

between 70 ns and 3  $\mu$ s. A few approach the radiative lifetime of about 5  $\mu$ s. The Stern-Volmer plots of  $\tau^{-1}$  versus pressure give quenching rates between  $2.2 \times 10^{-9}$  and  $6.5 \times 10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for both fast and slow levels below about 20 mTorr. The Stern-Volmer plots are dramatically curved and give quenching rates of only about  $2.2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> above 1 Torr. The low pressure quenching rates and zero pressure lifetimes for H<sub>2</sub>CO depend significantly on the *K*' and *J*' rotational quantum number within 4<sup>0</sup>. The large quenching rate constants and the curvature of the Stern-Volmer plots can be qualitatively understood in terms of mixed-state models of collision-induced radiationless decay.

#### *Flash-kinetic spectroscopy of HCO*

Formaldehyde vapor was photolyzed with a tunable pulsed UV laser. Flash kinetic absorption spectra of the HCO produced were recorded by intracavity dye laser spectroscopy with a time resolution of 1  $\mu$ s. The energy threshold for radical production was confirmed to be at  $86 \pm 1$  kcal mol<sup>-1</sup>. Photolysis at 294.1 nm produced HCO in its ground vibronic state (about 2/3) and with one quantum of vibrational excitation in either the bending (about 1/3) or CO stretching ( $10^{-1}$  -  $10^{-2}$ ) vibrations. Observation of the CO stretching hot band absorptions allowed that frequency to be determined as  $1868.4 \pm 1$  cm<sup>-1</sup>. Quantitative state-resolved measurements of concentration versus time were made in pure H<sub>2</sub>CO and in mixtures with O<sub>2</sub>, NO or Ar. The vibrational relaxation rate for the bending vibration of HCO in collisions with H<sub>2</sub>CO was  $(4.3 \pm 1) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Reaction rates for HCO + NO  $\rightarrow$  HNO + CO and HCO + O<sub>2</sub>  $\rightarrow$  HO<sub>2</sub> + CO were measured as  $(1.4 \pm 0.2) \times 10^{-11}$  and  $(4.0 \pm 0.8) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. Approximate rates were determined for the radical-radical reactions H + HCO  $\rightarrow$  H<sub>2</sub> + CO and 2HCO  $\rightarrow$  H<sub>2</sub>CO + CO as  $10^{-9.26 \pm 0.3}$  and  $10^{-10.2 \pm 0.5}$ , respectively. Since laser photolysis may be used to produce large accurately known concentrations of free radicals, radical-radical rate constants may be determined with good accuracy. By use of two photolysis lasers reactions between two different radicals or between two excited states may be studied.

## THE INFLUENCE OF TEMPERATURE ON UV ABSORPTION CROSS SECTIONS OF HALOCARBONS

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Aeronomic processes are initiated by the photodissociation of atmospheric constituents under the influence of the UV solar radiation. In the particular case of the stratosphere, a complete description of the prevailing chemical scheme has to take into account the numerous components present as traces, either of natural origin or artificially introduced. During the last few years, special attention has been paid to the case of halocarbons: owing to their intensive industrial uses and lack of chemical reactivity at low altitudes, these compounds slowly diffuse up to stratospheric altitudes where their concentrations have proved to retain significant values. Their photodissociation in the 200 nm wavelength range corresponding to the atmospheric optical window is their most important destruction mode and leads to the release of atomic chlorine which in turn initiates a catalytic destruction cycle for ozone. In order to evaluate the chlorine production above 30 km absorption cross sections are needed. When available, measurements have usually been restricted to room temperature conditions, although actual stratospheric temperatures can be as low as 220 K.

In the present work, UV absorption cross sections of chloromethanes (CH<sub>3</sub>Cl, CH<sub>2</sub>Cl, CHCl<sub>3</sub>, CCl<sub>4</sub>) and chlorofluoromethanes (CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, CFCl<sub>3</sub>) have been deter-

mined in the 200 nm wavelength range as a function of temperature, with a classical single beam equipment (deuterium source, monochromator, absorption cell, photomultiplier detection). As condensation conditions can restrict, for the less-volatile compounds, the use of fairly high gas pressures at low temperatures and consequently the access to low absorption cross sections, an absorption cell with a 2 m optical path has been constructed: its temperature regulation is achieved by the circulation of a refrigerating fluid through a double jacket. Analysis of exploratory experiments and comparison with results previously published in the case of  $\text{CF}_2\text{Cl}_2$  have pointed out the difficulty of defining the actual pressure and temperature conditions for the absorbing gas. Consequently, these parameters are estimated by taking into account both the temperature of the absorption cell walls, measured via thermic resistors, and the pressure decrease during refrigeration, followed by an *in situ* capacitance manometer MKS Baratron.

Chloromethanes and chlorofluoromethanes display continuous absorption in the region 180 - 240 nm, with absorption cross sections ranging roughly from  $10^{-21}$  to  $2 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . The progressive substitution of the H atoms of the basic methane entity by chlorine atoms leads to increased absorption and extension of the absorption range towards higher wavelengths. In contrast, the presence of fluorine atoms tends to stabilize the molecule whose absorption spectrum is depressed and shifted towards lower wavelengths.

At lower temperatures, absorption cross sections decrease by a factor which depends both on temperature, wavelength and the chemical nature of the compound itself; the effect is most important at low temperatures, in the vicinity of the absorption threshold and in the case of highly chlorinated substances. Intercomparison of the numerical results is performed, taking into account these particular features, and the incidence of the temperature effect on aeronomic budgets is discussed on the basis of photodissociation coefficients computed for actual stratospheric conditions.

## INTRACAVITY LASER DETECTION OF RADICALS FOLLOWING STATE-SELECTIVE DISSOCIATION

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The large ( $10^3 - 10^5$ ) enhancement in detection sensitivity achievable with intracavity laser detection (ILD) [1 - 4] has been used to observe the time-dependent concentrations of gas phase radicals following state-selective dissociations at low (millitorr) pressures. The role of radicals in the dissociation of polyatomic molecules is well

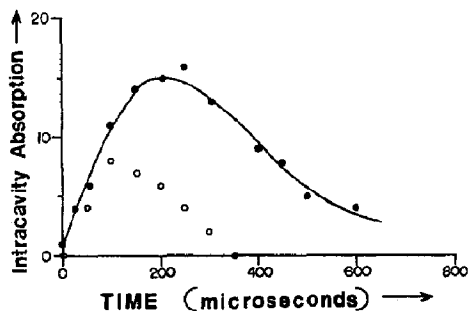


Fig. 1. The time-dependent concentration of HCO (as measured for the (0,9,0) ← (0,0,0) transition (R branch)) vs. time after the dissociation of  $\text{CH}_3\text{CHO}$ : ●, 200  $\mu\text{m}$   $\text{CH}_3\text{CHO}$ ; ○, 200  $\mu\text{m}$   $\text{CH}_3\text{CHO}$  + 10 Torr  $\text{N}_2$ .