

## WAVELENGTH AND FLUENCE DEPENDENCES OF THE IR MULTIPLE PHOTON DISSOCIATION OF $\text{CH}_3\text{NH}_2$ TO FORM GROUND STATE $\text{NH}_2$ RADICALS

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### Summary

Ground state  $\text{NH}_2$  radicals have been detected by laser excited fluorescence following the collisionless multiple photon dissociation of  $\text{CH}_3\text{NH}_2$  by a pulsed  $\text{CO}_2$  laser. The variation of dissociation yield with IR laser fluence and wavelength are reported for several  $\text{CO}_2$  lines overlapping the  $\text{CH}_3\text{NH}_2$  band. Dissociation is more efficient at wavelengths corresponding to initial absorption in the P branch of this transition than for excitation in the Q or R branches, with the difference in efficiencies being more pronounced at lower fluences. The mechanism of  $\text{NH}_2$  production appears to be direct C—N bond fission.

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### 1. Introduction

Several of the now numerous experimental studies of the collisionless dissociation of gas phase molecules brought about by pulsed IR laser radiation have provided considerable insight into the mechanism of the multiple photon absorption process itself. For  $\text{SF}_6$ , the molecule for which most experimental data have been reported, measurements of the dissociation yield as a function of two parameters, laser fluence (defined as the energy of the laser beam per unit area) and laser wavelength, have been of particular importance. Fluence (joules per square centimetre) has been found to be a more important parameter than laser intensity (watts per square centimetre) in controlling the dissociation yield [1, 2], which implies that linear non-coherent absorption processes dominate and that intensity-dependent effects, such as power broadening, play a minor role in determining the dissociation rate. Several measurements of the dependence of dissociation yield upon laser fluence have been reported [1, 3, 4] and recently compared with modelling calculations of the absorption process [5]; the results suggest that below the dissociation limit absorbed energy is not completely randomized amongst all the vibrational degrees of freedom. The wavelength dependence of the multiple photon dissociation yield and the observed shift

of its maximum to longer wavelengths than that of the single photon absorption spectrum have been used to explain how SF<sub>6</sub> can absorb multiple monochromatic photons in an isotopically selective fashion [3, 6]. Absorption of the first few photons occurs within the initially pumped vibrational mode, with rotational energy compensating for the vibrational anharmonicity, creating a set of essentially resonant absorption steps. Subsequent absorption from these levels takes place through a "quasi-continuum" formed by the high vibrational state density, which is caused in SF<sub>6</sub> by the large number of relatively low vibrational frequencies together with anharmonic splittings of vibrational overtones [7].

Multiple photon absorption processes are not confined to molecules having high densities of vibrational states, as recent studies of the production of NH<sub>2</sub> from the multiple photon dissociation (MPD) of NH<sub>3</sub> have demonstrated [8]. In this paper we report measurements of the wavelength and fluence dependences of the MPD of CH<sub>3</sub>NH<sub>2</sub> to produce NH<sub>2</sub> fragments, with the radicals detected in their ground electronic state by laser-excited fluorescence. This technique has recently been used by several groups [8, 9] to study a variety of radical fragments, with in some cases measurements made of their vibrational and rotational energy distributions, and their build-up with time during the dissociating laser pulse. The present experiments use laser-excited fluorescence simply as a detection technique for MPD products; time-resolved dissociation measurements will be described elsewhere [10].

## 2. Experimental

Figure 1 shows schematically the experimental arrangement of two pulsed laser beams, from a CO<sub>2</sub> laser and a tunable dye laser, intersecting at right angles inside an anodized aluminium reaction vessel. The line tunable CO<sub>2</sub> laser delivered a pulse consisting of a spike with a rapid risetime of about 20 ns which was approximately 150 ns wide, followed by a low intensity tail lasting for about 4 μs. Total pulse energy varied from line to line, but was typically 4 J with 25% of this in the main spike. The repetition frequency was 0.5 Hz. Partial mode beating was evident from the temporal structure of the pulse, and the spatial structure of the beam as measured from burn patterns on thermal paper indicated multimode operation. The beam was reduced in diameter from 32 mm at the output to 2.6 mm at the centre of the reaction vessel using a NaCl lens of focal length 380 mm.

