

INFRARED MULTIPLE PHOTON DISSOCIATION OF CH_3NH_2 and NH_3

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The infrared multiple photon dissociation of CH_3NH_2 and NH_3 to form ground state NH_2 radicals has been studied. A pulsed, line tunable CO_2 laser was used to dissociate the molecules, and a N_2 laser pumped dye laser used to monitor the fragments by laser excited fluorescence. Collisionless dissociation of both molecules has been studied as a function of CO_2 laser wavelength and fluence (laser energy per unit area), and measurements made of the build up of fragments during the CO_2 laser pulse.

Dissociation of CH_3NH_2 was studied between 9.46 - 9.70 μm , corresponding to initial absorption in the ν_8 C-N stretching vibration. NH_2 was detected in a combination of 1_{11} , 2_{12} and 3_{13} rotational levels of the $^2B_1(0,0,0)$ ground state by observing fluorescence following laser excitation at 492.55 nm. The fluorescence signal, measured in these experiments at a time delay of 1.0 μs from the peak of the CO_2 laser pulse, and proportional to the concentration of ground state NH_2 radicals, was found to be a linear function of pressure from the lowest pressure used, 0.01 torr, up to 0.5 torr, levelling off above this. This demonstrates that for the lowest pressures dissociation is collisionless, and that at higher pressures the dissociation yield is reduced after approximately 5 gas kinetic collisions. Fig. 1 shows the measured dependence of the fluorescence signal on laser fluence for four (001 - 020) CO_2 laser lines overlapping different regions of CH_3NH_2 absorption spectrum, as illustrated in Fig. 2; measurements were made at a pressure of 0.05 torr with time delay 1.0 μs . The dissociation yields are approximately equal for the three lines measured at the highest fluences, 30 J cm^{-2} , but diverge considerably at lower fluences. Fig. 2 shows the relative fluorescence signals, scaled to unity at P(24) laser line for the highest and lowest fluences common to all four lines, 17.1 and 10.9 J cm^{-2} respectively, together with relative signals from two shorter wavelength CO_2 lines measured at 17.1 J cm^{-2} . Dissociation at wavelengths corresponding to initial absorption within the CH_3NH_2 ν_8 P branch is clearly more efficient than Q or R branch excitation, an effect entirely analogous to that previously observed for the multiple photon dissociation of SF_6 . The relative efficiencies of the lines are seen to be a strong function of fluence, the differences being more pronounced at low fluences.

Dissociation of NH_3 in the same wavelength region with the P(24), P(28) and P(32) lines gave fluorescence signals a factor of approximately 20 lower than for CH_3NH_2 , with a slightly steeper dependence of dissociation yield upon fluence, but no marked variation with laser wavelength. These lines are essentially off resonance with the closest strong absorption feature of NH_3 , overlapping only isolated R branch lines of the ν_2 vibrational transition.

The time dependence of the build up of NH_2 fragments during the CO_2

laser pulse was measured for dissociation of 0.05 torr CH_3NH_2 with the P(24) laser line. Fig. 3 shows the CO_2 laser pulse, consisting of an initial spike of ~ 150 nsec duration and containing $\sim 25\%$ of the total energy (4.5 J) followed by a low energy tail extending to ~ 4 μs . Measured fluorescence signals are plotted as open circles in Fig. 3 out to a maximum of 1 μs ; at longer times signal was distorted by fragments moving out of the overlap region of the CO_2 and dye laser beams, both ~ 3 mm in diameter. The fluence dependence of dissociation yield measured for the P(24) line at a time of 1.0 μs after the CO_2 laser peak, and shown in Fig. 1, was used to calculate the fluorescence signal which would be expected as a function of time if the yield was dependent only upon laser fluence and not laser intensity, the integrated time dependence of the CO_2 laser pulse enabling the fluence delivered at a given time to be calculated. The results are shown as the filled circles of Fig. 3, normalised to fit the experimental data at 1 μs . Experimental and predicted points are seen to agree within 20% between 1.0 μs and 200 ns, but show significant deviations at shorter times. At 200 nsec, the fluence is 20 J cm^{-2} ; the present results suggest that at fluences above this, intensity effects are unimportant, but may be of influence at lower values. Further experimental results support these conclusions. Time dependences were measured under conditions in which the total laser energy was attenuated by a factor of 2 compared with that of Fig. 3. Marked deviations between measured and predicted values were seen over the whole range of fluences, $\leq 15 \text{ J cm}^{-2}$ in this case, with experimental points higher than those predicted; similar effects were observed when the CO_2 laser beam was expanded in size to reduce the fluence. Intensity effects, if they occur, would be expected to be more pronounced in the dissociation of NH_3 than in CH_3NH_2 , due to the far lower density of vibrational states in the former molecule. The time dependence of NH_3 dissociation with the P(24) line showed measured values consistently higher than those predicted from the fluence dependence, even up to the maximum fluence of 30 J cm^{-2} , in contrast to the CH_3NH_2 results. Further experiments with shorter CO_2 pulses are in progress to test these preliminary conclusions.

