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IR MULTIPLE-PHOTON FLUORESCENCE EXCITATION AND DISSOCIATION OF ELECTRONICALLY EXCITED NO_2

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The absorption of up to six CO_2-laser photons by excited NO_2 has been observed. The dissociation product NO has been detected by laser induced fluorescence The NO produced after 435.7 nm excitation and IR absorption of NO_2 has been studied no internally hot NO is found, confirming that the dissociation of NO_2 is a rapid process.

1. Introduction

The infrared (IR) multiple-photon excitation and dissociation (MPD) of polyatomic molecules has been in the past years increasingly the subject of intensive studies, experimentally and theoretically [1]. Dividing the MPD process, as is commonly done, into three energy regions, most information has been acquired about the excitation in the first region (I) of discrete energy levels and about the fragmentation mechanism in the third region (III), above the dissociation limit Much less is known about the excitation mechanism and energy distribution in the intermediate region (II) of quasi-continuum energy states. In this paper we wish to report a type of experiments which eventually may be suited to obtain further information about details of the process in region II as well as I and III.

In most investigations the pumping has been performed by intense infrared radiation of CO_2 laser at single wavelengths. Some investigations have been performed with excitation at two IR wavelengths. In few experiments dissociation has been achieved by multiple-photon absorption of CO_2-laser light followed by visible/ultraviolet absorption.

In this work we have performed multiple-photon excitation and dissociation of NO_2, by the succession of a one-photon absorption into an excited state below the dissociation limit followed by IR multiple-photon absorption. This leads either to a shift in the fluorescence spectrum of the parent molecule to shorter wavelengths or further to dissociation enabling direct detection of the fragment, NO, by laser excitation spectroscopy. In this paper we report first observations and measurements on both effects.

We have chosen the NO_2 molecule for various reasons. (1) as a triatomic it belongs to the simplest possible class of polyatomic molecules; (2) although the electronic spectrum at room temperature is very complex [2] the level density at high energies (e g. $0.5/cm^{-1}$ close to the dissociation limit) [3] is comparable to that of larger molecules at much lower energies; (3) the initial starting level for the IR pumping can, at least in principle, be selected by the wavelength of the visible photon; (4) the electronic excitation as well as the fluorescence lies in an experimentally convenient region, as compared to the IR region, (5) the process can be followed into the dissociation region in great detail by laser induced fluorescence spectroscopy of the NO fragment; (6) probing for the fragment recoil energy [4,5] provides the possibility of a complete analysis of the dynamics of the dissociation process.

2. Experimental

Nitrogen dioxide was taken from a cylinder (Messer Griesheim) purified by bubbling oxygen through the liquid at temperatures below 0°C and by degassing the solid several times at temperatures between –40°C and –196°C. During the experiments the NO_2 was kept at a temperature of –45°C and the vapour was pumped through a fluorescence cell at a speed such that the content of the cell volume was replenished between the laser pulses Experiments have been made at pressures between 0.5×10^{-6} and 10×10^{-6} bar in the cell, measured by a capacitance manometer.

Two different wavelengths have been used to excite the NO_2 the second harmonic of a Nd : YAG laser at 532 nm (pulse length 8 ns, pulse energy 5 mJ, 10 Hz repetition rate) and the stimulated first anti-Stokes Raman radiation at 435.7 nm (1 mJ pulse energy) produced by the 532 nm radiation in a high pressure (10 bar) Raman cell filled with hydrogen [6]. The diameter of these visible excitation beams was 2–4 mm in the centre of the fluorescence cell. The infrared excitation was carried out with radiation from a line tunable pulsed multimode TEA CO_2 laser focused by a (f = 151 mm) NaCl lens into the centre of the interaction chamber. The CO_2 laser pulse had a main peak of 200 ns duration and a tail of ≈1 μs. Its begin was time-delayed by usually 50 ns with respect to the visible excitation pulse. The two laser beams intersected each other at an angle of 60°. The detection, either of the NO_2 fluorescence directly or of the NO fragment by laser induced fluorescence, was started 1 μs after the visible laser pulse.

In the experiments on (VIS + IR) excitation of the NO_2 fluorescence the emission from the centre of the cell was collected by an optical system (f/2.5), wavelength selected through various interference filters (fwhm ≈600 cm^{-1}) and detected by a cooled photomultiplier (RCA 31034) Pulses from the photomultiplier were amplified and stored in a gated counter for a preselected number of laser pulses. Although the radiative lifetime of the observed fluorescence is several 10 μs the gate of the counter was opened for only 1 μs to avoid the influence of collisions.