The tunable dye laser (Molelectron DL200) was pumped by a pulsed N<sub>2</sub> laser (Molelectron UV 14) and the output beam was collimated to a diameter of 3 mm so that it intersected the whole of the CO<sub>2</sub> beam at right angles at the centre of the reaction vessel.

The wavelength of the dye laser was tuned to a strong absorption feature of the NH<sub>2</sub> radical; in these experiments this was chosen to be an overlap of the 3<sub>03</sub> - 3<sub>13</sub>, 2<sub>02</sub> - 2<sub>12</sub> and 1<sub>01</sub> - 1<sub>11</sub> rotational lines in the <sup>2</sup>A<sub>1</sub> Σ (0,13,0) - <sup>2</sup>B<sub>1</sub> (0,0,0) transition at a wavelength of 492.55 nm [11]. The

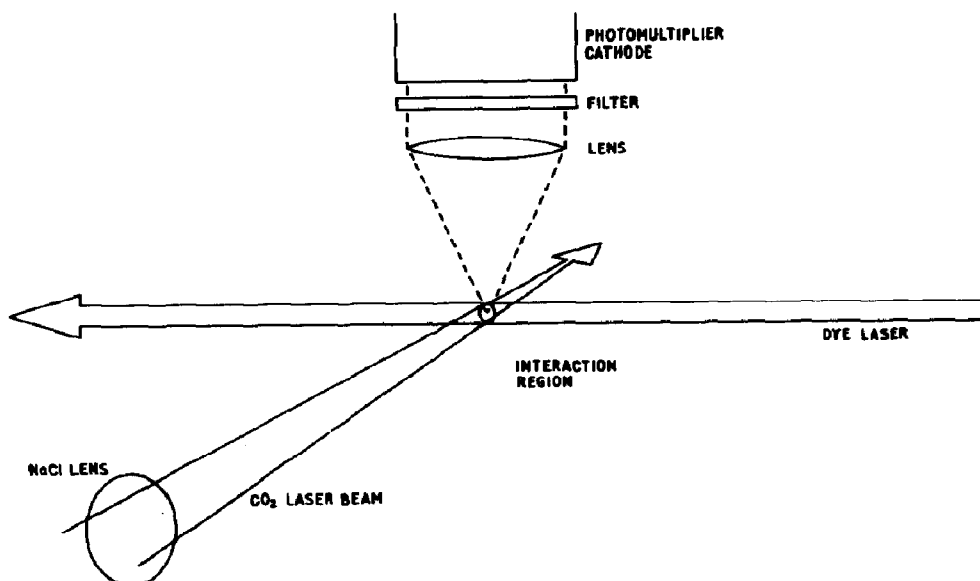


Fig. 1. Schematic diagram of the apparatus used for the detection of  $\text{NH}_2$  fragments formed in the IR multiple photon dissociation of  $\text{CH}_3\text{NH}_2$ , showing the crossed  $\text{CO}_2$  and dye laser beams and the photomultiplier detection system.

dye used was a  $10^{-2}$  M solution of Coumarin 152A in dioxan, and this produced an output pulse typically  $200 \mu\text{J}$  in energy and 7 ns wide with a bandwidth of 0.03 nm. The dye laser was fired at a time delay adjustable with respect to the  $\text{CO}_2$  laser pulse which was reproducible to  $\pm 10$  ns from shot to shot.

