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 CF_2Cl_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 2×10^{-18} cm^2 $molecule^{-1}$. 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

G. H. ATKINSON and R. J. GILL

Department of Chemistry, Syracuse University, Syracuse, N.Y. 13210 (U.S.A.)

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
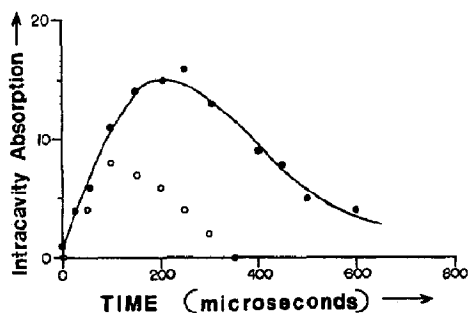

Fig. 1. The time-dependent concentration of HCO (as measured for the (0,9,0) ← (0,0,0) transition (R branch)) *vs.* time after the dissociation of CH_3CHO: ●, 200 μm CH_3CHO; ○, 200 μm CH_3CHO + 10 Torr N_2.

recognized as a general phenomenon, but its relationship to the initial molecular properties of the parent molecule is not well understood. The capabilities of ILD have made it possible to examine this relationship in great detail for a wide range of radical species. Specifically, one can use ILD to obtain information on (1) the energetic onsets in the photolysis of the parent into radicals, (2) the time-dependent internal energy content of radicals after their photolytic production, (3) the pathways and efficiencies for vibrational and rotational energy transfer within the energy levels of the radical and (4) the rates of reaction between radicals in specific excited-state energy levels with stable species (e.g. $HCO + H_2CO$). When combined with state-selective excitation, ILD can correlate data of the type 1 - 3 with the initially populated states of the dissociating parent molecule.

Results for a variety of dissociative reactions yielding radical products will be presented. The dissociation of CH_3CHO into HCO provides an excellent example. The time for the appearance of HCO following excitation exhibits a strong dependence on the accompanying collision partners. Data in Fig. 1 illustrate this behavior for N_2. The maximum HCO concentration for pure CH_3CHO occurs at 250 μs while the addition of N_2 reduces this time to about 100 μs [5].

The ILD instrumentation used in this work (utilizing a CW dye laser and optical multichannel detection) will also be described.

1 N. C. Peterson, M. J. Kurylo, W. Braum, A. M. Bass and R. A. Keller, J. Opt. Soc. Am., 61 (1971) 746.
2 T. W. Hansch, A. L. Schlawlow and P. E. Toschek, IEEE J. Quantum Electron., QE-8 (1972) 802.
3 G. H. Atkinson, A. H. Laufer and M. J. Kurylo, J. Chem. Phys., 59 (1973) 350.
4 G. H. Atkinson, T. N. Heimlich and M. W. Schuyler, J. Chem. Phys., 66 (1977) 5005.
5 R. Gill and G. H. Atkinson, submitted to Chem. Phys.

TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY

G. H. ATKINSON, R. B. SRIVASTAVA and L. R. DOSSER

Department of Chemistry, Syracuse University, Syracuse, N.Y. 13210 (U.S.A.)

Time-resolved resonance Raman (TR^3) spectroscopy offers the opportunity to obtain simultaneously structural and kinetic information on reaction intermediates. Thus, not only can TR^3 spectroscopy be used to identify the presence of conformationally distinct intermediates, but it can measure their time-dependent lifetime during each stage of a reaction.

TR^3 spectra have been obtained with multiwavelength detectors such as intensified vidicons and pulsed tunable laser excitation. The reactions under study are initiated photolytically by a second pulsed laser. The overall measurement has a typical time resolution of 10 ns. The frequency used to generate TR^3 scattering is chosen so as to yield maximum resonant intensity enhancements for specific chromophores.

TR^3 experiments have examined the ligation reactions of hemoglobin (Hb) with O_2 and CO. The reaction is initiated by the photolytic dissociation of HbO_2 or HbCO. The ligation reaction is then followed by monitoring band intensities of HbO_2, HbCO and Hb in the appropriate TR^3 spectrum. At least two distinct rates of reaction are observed (with rate constants of 2.2×10^7 M^{-1} s^{-1} and 1.3×10^8 M^{-1} s^{-1}).

Previous workers using flash photolysis and transient absorption techniques have also measured two rates of ligation, the faster rate constant being about 2×10^7 M^{-1} s^{-1}. This correlates well with the slower rate measured in this work. Thus, the faster rate observed in our work derives from a stage of the reaction not previously observed. It may correspond with a fast conformational rearrangement of Hb or one step in the sequential binding of the four O_2 molecules bound to Hb.