Multiple photon absorption in polyatomic molecules

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Absorption data for silicon tetrafluoride ($\tilde{\nu}_{irr}$ = 1025.3 cm^{-1}), cyclobutanone ($\tilde{\nu}_{irr}$ = 1073.3 cm^{-1}), ammonia ($\tilde{\nu}_{irr}$ = 1076.0 cm^{-1}) and hexafluorobenzene ($\tilde{\nu}_{irr}$ = 1023.2 cm^{-1}) over a range of pressures P (0.4 - 50 Torr) and fluences F (0.03 - 0.8 J cm^{-2}) are presented. The integral experimental absorption data can be represented in terms of an empirical differential equation

$$n(P,F) = \frac{A_1(P)F + A_2(P)F^2}{1 + B_1(P)F} \frac{1}{h\nu} \frac{RT}{P}$$

where

$$n(P,F) = -\frac{dF}{dl} \frac{1}{h\nu} \frac{RT}{P}$$

is the number of photons absorbed per molecule in a volume element with pressure P and fluence F. These data can be transformed to obtain absorption cross sections $\sigma_{exp}(\bar{E})$ for molecules with average energy $\bar{E}$. The experimental values are compared with model net absorption cross sections $\sigma_{net}(E)$ for molecules in "energy shell" E. In all cases $\sigma_{exp}(\bar{E})$ decreases with increasing $\bar{E}$, the rate of decrease being most pronounced for ammonia and least pronounced for hexafluorobenzene. Reasons for the energy dependence of σ_{exp} are considered. The consequences of these variations, as well as other factors, in affecting the efficiency of both direct and sensitized reactions are discussed.

Short-pulse CO_2 laser photochemistry of CH_3NH_2

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Multiphoton absorption (MPA) and multiphoton decomposition (MPD) of CH_3NH_2 were studied using a variable pulse length (2 - 60 ns) CO_2 laser. The laser pulse had a smooth temporal profile and an energy contrast ratio of at least 10. The MPA was measured either by transmission or by use of an optoacoustic detector to cover fluences from 0.001 to 45 J cm^{-2} over a pressure range 0.1 - 1.3 kPa (0.06 - 0.7 collisions during a pulse of 6 ns full width at half-maximum). The MPD was studied by measuring final stable product yields (H_2,

CH_4 and N_2) as functions of laser fluence (5 - 100 J cm^{-2} over a pressure range sure (0.1 - 1.3 kPa) with the short smooth CO_2 laser pulse. (Previous experiments have involved long multilongitudinal mode CO_2 laser pulses.) H_2 is formed via a reaction channel involving about half the enthalpy of that giving CH_3. We assume that CH_4 results from hydrogen abstraction by CH_3. A comparison of H_2 and CH_4 yields gives information concerning the intensity dependence of branching ratios.

Unimolecular decompositions sensitized by the multiphoton excitation of silicon tetrafluoride

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High purity silicon tetrafluoride containing 1 part in 35 of cyclobutanone, a mixture of cyclobutane and cyclopropane or a mixture of cyclobutanone and cyclohexene was irradiated with a carbon dioxide–triethylamine laser tuned to the P42 line of the 9.6 μm band at 1025 cm^{-1}. The laser beam was collimated to a rectangular cross section of 0.5 cm × 0.3 cm, with fluences between 0.9 and 1.6 J cm^{-2} attained by attenuation with polyethylene films. A single pulse was used to excite 0.5 cm^3 of silicon tetrafluoride vibrationally at pressures of 10 - 30 Torr. A direct calorimetric measurement of the energy absorbed was interpreted as a transient increase in the temperature of the silicon tetrafluoride heat bath to the 2000 - 3500 K range. The relative decomposition rates of the substrate compounds were determined by measuring product ratios at small conversion. The values so obtained differed drastically from those calculated using the well-known Arrhenius parameters for the high pressure limits. These results are consistent with very large relative decreases in the high pressure rate constants. Detailed results are presented to provide an experimental basis for the development of the collisional energy transfer models needed to explain this extraordinary "fall-off" behavior at high temperatures.