Scattered fluorescence from  $\text{NH}_2$  radicals, which were formed in their ground electronic state by multiple photon dissociation and excited by the pulsed dye laser, was collected by a lens and detected at a wavelength of about 532 nm by a fast risetime photomultiplier (Mullard 56 AVP). This fluorescence wavelength corresponds to the non-resonant  ${}^2A_1 \Sigma (0, 13, 0) - {}^2B_1 (0, 1, 0)$  transition; scattered light from the dye laser, which was not completely removed by the baffles inside the reaction vessel, was blocked with a cut-off filter (Schott OG 515). The photomultiplier output was digitized with 10 ns resolution by a transient recorder (Biomation 8100) and the signals were accumulated over a fixed number of pulses, eight in all the present experiments, by a signal-averaging system (Nicolet 1070). The observed fluorescence consisted of a rapidly rising pulse (risetime less than 10 ns) followed by an exponential decay (typically 700 ns under the present experimental conditions). Extrapolation of the decay curve to the time of firing of the dye laser gave the initial fluorescence signal, which was proportional to the concentration of  $\text{NH}_2$  radicals excited in the  ${}^2A_1 \Sigma (0, 13, 0)$  state by the pulsed dye laser and hence to the concentration of ground state  $\text{NH}_2$  radicals produced by MPD.

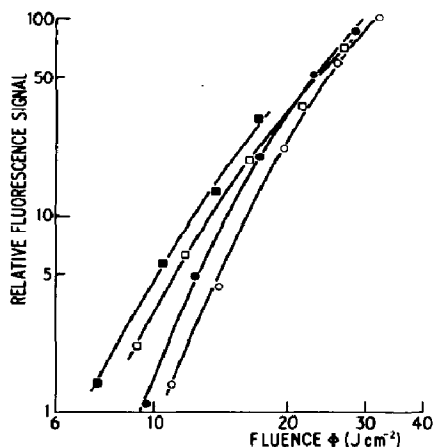


Fig. 2.  $\text{NH}_2$  fluorescence signals as a function of laser fluence for the multiple photon dissociation of  $\text{CH}_3\text{NH}_2$  with four  $\text{CO}_2$  (0,0,1 - 0,2,0) laser lines: ○, P(24); ●, P(28); □, P(32); ■, P(36). The signals were measured at 1.0  $\mu\text{s}$  delay from the  $\text{CO}_2$  laser peak; the  $\text{CH}_3\text{NH}_2$  pressure was 0.05 Torr.

The total  $\text{CO}_2$  laser fluence per pulse at the intersection of the two laser beams was calculated from the total energy of the beam, which was measured using a calibrated joulemeter, and its cross-sectional area which was measured from burn patterns taken on thermal paper with the beam highly attenuated. Allowances were made for reflection losses at the NaCl lens and entrance window. The fluorescence signal was measured, as described later, at fixed times of 1.0 and 3.0  $\mu\text{s}$  from the initial peak of the  $\text{CO}_2$  laser pulse, and hence the total IR energy had not been delivered at these times. A fast (20 ns) risetime linear-response pyroelectric detector was used to record the intensity of the  $\text{CO}_2$  pulse as a function of time, and the fluence at 1.0 and 3.0  $\mu\text{s}$  could then be calculated from the integral of the pulse shape which gave the energy delivered as a function of time. Fluences were varied over a factor of 3 in these experiments using previously calibrated polyethylene attenuators.

Shot to shot variations in the total laser output energy were measured to be 10%, although this effect tended to be averaged over the number of pulses. The uncertainty in the absolute values of the fluence depends upon the calibration of the joulemeter, the estimate of the beam size on the thermal paper and the calculated energy losses from the optics. Overall these effects were estimated to give a 20% uncertainty in the absolute fluence values, but relative fluences were considered to be accurate to within 10%.

Pressures inside the reaction vessel were measured using a capacitance manometer (Granville Phillips).  $\text{CH}_3\text{NH}_2$  (BDH 98%) and  $\text{NH}_3$  (BOC 99.98%) were purified by freeze-thaw cycling.  $\text{CD}_3\text{NH}_2$  was prepared from the hydrochloride (Aldrich 98%) by reaction with saturated KOH solution.

