A detailed analysis of the results is in preparation [8], but one may speculate that a statistical model involving the strongly bound CH_2^+ complex is adequate. From symmetry arguments it follows that the system can reach the upper electronic state only via a non-adiabatic “surface hopping” process.

Figure 2 shows a series of spectra obtained in the $C^+ + O_2$ system between 1 and 1000 eV. At high energy only emission from charge transfer products (O_2^+ , C, C^+ and O^+) is observed, illustrating the competition between luminescent charge transfer and CLIMAX, which often has a small cross section (e.g. about 10^{-18} cm²). Around 10 eV $CO^+(A^2\Pi)$ is formed, in an exothermic reaction, and emits the well-known comet tail bands. The very blurred structure indicates again a very high rotational excitation of $CO^+(A)$, approximating a 30 000 K thermal rotational distribution [6]. The possibility of metastable C^+ reactant ions and of a metastable O product was explored, and a correlation diagram shows again the non-adiabatic nature of the reaction.

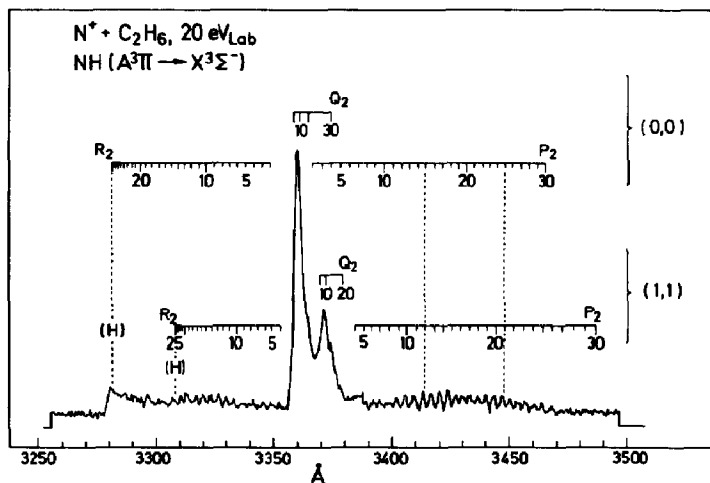


Fig. 3. Spectrum from the $N^+ + C_2H_6$ reaction.

Reactions between N^+ ions and hydrogen or hydrocarbons give chemiluminescence from the $NH(A^3\Pi)$ product, while no NH^+ radiation is observed. Figure 3 shows an example. At 2 Å FWHM resolution, band and line structure is resolved, from which the vibrational-rotational population distribution was again determined. Particularly interesting is the emission cross section σ as a function of energy. Figure 4 gives the results. With the hydrocarbons, σ reaches up to 1 Å² at low energy. In this regime the reaction approx-

