Multiple photon absorption in polyatomic molecules

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Absorption data for silicon tetrafluoride ($\bar{\nu}_{irr}$ = 1025.3 cm^{-1}), cyclobutanone ($\bar{\nu}_{irr}$ = 1073.3 cm^{-1}), ammonia ($\bar{\nu}_{irr}$ = 1076.0 cm^{-1}) and hexafluorobenzene ($\bar{\nu}_{irr}$ = 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,