### 3. Results

Lines within the  $9.6 \mu\text{m}$  (0,0,1 - 0,2,0) band of the  $\text{CO}_2$  laser overlap with the P, Q and R branches of the  $\nu_8$  C-N stretching vibration in  $\text{CH}_3\text{NH}_2$  [12]. The dependence of the fluorescence signal upon fluence in the region  $10 - 30 \text{ J cm}^{-2}$  was measured for MPD by the P(24), P(28), P(32) and P(36) lines, and the results are shown in Fig. 2 as log-log plots in a similar way to previous results for  $\text{SF}_6$  [1, 4]. The P(24) line at  $9.59 \mu\text{m}$  ( $1043.2 \text{ cm}^{-1}$ ) lies in the  $\nu_8$  Q branch with the other three lines in the longer wavelength P branch, as illustrated in the lower part of Fig. 3 in which the  $\text{CH}_3\text{NH}_2$  single photon IR absorption spectrum is shown with the line positions marked relative to it. The total pressure of  $\text{CH}_3\text{NH}_2$  in these experiments was 0.05 Torr and the fluorescence signals were measured at a time of  $1.0 \mu\text{s}$  from the peak of the  $\text{CO}_2$  laser pulse. After  $1 \mu\text{s}$  an appreciable fraction of the  $\text{CO}_2$  laser pulse energy, between 50 and 60% depending upon laser wavelength, was incident upon the sample, yielding easily measurable signal levels. The time, however, was short enough to prevent loss of signal by dissociation products formed at earlier times moving out of the path of the dye laser beam. Signal loss of this kind was estimated by comparing the fluorescence measured at  $1 \mu\text{s}$  with that at a time of  $3 \mu\text{s}$  for the same fluence, with the result that at high fluences (above  $20 \text{ J cm}^{-2}$ ) the  $3 \mu\text{s}$  signal was some 25% lower than that at  $1 \mu\text{s}$ . This loss was shown not to be due to the different rates at which energy was being delivered in the 1 and  $3 \mu\text{s}$  cases, *i.e.* an intensity effect, by a further experiment in which the  $\text{CO}_2$  laser beam was expanded in area by a factor of 4 with the result that the 1 and  $3 \mu\text{s}$  signals were approximately equal at the same fluences. The loss can thus be attributed to fragments moving out of the dye laser beam between the times of 1 and  $3 \mu\text{s}$ . An approximate calculation showed that at times less than  $1 \mu\text{s}$  this effect would be negligible. Further experiments are in progress in this laboratory to measure the translational energies of MPD products by a time-of-flight method, and preliminary results have shown that the mean velocities of  $\text{NH}_2$  radicals from  $\text{CH}_3\text{NH}_2$  dissociation are low and would not affect fluorescence signals measured at  $1 \mu\text{s}$ .

At the pressure of the present experiments (0.05 Torr) a  $\text{CH}_3\text{NH}_2$  molecule experiences one gas kinetic collision about every  $2 \mu\text{s}$ . To check that collisions were not affecting the observed  $1 \mu\text{s}$  signal, the pressure dependence of the fluorescence signal was measured and was shown to be linear from 0.01 Torr, the lowest pressure used, up to 0.5 Torr and flattened off at higher pressures. These results demonstrate that the process is collisionless at low pressures, and that up to about five gas kinetic collisions are needed before the dissociation yield is reduced.

No estimate of the absolute probability of dissociation, as was previously reported for the MPD of  $\text{SF}_6$ , could be made in the present experiments, mainly because the absorption coefficients for the lines pumped by the dye laser and the Franck-Condon factor for the observed non-resonant fluorescence transition were not known. However, the fluores-