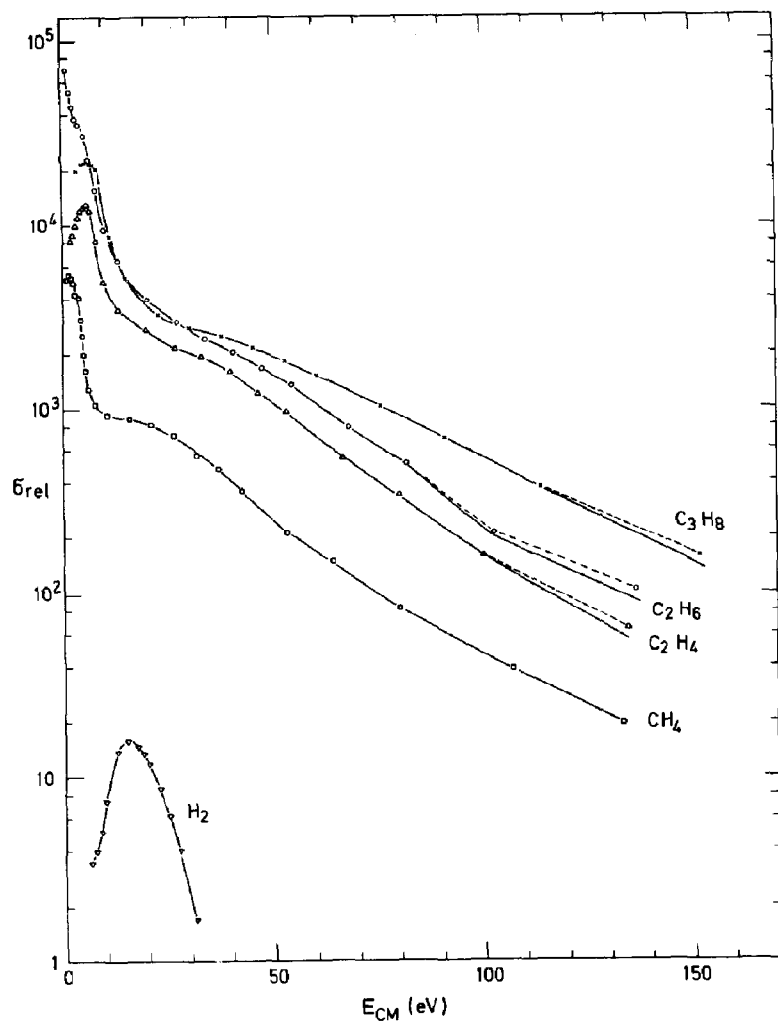


Fig. 4. Cross sections for the production of NH(A) in collisions of N^+ ions with five reactant gases, as a function of the collision energy (ordinate scale in arbitrary units).

imates the stripping mechanism, especially in the case of CH_4 , as could be directly verified from the rotational distribution. Above 10 - 20 eV stripping is no longer possible, and as a result σ drops sharply. However, except in the H_2 case, NH(A) is still formed up to the very high energy of 150 eV_{CM}. This is surprising in view of the low bond strength of NH(A) ($D_e = 2$ eV). The explanation is a two-step mechanism for the high energy reactions. The incoming projectile is initially slowed down by an N^+ -collision, which is very effective for the two nearly equal masses. Subsequently, the slow N^+ is able to capture H^- to form NH(A). This view was confirmed by trajectory calculations in the case of CH_4 , which gave a fall-off of σ with energy in good agreement with experiment.

This report summarizes work done jointly with J. Appell, D. Brandt, I. Kusunoki, J. Simonis and S. Zimmermann.

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THE PHOTOPHYSICS AND PHOTOCHEMISTRY OF FORMALDEHYDE INVESTIGATED BY LASER FLASH PHOTOLYSIS

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Laser excitation of formaldehyde is used to measure fluorescence lifetimes of individual rovibronic levels of the first excited singlet state. Both collision-free and collision-induced radiationless processes are observed. Intracavity dye laser spectroscopy is used to study the HCO produced by laser photodissociation of H₂CO. Vibrational relaxation rates and both radical-molecule and radical-radical reaction rates are determined. End product analysis of laser-photolyzed formaldehyde mixtures gives absolute quantum yields for radical, H + HCO, and molecular, H₂ + CO, photodissociation for individual vibronic bands. Selective photolysis of single lines in the ¹⁴CH₂O spectrum yields CO enriched by as much as 150 times in ¹⁴C. Significant improvements in ¹⁴C dating may be possible.

Lifetimes of S₁ formaldehyde

The decay of fluorescence from the 4⁰ and 4¹ levels of the S₁ (\tilde{A}^1A_2) state of H₂CO and D₂CO has been monitored as a function of pressure after selective, pulsed laser excitation. For D₂CO, single exponential decays modified by 4⁰ ↔ 4¹ energy transfer were observed over the entire pressure range 4 × 10⁻⁵ - 4 Torr. The zero pressure lifetimes τ₀(4⁰) = 7.8 ± 0.7 μs and τ₀(4¹) = 6.0 ± 0.4 μs are probably the radiative lifetimes. The rate of 4¹ ↔ 4⁰ energy transfer in D₂CO was found to be (9.6 ± 0.4) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, about three times the gas kinetic rate. For H₂CO at pressures above 0.1 Torr, fluorescence decays were also single exponentials modified by 4⁰ ↔ 4¹ energy transfer. However, in the range 2 × 10⁻⁴ - 0.1 Torr, the decays of the individual 4⁰ and 4¹ vibronic levels were multiexponential. Lifetimes of individual rovibronic levels vary

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