Triplet Quenching by Oxygen in a Rhodamine 6G Laser

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Measurements of dye laser output power vs. oxygen content of the dye solution are reported and compared with a simple theoretical model. The triplet lifetime of rhodamine 6G in oxygen-free methanol at room temperature is seen to lie between 1 and 100 μsec, with 2 μsec giving the best fit of the experimental data.

Triplet-triplet absorption losses in dye lasers can be reduced by the use of triplet quenchers. It was first shown by Snavely and Schäfer [1] that the oxygen content of an air-saturated rhodamine 6G solution reduces the steady state triplet population so far that cw-operation of a laser using this solution as active medium is possible. It is necessary to know the exact functional dependence of laser output on oxygen content of a dye solution for a choice of the optimum operating conditions. In addition, an analysis of this functional dependence will yield information on the molecular mechanisms involved.

In the present work we used a dye laser that was essentially the same as in the work of Snavely and Schäfer and described in more detail by Snavely [2]. Oxygen-nitrogen mixtures saturated with methanol vapour were bubbled through the dye solution for at least fifteen minutes before the laser was fired and the laser output measured with a calibrated photodiode. For every shot the reservoir and cuvette were filled with fresh solution to avoid photochemical decomposition of the dye influencing the results. The dye solution was rhodamine 6G (BASF) in methanol at a concentration of $3 \cdot 10^{-4}$ mole/l. The laser peak power at $p_{O_2} = 0.5$, $W_{1/2}$, was 200 W, the pulse width (FWHM) 100 μs. The results of laser peak power measurements with gas mixtures of different oxygen content are indicated by crosses in Figure 1.

For an interpretation of the experimental results we first note that the laser output power W is approximately proportional to the single pass amplification. For small signals this is proportional to the population of the first excited singlet level, n_S, and inversely proportional to the population of the triplet state, n_T, since the latter is proportional to the triplet-triplet absorption losses. We thus have $W \sim n_S/n_T$. On the other hand we can obtain n_S/n_T from the steady state condition of the triplet population. Equalizing the triplet production and deactivation yields

$$(k_{ST} + k_{QS}[O_2])\, n_S = (k_{TG} + k_{QT}[O_2])\, n_T ,$$

where k_{ST} is the intersystem crossing rate from the first excited singlet to the triplet state, k_{TG} is the deactivation rate of the triplet state in the absence of oxygen, k_{QS} and k_{QT} are the quenching constants of the excited singlet and the triplet state, respectively, while $[O_2]$ is the concentration of oxygen in the solution. The latter is a function of the partial pressure of oxygen in the gas mixture bubbling through the solution. With the help of solubility data for oxygen in methanol [3] it can be written as $[O_2] = 1.01 \cdot 10^{-2} \cdot p_{O_2}$, where $[O_2]$ is measured in moles/liter and p_{O_2} in atmospheres. From the literature we have $k_{ST} = 2 \cdot 10^7$ sec^{-1} for rhodamine 6G [4],

$$k_{QT} = 3.3 \cdot 10^9 \text{ l/(mole} \cdot \text{sec)},$$

and

$$k_{QS} = 3 \cdot 10^{10} \text{ l/(mole} \cdot \text{sec)}$$

for some aromatic molecules of similar size and electron structure as rhodamine 6G [5, 6]. We thus have

$$W \sim \frac{n_S}{n_T} = \frac{k_{TG} + 3.3 \cdot 10^7 \cdot p_{O_2}}{2 \cdot 10^7 + 3 \cdot 10^8 \cdot p_{O_2}} .$$

The resulting curve of W vs. p_{O_2} for $k_{TG} = 5 \cdot 10^5$ sec^{-1} is given as the solid line in Fig. 1, while the upper broken curve results with $k_{TG} = 10^6$ sec^{-1} and the lower one with $k_{TG} = 10^4$ sec^{-1}. Since k_{TG} is the reciprocal of the triplet lifetime without oxygen quenching, the latter is seen to lie between 1 and