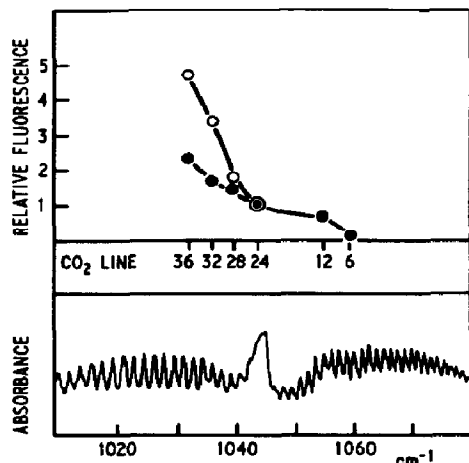


Fig. 3.  $\text{NH}_2$  fluorescence signals as a function of  $\text{CO}_2$  laser line within the  $(0,0,1 - 0,2,0)$  band for the multiple photon dissociation of  $\text{CH}_3\text{NH}_2$  at two fluences: ●,  $17.1 \text{ J cm}^{-2}$ ; ○  $10.9 \text{ J cm}^{-2}$ . Both signals are normalized to unity at the P(24) line. The line positions are shown relative to the  $\nu_8$  absorption band of  $\text{CH}_3\text{NH}_2$  in the lower part of the figure.

cence signals of Fig. 2 do accurately reflect the relative efficiencies of the different  $\text{CO}_2$  laser lines in producing  $\text{NH}_2$  radicals at any given fluence. The effect is illustrated in Fig. 3, where relative fluorescence signals taken from the data of Fig. 2 are plotted as a function of  $\text{CO}_2$  laser wavelength at the highest and lowest fluences common to all four lines, *i.e.*  $17.1$  and  $10.9 \text{ J cm}^{-2}$ . For clarity the P(24) fluorescence signal is taken as unity in both cases. Also shown in Fig. 3 are the fluorescence signals obtained with the P(12) and P(6) lines which, as shown in the figure, lie within the  $\nu_8$  R branch. Signals were measured at fluences of  $20.6$  and  $18.5 \text{ J cm}^{-2}$  respectively, but are corrected in the figure to fluences of  $17.1 \text{ J cm}^{-2}$  in order to compare with the other data by assuming the same fluence dependence as the P(24) line over this relatively small range. As can be seen, the fluorescence signal, proportional to the dissociation probability, increases at longer wavelengths with the wavelength dependence being more pronounced at lower laser fluences.

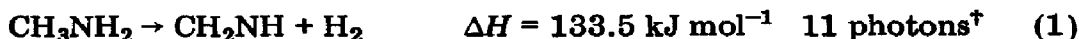
Collisionless MPD of  $\text{CH}_3\text{NH}_2$  to form excited state  ${}^2A_1 \text{ NH}_2$  radicals did not take place at the fluences used in the present experiments as no fluorescence signal was observed at pressures of  $0.05$  Torr with the dye laser beam blocked (so-called "luminescence"). Luminescence was observed at pressures above  $1$  Torr, but at times delayed with respect to the  $\text{CO}_2$  laser pulse, and clearly was the result of collisional processes forming the excited species.

## 4. Discussion

### 4.1. Mechanism

The present experiments demonstrate that ground state  $\text{NH}_2$  radicals are produced in the collisionless MPD of  $\text{CH}_3\text{NH}_2$ , but the laser-excited

fluorescence technique is unable to establish whether or not this is the predominant dissociation channel as fragments other than  $\text{NH}_2$  cannot be detected with the present apparatus. Previous experimental evidence of MPD in other molecules indicates that the lowest energetically accessible dissociation channel will predominate [13]. For methylamine photolysis this appears to be the elimination of molecular hydrogen to form methylenimine:

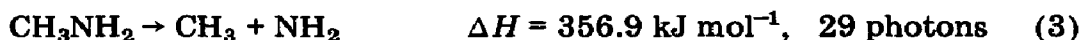


Methylenimine has IR absorption features at wavelengths close to the  $\text{CO}_2$  laser lines used in the present experiments [18] and would probably absorb further to dissociate:

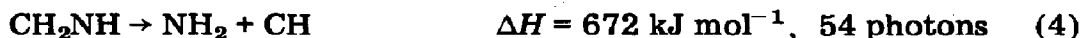


HCN was detected by IR absorption as a major end product in MPD experiments in high pressure (7 Torr)  $\text{CH}_3\text{NH}_2$ , but lack of experimental sensitivity precluded such measurements under low pressure collision-free conditions.

