

SATURATION OF THE a(6, 0) TRANSITION IN THE ν_2 BAND OF NH_3 BY IRRADIATION
WITH A TEA CO_2 LASER

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Experimental Study

As a prerequisite to the study of NH_3 sensitised laser induced reactions, the absorption coefficients of NH_3 at the R16 line (1075.99cm^{-1}) of a CO_2 TEA laser have been measured in the pressure range 10-200 torr. A typical (0.1-1 J pulse⁻¹, 5Hz) pulse from the CO_2 TEA laser exhibited a 200ns width at half maximum followed by low intensity (<5% of major peak) secondary pulses of longer duration. Measurement of the incident and transmitted intensities was carried out in a conventional optical system incorporating front and rear NaCl beam splitters, 1.6cm pathlength cell and dual detection system of calibrated photon drag detectors.

The aR(6,0) and aR(6,1) absorption line centres of the ν_2 fundamental mode in NH_3 occur at 1076.01cm^{-1} and 1075.88cm^{-1} respectively.¹ Line broadening coefficients (FWHM) of 8.9 MHz torr⁻¹ and 10.7 MHz torr⁻¹ measured for these lines², under non-saturation conditions, ensure that contribution to the absorption coefficient by the a(6,1) transition does not exceed circa 12% at the highest pressure.

At incident doses greater than $\sim 0.1 \text{ J cm}^{-2}$ the optical density, defined by $\log_{10} D_o/D_t$, where D_o and D_t are the corrected incident and transmitted doses respectively exhibits saturation as demonstrated in fig. 1. The linear dependence of the optical density on absorbed dose,

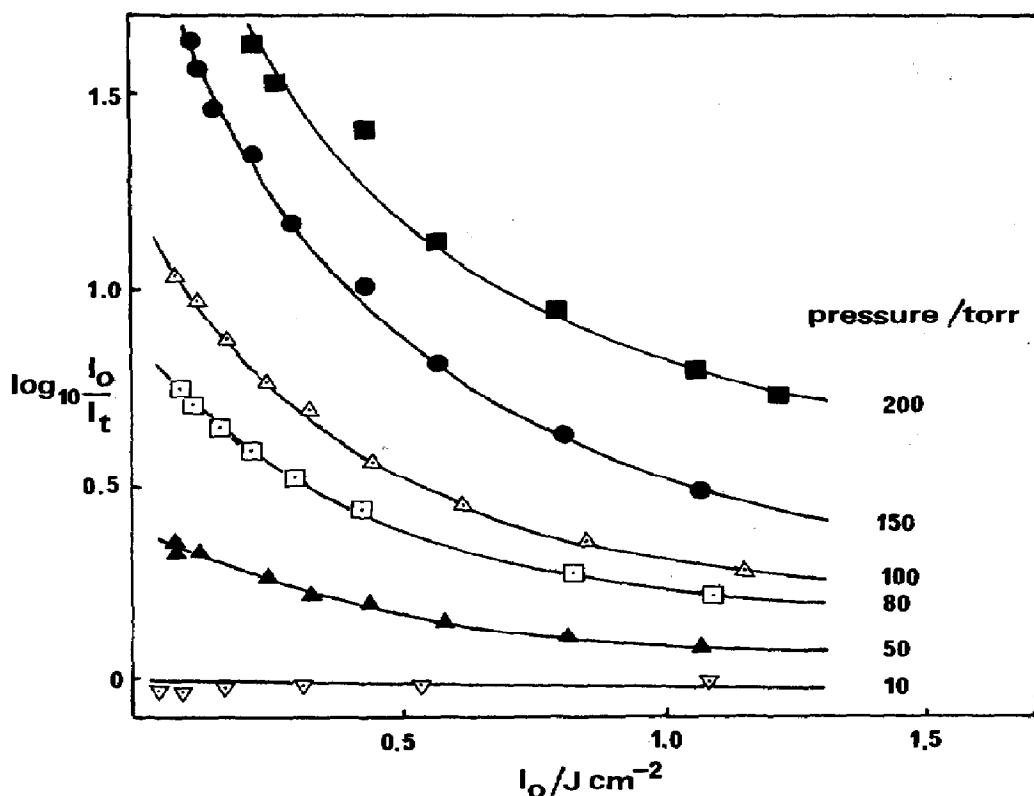


Figure 1. Dependence of the optical density of NH_3 on the incident laser dose, I_0 , at 1075.99cm^{-1} . Optical path length = 1.6cm ; NH_3 pressures; \blacksquare , 200 torr; \bullet , 150 torr; Δ , 100 torr; \square , 80 torr; \blacktriangle , 50 torr; ∇ , 10 torr.

fig. 2, allows measurement, by extrapolation, of the absorption coefficient, α/cm^{-1} , at low incident doses. Comparison of the pressure dependence of α acquired in the present study, as in fig. 3, with that measured at Brandeis University³ and that published by Chang and McGee² demonstrate that;

- (i) linear extrapolation of the optical density, measured under saturation conditions, to zero absorbed dose is a satisfactory procedure and, moreover, the optical density may be empirically related to the absorbed dose, thus,

$$\log_{10} \frac{D_o}{D_t} = -\frac{B}{2.303} (D_o - D_t) + \frac{AL}{2.303}$$

where A and B are constants and L is the optical pathlength.