In the experiments on the (VIS + IR) dissociation of NO_2 the product NO was detected by laser induced fluorescence (LIF) [5,7] using the frequency doubled output of a dye laser which was pumped by the third harmonic of a Nd:YAG laser. The levels $v'' = 0, 1$ have been probed by excitation of the NO ($A\,^2\Sigma^+$–$X\,^2\Pi$) system in the ultraviolet. The red-shifted NO fluorescence was detected through an interference filter (λ_{max} = 260 nm) by the same photomultiplier and counting system mentioned above. NO excitation spectra have been measured by scanning the dye laser wavelength with a stepping motor. The accumulated count rate of 20 laser pulses is converted into an analog voltage and recorded.

3. Results and discussion

3.1. *Fluorescence excitation of NO_2*

In the experiments on the NO_2 fluorescence we have worked at the visible wavelength λ_{VIS} = 532 nm (18797 cm^{-1}). Fig. 1 shows the spectral distribution of the NO_2 fluorescence obtained after the successive absorption of the 532 nm radiation followed by the CO_2-laser light, once of 949.5 cm^{-1} (round dots) and once of 1046.8 cm^{-1} (squares). The CO_2-laser pulse energy was 1 J/pulse in both cases. Signals have not been corrected for the spectral response of the photomultiplier. Also shown (open circles) is the fluorescence signal measured when the CO_2-laser light was blocked in front of the fluorescence cell. This signal is thus caused by the 532 nm radiation alone. Its spectral extension into the region of wavelengths shorter than 532

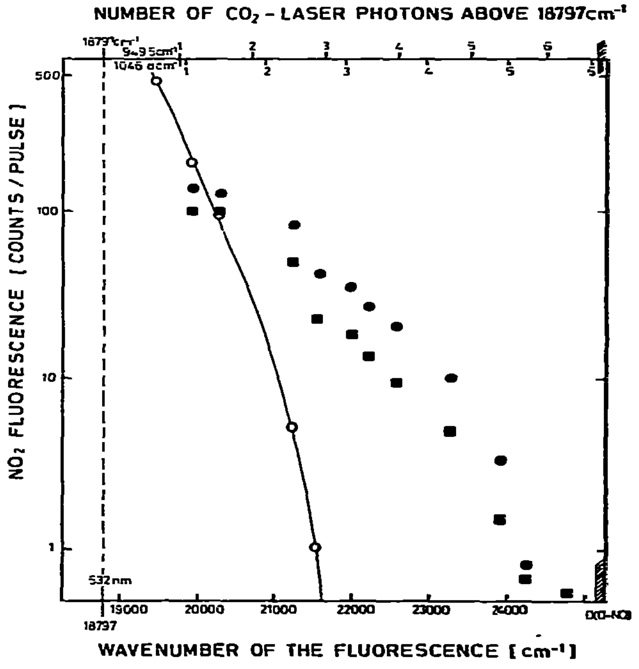

Fig. 1. Fluorescence of NO_2 excited by (1 VIS + n IR)-photon absorption. Spectral fluorescence distribution produced by 532 nm alone (open circles); fluorescence enhancement by CO_2-laser radiation of 1046.8 cm^{-1} (full squares) and 949.5 cm^{-1} (full circles). CO_2-laser energy: 1 J/pulse. NO_2 pressure: 5×10^{-6} bar at signals smaller than 10 counts/pulse, 0.5×10^{-6} bar at higher signals.

nm is to a large extent due to the broad transmission characteristics (fwhm 600 cm^{-1}) of the interference filters used and to a smaller part due to some contribution from the spread of thermal population of NO_2 in the ground state at room temperature. The CO_2-laser radiation however clearly causes fluorescence shifted towards wavelengths shorter than that of to the visible excitation It in fact extends up to the dissociation limit D(O–NO) of 25125 cm^{-1} [8], indicated in fig. 1. The numbers of CO_2 photons corresponding to the energy gap from the visible excitation wavelength to the dissociation limit are indicated in the upper scale of fig. 1 for the two IR wavelengths.

The CO_2-laser line at 949.5 cm^{-1} is evidently more effective in exciting the blue-shifted fluorescence than is the 1046.8 cm^{-1} line, although the single photon energy is smaller. Experiments at other than these two CO_2 laser lines confirmed this trend, namely that the lines below 1000 cm^{-1} are more effective than the shorter wavelength lines. A possible explanation for this behaviour could be that the lower energy lines are closer to a vibrational frequency in excited NO_2. This would be consistent with Douglas and Huber who have found a vibrational spacing of $\Delta G' = 890$ cm^{-1} in the blue region of the absorption spectrum.