The lowest overall energy pathway to produce  $\text{NH}_2$  radicals is the direct C-N bond fission



which is clearly, on energetic grounds, a considerably less probable process than step (1) even with the possibility of an activation energy barrier for the  $\text{H}_2$  elimination. However, several two-step dissociation pathways are possible, which although requiring more overall energy than process (3) comprise an initial step with lower or similar  $\Delta H$ . The first possibility would be the further dissociation of the methylenimine formed in step (1) to produce  $\text{NH}_2$  and CH radicals:



Clearly step (2) would predominate in methylenimine dissociation, but this sequence needs to be considered if step (1) were effectively to remove all methylamine molecules rapidly, precluding the direct dissociation step (3). Some experimental evidence, although not conclusive, was obtained which suggests that process (4) does not occur. The MPD of  $\text{CD}_3\text{NH}_2$  with the R(14) line of the (001 - 100)  $\text{CO}_2$  laser band, which, at  $10.29 \mu\text{m}$ , lies within the Q branch of the  $\nu_8$  (C-N) stretching vibration [12], produced approximately the same  $\text{NH}_2$  signal as did MPD of  $\text{CH}_3\text{NH}_2$  with the P(24) line at the same fluence of about  $30 \text{ J cm}^{-2}$ . Furthermore, no laser-excited fluorescence from  $\text{ND}_2$  radicals could be observed in the MPD of  $\text{CD}_3\text{NH}_2$  when the dye laser was tuned to a strong absorption feature of  $\text{ND}_2$  at  $502.01 \text{ nm}$

<sup>†</sup>The heats of reaction were taken from ref. 14 except for the following species:  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_2\text{NH}_2$  and  $\text{CH}_3\text{NH}$  from ref. 15;  $\text{CH}_2\text{NH}$  from ref. 16;  $\text{NH}_2$  from ref. 17. The number of photons required refers to MPD with the P(24) line at  $9.59 \mu\text{m}$  (photon energy,  $12.48 \text{ kJ mol}^{-1}$ ).

[11]. The experimental detectivity for ND<sub>2</sub> radicals at this wavelength had been previously shown to be approximately the same as for NH<sub>2</sub> excited at 492.55 nm by comparing the signal obtained from ND<sub>2</sub> radicals generated in a fast flow system by a microwave discharge in a mixture of ND<sub>3</sub> and argon, with that from NH<sub>2</sub> produced by a discharge in a mixture of NH<sub>3</sub> and argon. No ND<sub>2</sub> was observed following MPD of CD<sub>3</sub>NH<sub>2</sub> with the P(24) laser line at 9.59 μm, whereas NH<sub>2</sub> was again detected with approximately the same yield as for CH<sub>3</sub>NH<sub>2</sub> dissociation.

Several routes for the elimination of isotopic variants of molecular hydrogen from CD<sub>3</sub>NH<sub>2</sub> can be envisaged which differ in the energy inputs required by the zero point energies of the products [18]. The mechanism with the lowest Δ*H* value involves the rearrangement step

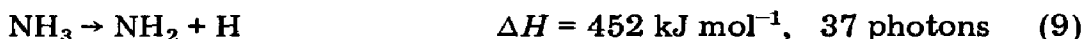
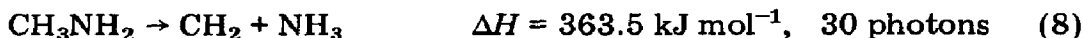


Lack of a signal from ND<sub>2</sub> appears to eliminate this two-step dissociation route, despite CD<sub>2</sub>ND possessing IR absorption features at CO<sub>2</sub> laser wavelengths [18]. If step (5) does not take place, the similarly complex rearrangements



followed by CH<sub>2</sub>ND or CHDNH dissociation to form NH<sub>2</sub> seem highly unlikely, particularly as both processes (6) and (7) are 8 kJ mol<sup>-1</sup> more endothermic than step (5). Formation of other deuterated methylenimines by elimination of HD could not result in further dissociation to give NH<sub>2</sub>; from the similar magnitudes of the NH<sub>2</sub> signals from the MPD of CD<sub>3</sub>NH<sub>2</sub> and CH<sub>3</sub>NH<sub>2</sub> it seems likely that the radicals are formed directly by step (3).