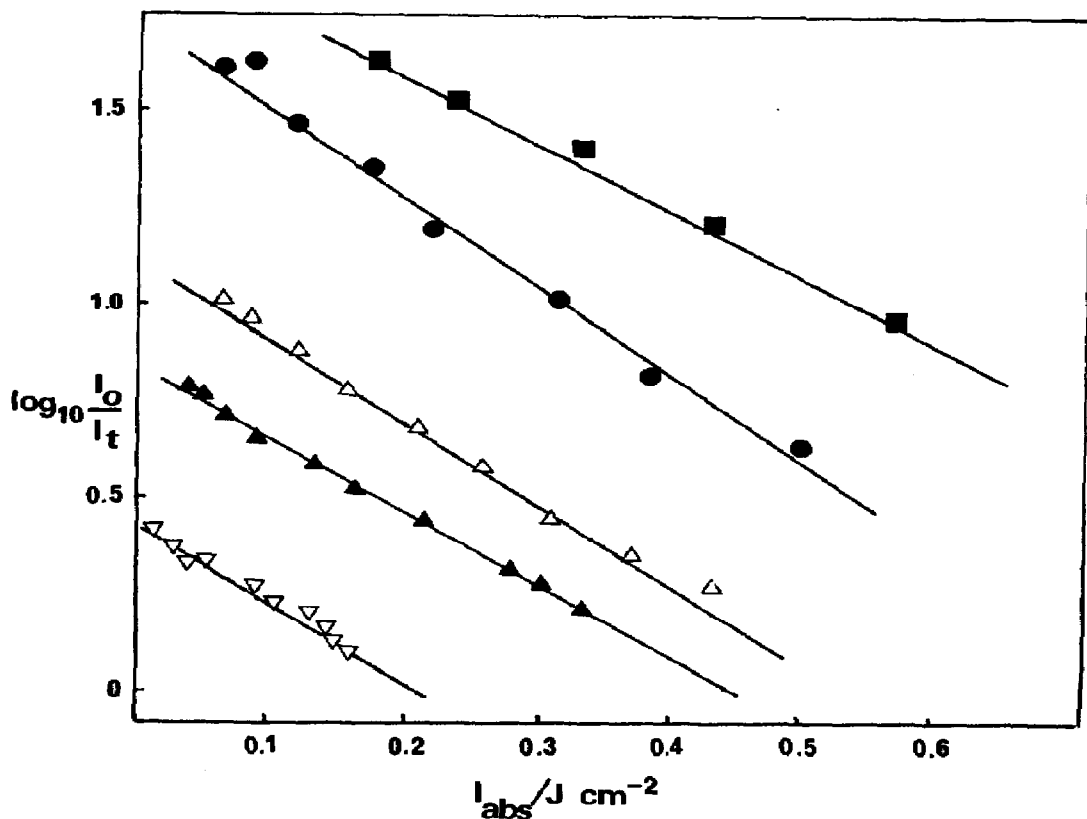


Figure 2. Variation of the optical density of NH_3 with absorbed dose, I_{abs} , at 1075.99cm^{-1} . Optical path length = 1.6cm . NH_3 pressures; \blacksquare , 200 torr; \bullet , 150 torr; Δ , 100 torr; \blacktriangle , 80 torr; ∇ , 50 torr.

- (ii) the present data, computed as a mean of at least five determinations at each pressure, is within the combined experimental error of the other studies^{2,3}.
- (iii) verification that rapid inter and/or intramolecular R-R and V-V relaxation processes play an integral part in the absorption process is obtained from the average number of quanta absorbed per molecule, $\langle n \rangle$, since,