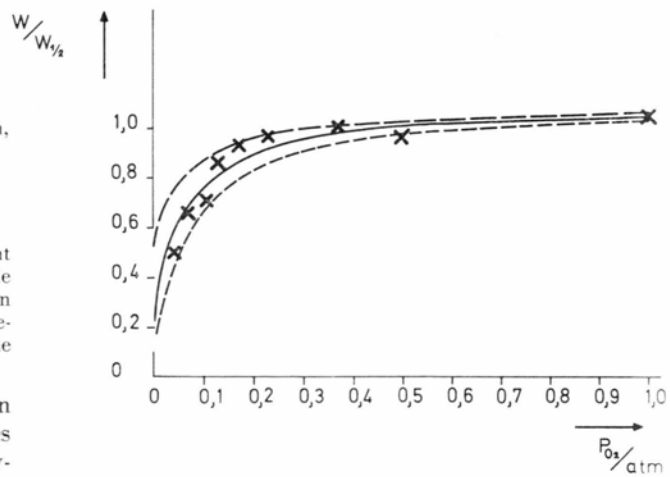

Fig. 1. Normalized laser output $W/W_{1/2}$, vs. oxygen partial pressure, P_{O_2}, in the gas mixture over the solution. Crosses: measurements; solid line: theoretical result for $k_{TG} = 5 \cdot 10^5$ sec^{-1}; upper dashed curve: same but for $k_{TG} = 10^6$ sec^{-1}; lower dashed curve: same for $k_{TG} = 10^4$ sec^{-1}.

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100 μsec, with 2 μsec giving the best fit of the experimental data. For large values of p_{O_2} the ratio n_S/n_T reaches the asymptotic value 1/9. However, even at $p_{O_2} = 0.2$ atm (corresponding to air) this plateau is almost reached. Thus it seems neither necessary nor advisable to use higher oxygen pressures, since the presence of oxygen might enhance the photodecomposition of the dye molecules. In this respect, other triplet quenchers, using triplet-singlet energy transfer [7, 8] are to be preferred.

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Desorientierung von optisch ausgerichteten Na-Atomen durch Stöße mit gesättigten Kohlenwasserstoffen *

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Disorientation of Optically Oriented Na-atoms in Collisions with Saturated Hydrocarbons

Cross sections for collisionally induced disorientation of of the Na ($3\,^2S_{1/2}$) sublevels have been measured for the C_1–C_4 saturated hydrocarbons. The strong increase of the cross sections with the number of buffer gas electrons can be explained by using the model of spin-orbit-relaxation.

Die Relaxation von Alkali-Atomen, die im $^2S_{1/2}$-Grundzustand optisch gepumpt sind, kann durch Stöße mit der Wand, mit gleichartigen Atomen sowie Fremdatomen verursacht werden. Besonders die Desorientierung durch Edelgasstöße ist theoretisch und experimentell eingehend untersucht worden [1]. Danach werden zwei verschiedene Wechselwirkungen vorgeschlagen, um die Spin-Relaxation zu erklären: Einmal die Kopplung des orientierten Elektronenspins mit dem relativen Bahndrehimpuls der beiden Stoßpartner und zum anderen der Spin-Austausch zwischen dem orientierten Elektronenspin des Alkaliatoms und dem Kernspin des Fremdgasatoms [2]. Für die gemessenen Desorientierungsquerschnitte kann auf Grund dieser beiden Mechanismen die richtige Größenordnung, die Änderung mit der Elektronenzahl des Stoßpartners sowie der Unterschied von He_3 und He_4 befriedigend gedeutet werden [3].