Laser excited fluorescence has the disadvantage of looking only at selected fragments of the dissociation process, in the present case the NH_2 radical in its ground state. The lowest energetically accessible channel for the dissociation of CH_3NH_2 , which, from comparison with multiple photon dissociation studies of other molecules, would be expected to predominate, does not involve NH_2 formation, but instead molecular hydrogen elimination with the production of methylenimine



The direct C-N bond cleavage step



is however the lowest energy pathway producing NH_2 radicals, and is expected to be the dissociation mechanism observed in the present experiments.

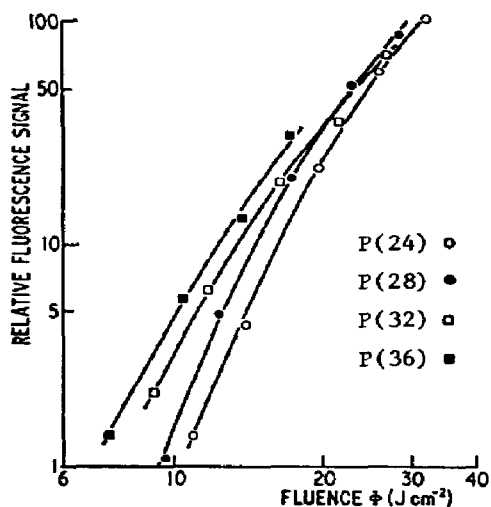


Fig. 1

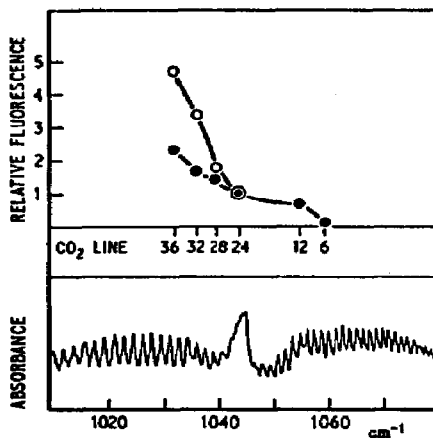


Fig. 2

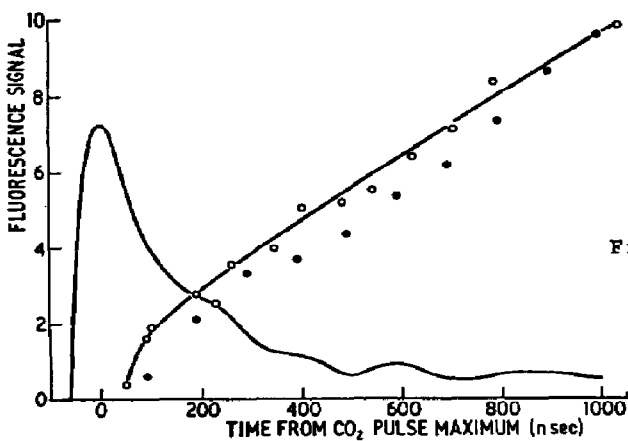


Fig. 3.

Fig.1. Dependence of NH_2 fluorescence on CO_2 laser fluence for multiple photon dissociation of CH_3NH_2 .

Fig.2. Fluorescence signals as a function of CO_2 laser wavelength, normalised to 1 for the P(24) signal; \bullet 17.1 J cm^{-2} , \circ 10.9 J cm^{-2} . The lower part of the figure illustrates the ν_8 band of CH_3NH_2 .

Fig.3. P(24) CO_2 laser pulse (solid line); \circ NH_2 fluorescence signal; \bullet predicted signal assuming no intensity dependence.