$$\langle n \rangle = A^1 D / (1 + BD)$$

where

$$A^1 = 1.648 \times 10^4 AT / \nu_{\text{CO}_2} P$$

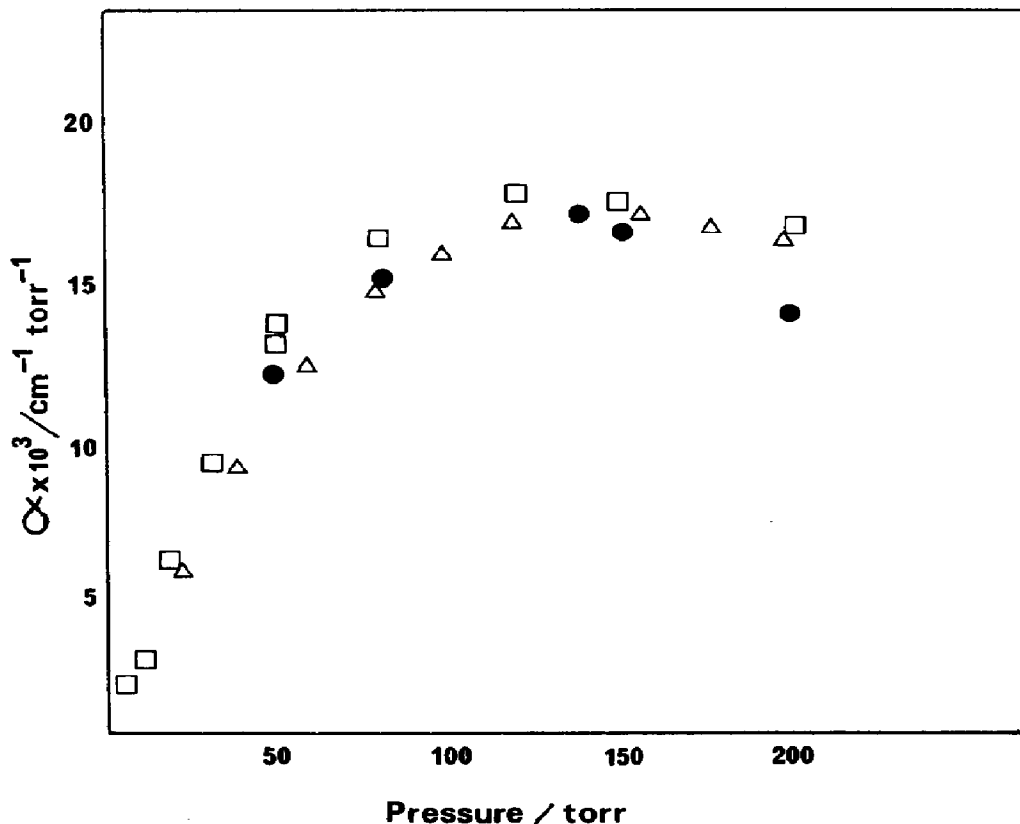
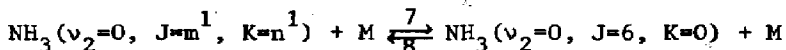
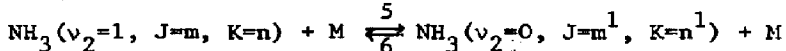
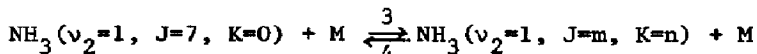
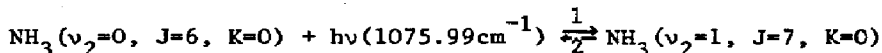


Figure 3. Comparison of the pressure dependences of the absorption coefficient, α , for the $a(6,0)$ transition in the ν_2 band of NH_3 . ●, present work; Δ, ref. 2; □, ref. 3.

T is the translational temperature; ν_{CO_2} the frequency of the incident laser pulse; D the absorbed dose and P the pressure of NH_3 . The experimental data and related theoretical study, *vide infra*, demonstrates that $\langle n \rangle$ asymptotically reaches a maximum value, $\langle n \rangle_{\text{max}} = A^1/B$, which exceed 0.5. A treatment of the saturation phenomena in terms of a simple two level system is thus precluded.

Whereas the linear relationship between the optical density versus absorbed dose in fig. 2 may be predicted from steady state solutions to a molecular mechanism, described below, incorporating rapid intermolecular, vibrational and rotational relaxation processes, the pressure dependence of

the gradients cannot be so reconciled.



The set of coupled differential equations representing equations(1)-(8) have been solved numerically using Gill's modification⁴ of the Runge-Kutta procedure. Initial populations of the a(6,0) and s(7,0) states, prior to irradiation, were obtained from a Boltzmann distribution calculated from the established energy levels of the (J,K) rotational sublevels of the ν_2 band in NH_3^1 . Calculations of the time dependent populations of the pumped and terminal levels during a laser pulse have been performed employing a range of intermolecular relaxation rate constants encompassing the range 8.9 MHz torr⁻¹(ref. 2) to 40 MHz torr⁻¹(collisional efficiency of approx. unity). The rates of the reverse reactions were obtained from detailed balancing. Values of $\langle n \rangle$ and thence $\log_{10} D_o/D_t$ have been calculated integrated over the optical pathlength.

Whilst agreement between the theoretical model and the experimental data is satisfactory at high pressures, a disparity occurs at lower pressures. The implications of this fact with respect to multi-photon absorption processes will be discussed.

References

1. H.M. Mould, W.C. Price and G.R. Wilkinson, *Spectrochem.Acta*, 15,313 (1959).
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3. C. Steel, private communication.
4. S. Gill, *Proc.Camb.Phil.Soc.*, 47,96.