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Die gesättigten Kohlenwasserstoffe sind wegen ihres chemisch inerten Verhaltens gegenüber Alkalidämpfen auch als Puffergase zu verwenden. In einem konventionellen optischen Pumpexperiment wurde die longitudinale Relaxationszeit als Funktion der Fremdgasdichte N gemessen [4]. Unter der Annahme, daß die Orientierung an der Gefäßwand verschwindet, kann die Relaxationsrate als Summe von zwei Anteilen geschrieben werden.

$$1/T = \text{const} \cdot D_0/N + \text{const} \cdot \sigma N .$$

Der erste Ausdruck beschreibt die Wandrelaxation nach der Diffusion der orientierten Alkali-Atome durch das Fremdgas, wobei D_0 der Diffusionskoeffizient ist, bezogen auf Normalbedingung (0 °C, 760 Torr). Der zweite Anteil mit dem Desorientierungsquerschnitt σ stellt die Relaxationsrate auf Grund der Fremdgasstöße dar. Durch eine Anpassung der experimentellen Werte $T(N)$ lassen sich die beiden Parameter D_0 und σ bestimmen. Die so ermittelten Werte sind in Tab. 1 zusammengestellt, wobei der Fehler für σ und D_0 maximal 15% beträgt.

Na $^2S_{1/2}$	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}
σ (10^{-24} cm^2)	0,27	7,9	21,4	71,2
D_0 (cm^2/s)	0,59	0,39	0,32	0,26

Die Diffusionskoeffizienten sind alle in der zu erwartenden Größenordnung. Sie liegen um einen Faktor 2 über den mit Hilfe der kinetischen Gastheorie berechneten Werten.

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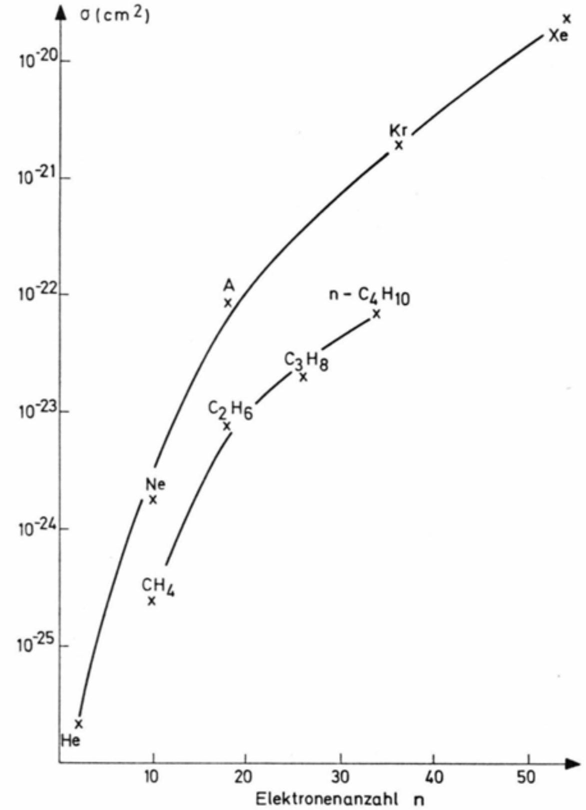

In Abb. 1 sind die Desorientierungsquerschnitte für die ersten Kohlenwasserstoffe zusammen mit entsprechenden Werten für die Edelgase eingetragen [1]. Wie nach der Spin-Bahn-Theorie zu erwarten, wächst der Querschnitt mit der Elektronenanzahl des Fremdgases. Offensichtlich folgt der Querschnitt bei den Alkanen jedoch nicht so stark der Elektronenzahl wie bei den Edelgasen. Wahrscheinlich spielt bei den größeren Molekülen die Abschirmung der Kohlenstoffelektronen durch die äußeren Wasserstoffatome eine Rolle.

Die Änderung des Querschnittes σ mit der Elektronenzahl n der Alkane läßt sich recht gut durch die Funktion $\sigma = \text{const} \cdot n^3$ wiedergeben, eine Beziehung, die mit Hilfe der Spin-Bahn-Wechselwirkung erklärt werden kann und auch für Edelgase recht gut erfüllt ist. Aus den gemessenen Querschnitten für die Alkane ergibt sich somit kein Hinweis darauf, ob eine weitere Relaxationswechselwirkung bei diesen Molekülen vorliegt. Dagegen sind bei einigen Fremdgasen mit permanentem elektrischen Dipolmoment (NH_3, CO) für die Rb-Relaxation erstaunlich große Querschnitte ermittelt worden, die zu einer Diskussion von elektrostatischen Wechselwirkungen führten [5]. Theoretische Überlegungen schließen eine direkte elektrostatische Relaxation aus, doch ist eine experimentelle Prüfung wünschenswert. Untersuchungen zu dieser Frage sind im Gange.