A second possibility for two-step dissociation is the sequence



comprising an initial step with essentially the same energy requirement as step (3). Isolated absorption features of NH<sub>3</sub> exist in the wavelength region of the CO<sub>2</sub> laser and could cause further dissociation. To test this mechanism experiments were carried out to study the dissociation of pure NH<sub>3</sub> under the same conditions as for CH<sub>3</sub>NH<sub>2</sub>. NH<sub>2</sub> was again detected but with dissociation yields a factor of 20 lower than for CH<sub>3</sub>NH<sub>2</sub> with the P(24) line. Unless NH<sub>3</sub> is produced in step (8) with considerable internal excitation which will increase its MPD cross section by this factor, the reaction sequence (8) and (9) seems highly unlikely.

Other two-step dissociations forming NH<sub>2</sub>, such as those involving initial dissociation to form CH<sub>2</sub>NH<sub>2</sub> or CH<sub>3</sub>NH, require more energy than does process (3) and are thus considered unlikely.



From the evidence presented it would appear that the direct bond fission step (3) produces the  $\text{NH}_2$  radicals observed, although the present experiments do not conclusively distinguish this from the other mechanisms discussed.

#### 4.2. Wavelength and fluence dependences

The observed dependence of dissociation yield upon wavelength and its comparison with the single photon IR absorption spectrum shown in Fig. 3 are clearly very similar to those observed for the MPD of  $\text{SF}_6$  [6], namely that irradiation in the P branch of the single photon absorption band is more efficient than in the Q or R branches. Rotational compensation of vibrational anharmonicity, invoked to explain multiple photon absorption of  $\text{SF}_6$  [6] and, more recently,  $\text{OsO}_4$  [19], and implying peaking of the dissociation spectrum at wavelengths corresponding to the P branch of the single photon spectrum, also appears to operate in the case of  $\text{CH}_3\text{NH}_2$ .

The fluence dependences of Fig. 2 again show remarkable similarity to those measured for the MPD of  $\text{SF}_6$  with the P(20)  $\text{CO}_2$  laser line, which, at  $10.6 \mu\text{m}$ , overlaps the  $\text{SF}_6$  spectrum in the middle of its P branch and is close to the maximum of the dissociation spectrum. The dissociation yield *versus* fluence plot shows a slope of about 3 on a log-log scale for fluences in the range  $2.5 - 10 \text{ J cm}^{-2}$ , increasing to higher values at lower fluences [4]. All four lines used in the present experiments show very similar behaviour to this, except that the region of cubic dependence is at considerably higher fluences ( $15 - 30 \text{ J cm}^{-2}$ ). Furthermore, this region extends to lower fluences for the lines which are more efficient at MPD, namely those at longer wavelengths. At high fluences (about  $30 \text{ J cm}^{-2}$ ) the P(24), P(28) and P(32) lines have almost identical dissociation efficiencies, possibly indicating the onset of saturation with a high efficiency of  $\text{CH}_3\text{NH}_2$  dissociation. The higher fluence at which this occurs for  $\text{CH}_3\text{NH}_2$  than for  $\text{SF}_6$  does reflect the difference in vibrational state density in the quasi-continuum for the two molecules which is due to the higher vibrational frequencies in  $\text{CH}_3\text{NH}_2$ , but a contributing cause may be that the observed process of  $\text{NH}_2$  production is almost certainly not the predominant dissociation pathway.

No dissociation threshold effects were observed in the present experiments. The lowest fluorescence signals observed were at what was considered to be the limit of detectivity of the present apparatus, and appear to be at fluences above any dissociation threshold, should this exist.

#### 5. Conclusions

The fluence and wavelength dependences of the MPD of  $\text{CH}_3\text{NH}_2$  have been shown to bear a close resemblance to similar measurements previously reported for  $\text{SF}_6$ . Models of the multiple photon absorption process invoked to explain such dependences in  $\text{SF}_6$  do seem to have applicability to less symmetric molecules with lower vibrational state densities.

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