The collision free nature of the whole pumping process and of the fluorescence within the time interval of observation (≈ 2 μs) was checked by measuring the pressure dependence of the fluorescence at 23250 cm^{-1} (filter peak transmission). The result was a linear increase with NO_2 pressure in the range from 0 5 to 18 μbar.

Fig. 2 shows the CO_2-laser energy dependence of the fluorescence intensity observed at 22000 cm^{-1} (filter peak transmission). Saturation occurs at a CO_2-laser pulse energy of about 0 5 J which corresponds to a fluence of the order of 25 J/cm^2. The same qualitative behaviour has been found for the fluorescence at other wavelengths 22570 cm^{-1} and 23250 cm^{-1}. As to the dependence of the CO_2-laser enhanced fluorescence on the intensity of the 532 nm light, measurements for instance at 23250 cm^{-1} showed that it increased linearly with intensity up to 3.5 mJ pulse energy.

The decrease of the fluorescence intensity at shorter wavelengths might be explained by a bottleneck effect, i.e. a decrease of IR absorption cross section as the energy increases towards the dissociation limit. However, with the present experimental results it is not possible to relate the observed intensity distribution to a NO_2 population distribution at corresponding excitation energies. For this one would need to observe resolved fluorescence spectra from the energy levels populated by the IR excitation. Furthermore, the excitation by the visible photons produces a distribution of excited rovibronic states because one starts already with the thermal population distribution of NO_2 in the ground state which means, in turn, that the IR absorption also starts from a correspondingly undefined energy. Experiments with defined and selected initial states of the parent molecule and with higher spectral resolution of the emission are in progress.

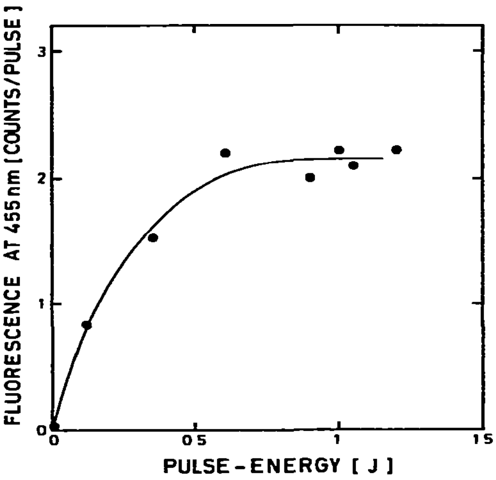

Fig 2 Dependence of the fluorescence enhancement observed at 455 nm (22000 cm^{-1}) on CO_2-laser pulse energy. Visible excitation wavelength 532 nm, CO_2-laser line 949.5 cm^{-1}

Herman et al. [9] have performed IR–optical double resonance experiments in NO_2, using cw lasers. They found evidence that at the wavelengths of the Ar-ion laser very short lived (0.6 ± 0.2)μs levels are participating We have found that the major part (more than 95%) of the CO_2-laser enhanced fluorescence at 443 nm is not sensitive to the time delay between excitation laser (532 nm) and CO_2-laser pulse in the range from 50 ns to 2 μs. So, most excited states populated by 532 nm radiation which participate in the CO_2-laser photon absorption have longer lifetimes.

3.2. *Dissociation of NO_2*

Dissociation experiments have been carried out with two visible wavelengths: 435.7 nm (22952 cm^{-1}) and 532 nm (18797 cm^{-1}) and with two CO_2-laser lines: 1046.8 cm^{-1} and 944.2 cm^{-1}.

435.7 nm. After the excitation by 435.7 nm radiation the NO_2 has to absorb a minimum of two additional CO_2 laser photons in order to reach the dissociation limit of 25125 cm^{-1} [8]. An energy defect of 79 cm^{-1} for the 1046 8 cm^{-1} line can be compensated for most of the NO_2 molecules by their thermal internal energy. For the 944.2 cm^{-1} line the energy defect of 285 cm^{-1} can be compensated of course by correspondingly fewer NO_2 molecules in the upper half of the rovibronic room temperature distribution. Those with less initial internal energy need three additional IR photons.

Fig. 3 shows in the upper part (A) an excitation spectrum of NO from the vibrational ground state ($v'' = 0$) obtained with the 435.7 nm radiation followed by radiation of 944.2 cm^{-1} at a CO_2-laser energy of 1 J/pulse The lower part (B) of fig. 3 also represents an NO ($v'' = 0$) excitation spectrum taken, however, without irradiation by the CO_2-laser light, i.e. by 435.7 nm alone. This background NO spectrum is due to No present as an impurity in the NO_2 sample at a concentration of the order of 0.2%. The same NO excitation spectrum was obtained also without the 435.7 nm light. Comparison of the signal strengths shows that the background spectrum (B) is weaker than (A) by about an order of magnitude. Taking the impurity to be 0.2% this indicates that at least 1% of the NO_2 in the crossing region of the three laser beams was dissociated.