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Dissociative Excitation and Ionization Excitation in N_2O with Synchrotron Radiation

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The formation of N_2O^+ ($\tilde{A}\,^2\Sigma^+$) from N_2O by photons is strongly influenced by the Rydberg states $3p\pi$ and $4p\pi$ converging to $\hat{C}\,^2\Sigma^+$. N($3s\,^4P$) can be formed by partial photodissociation of N_2O only together with metastable NO.

The absorption cross section of N_2O in the vuv is the sum of the cross sections for several processes such as ionization, ionization excitation, dissociative excitation etc. The aim of this work was to study the following processes:

$$\text{a)}\quad N_2O + h\,\nu_p \rightarrow N_2O^{+*} + e^- \;\hookrightarrow N_2O^+ + h\,\nu_s$$

$$\text{b)}\quad N_2O + h\,\nu_p \rightarrow NO + N^* \;\hookrightarrow N + h\,\nu_s$$

We used the synchrotron radiation as a light source. The intensity at the exit slit of the first monochromator amounted to about 10^9 photons/sec·Å at 600 Å; it was 10^8 photons/sec·Å at 400 Å [1]. The wavelength resolution was 3.5 Å.

In order to study process a) the fluorescence in the near uv was scanned with a second monochromator at 24 Å resolution. The signal was detected with a cooled multiplier (EMI 6256S). Process b) was measured with a LiF-window and a Bendix Channeltron. This device is sensitive to light in the

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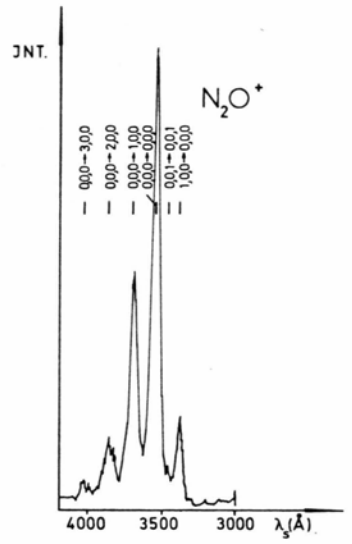

Fig. 1. Emission spectrum of N_2O^+ obtained by irradiating N_2O with 17.5 eV photons.

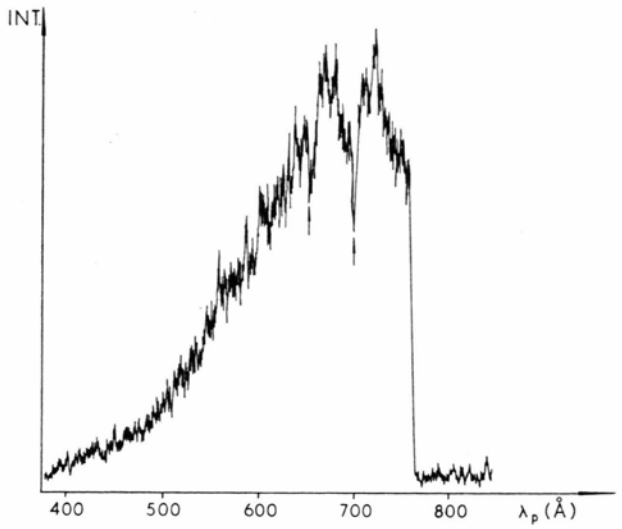

Fig. 2. Fluorescent yield of N_2O^+ ($\tilde{A}\,^2\Sigma^+(0,0,0) \rightarrow \tilde{X}\,^2\Pi_i(0,0,0)$).

wavelength region from 1050 Å to about 1300 Å. The pressure within the collision chamber was varied between 10^{-3} Torr and $5 \cdot 10^{-2}$ Torr.

Figure 1 shows a spectrum of N_2O^+ which was obtained at a primary photon energy of 17.5 eV. This radiation is due to the transition N_2O^+ ($\tilde{A}\,^2\Sigma^+ \rightarrow \tilde{X}\,^2\Pi_i$) [2]. The spectrum shows different vibrational transitions which are designated in Figure 1. The vibrational quantum numbers were determined by using photoelectron spectroscopy data [3]. Since the ground state is a doublet, every component consists of two lines which could not be resolved in our experiment [4].

Figure 2 shows the fluorescent emission at about 3550 Å as a function of the primary wavelength. It has not been corrected with respect to the intensity of the primary photons. There is a sharp structure at 700 Å and 654 Å. A similar window-structure was found in Reference [2]. In that paper the relative fluorescent yield of all lines shown in Fig. 1 was measured with a set of filters. The ground state of N_2O is $1\sigma^2 \ldots 6\sigma^2\ 1\pi^4\ 7\sigma^2\ 2\pi^4\ \tilde{X}\,^1\Sigma^+$. If the primary photon ejects a 7σ electron the excited ion N_2O^+ ($\tilde{A}\,^2\Sigma^+$) is formed. On the other hand a 6σ electron can be raised to the Rydberg orbitals $3p\pi$, $4p\pi$ [5] the energy of which coincides with the energy of the window-structure in Figure 2. Therefore this structure is due to the interaction of these Rydberg states with the corresonding continuum of $\tilde{A}\,^2\Sigma^+$ (0, 0, 0).

Figure 3 shows the fluorescent radiation in the wavelength region from 1300 Å to 1500 Å as a function of the primary wavelength. Since the primary photon intensity falls off from 800 Å to 600 Å [1] the cross section has its largest values at the two broad maxima between 600 Å and 400 Å.

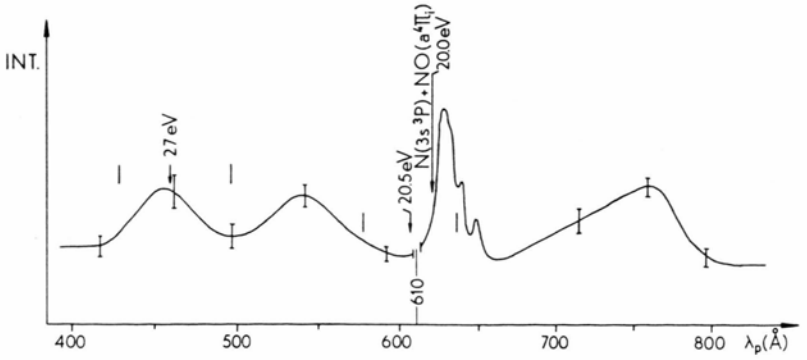

Fig. 3. Radiation produced in the dissociative excitation of N_2O. The measurements was interrupted at 610 Å. Correction: The excited state of N is N(3s ^{4}P).

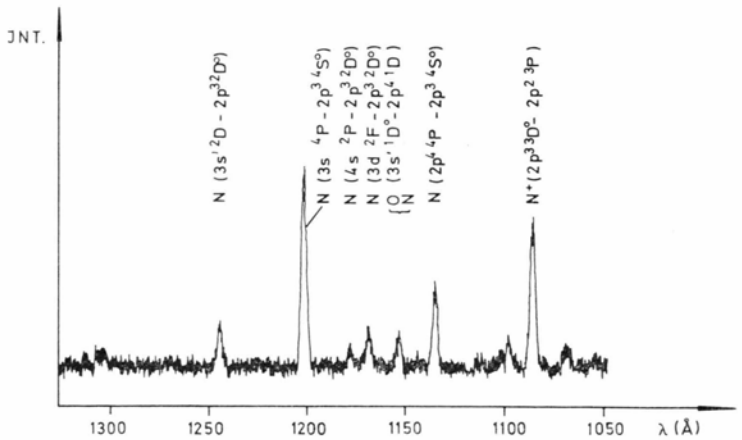

Fig. 4. Vacuum ultraviolet spectrum obtained by electron impact on N_2O.

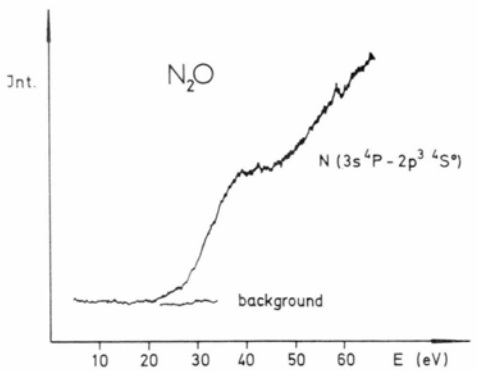

Fig. 5. Electron excitation function of $N(3s\,^4P \rightarrow 2p^3\,^2D^0)$.

Figure 4 shows the spectrum between 1300 Å and 1050 Å obtained by bombardment of N_2O with 158 eV electrons. The apparatus for this experiment is described in Reference [6]. According to the selection rules every line which is excited by photons must also appear in the electron collisional process. Since the appearance potential of the state N^+ ($2p^3\,^3D^0$) amounts to 40 eV this line cannot give a contribution to the radiation shown in Figure 3. The electron excitation function of the state N ($3s\,^4P$) is given in Figure 5. It has critical potentials at 20.5 ± 1 eV and 27 ± 2 eV. The values are marked in Figure 3. Thus we can assume that the structure shown in Fig. 3 is due to the transition $N\,(3s\,^4P \rightarrow 2p^3\,^4S^0)$ which is the most intense line in Figure 4. Since the state N ($3s\,^4P$) appears in the photodissociation process the transition from the ground state $N_2O\,(\tilde{X}\,^1\Sigma^+)$ to the repulsive molecular state must be optically allowed. At 20.5 eV the energy is not sufficient for total dissociation of N_2O and additional excitation of N ($3s\,^4P$). On the other hand the NO molecule cannot be in a doublet state since the combination of a doublet and a quartet does not result in a singlet state. The NO molecule can only be in one of the quartet states $a\,^4\Pi_i$ or $b\,^4\Sigma^-$. It follows from the Wigner-Witmer correlation rules that the repulsive state of N_2O must be $^1\Sigma^+$ or $^1\Pi$. The formation of N ($3s\,^4P$) can be written:

$$N_2O\,(\tilde{X}\,^1\Sigma^+) + h\nu_p \rightarrow N_2O^*\,(^1\Sigma^+ \text{ or } ^1\Pi) \rightarrow N^*\,(3s\,^4P) + NO^*\,(a\,^4\Pi_i \text{ or } b\,^4\Sigma^-) \rightarrow N\,(2p^3\,^4S^0) + h\nu_s\,(1200\,\text{Å}).$$

The minimum energies required for N ($3s\,^4P$) + NO ($b\,^4\Sigma^-$) and NO ($a\,^4\Pi_i$) are 21.1 eV and 20.0 eV. It follows from Fig. 3 that the repulsive potential curve of N_2O ($^1\Sigma^+$ or $^1\Pi$) crosses the FC region between about 20.5 eV and 24.5 eV and may have a minimum at larger distances. The measurement implies that N ($3s\,^4P$) is formed together with metastable NO and the kinetic energy of the dissociation products has an upper limit of about 4 eV. By similar considerations it follows that the maximum at about 460 Å in Fig. 3 is most probably due to total dissociation

$$N_2O\,(\tilde{X}\,^1\Sigma^+) + h\nu \rightarrow N^*\,(3s\,^4P) + O + N.$$

The oxygen and nitrogen atoms may be in one of the states

$$O\,(^3P) + N(^4S^0),\quad O\,(^3P) + N(^2D^0),\quad O\,(^1D) + N(^4S^0).$$

A more extensive report will be given in a later paper.

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