As to the rotational energy distribution of the NO fragment, the spectral distribution of spectrum (A) is similar to that of spectrum (B), indicating that the NO fragment is produced with roughly room temperature rotational distribution in the $v'' = 0$ state. The excitation by the CO_2-laser radiation did not produce NO in the excited vibrational state $v'' = 1$. By comparing the fluorescence intensity of the thermal excitation spectrum from $v'' = 1$ of the impurity NO with the noise

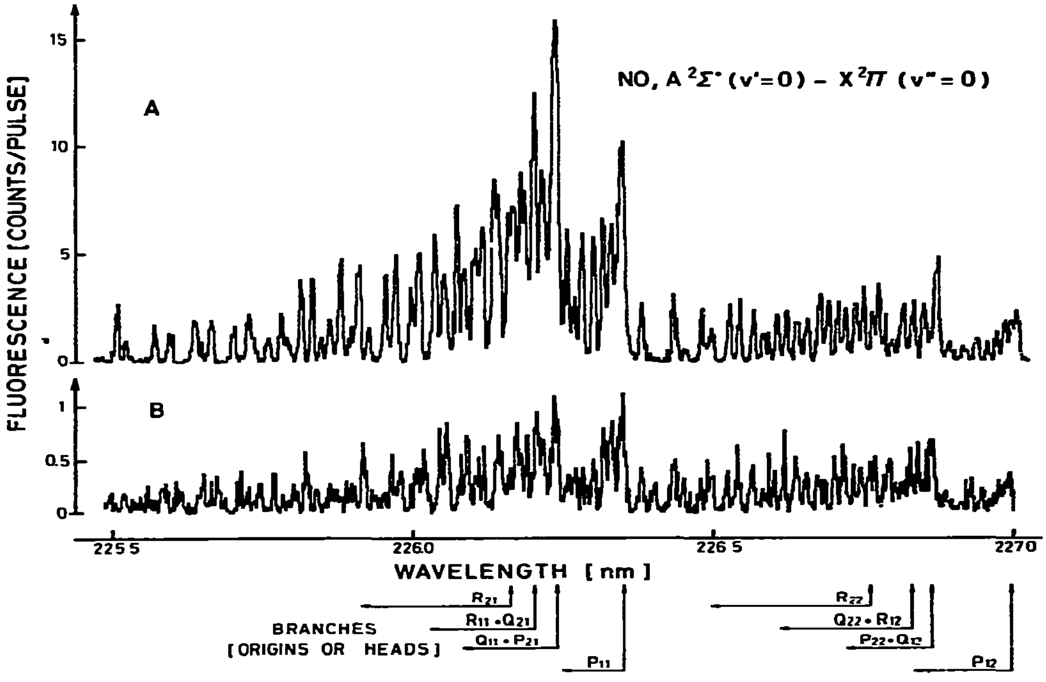

Fig. 3. NO_2 dissociation by (1 VIS + *n* IR)-photon absorption. Excitation spectra of NO($A\,^2\Sigma^+$, $v' = 0 \leftarrow X\,^2\Pi$, $v'' = 0$). Upper spectrum (A). NO_2 irradiated by 435 7 nm (energy 1 mJ/pulse) plus CO_2-laser light at 944.2 cm^{-1} (energy 1 J/pulse), NO_2 pressure 3×10^{-6} bar. Lower spectrum (B) NO background excitation spectrum. Conditions as in (A), however without CO_2-laser irradiation.

level it was possible to estimate an upper limit of the relative dissociation yield of about 10^{-5} for NO ($v'' = 1$) to NO ($v'' = 0$). The thermal rotational distribution of NO in $v'' = 0$ and the virtual absence of vibrationally excited NO is consistent with the commonly accepted MPD mechanism according to which the dissociation is explained by the RRKM model with statistical energy distribution. Because of the few degrees of freedom of the molecule the dissociation rate of NO_2 after absorption of up to one CO_2-laser photon above the dissociation limit is so large (10^{11}–10^{12}) s^{-1} [3,10] that the probability of absorption of another photon is very small at the intensities applied (10^{28} photons s^{-1} cm^{-2} by order of magnitude) If more CO_2 photons were absorbed one would expect internal excitation of NO.

To ascertain the collisionless nature of the (VIS + IR) dissociation process the dependence of the NO laser excited fluorescence intensity on the NO_2 pressure was measured. Fig. 4 shows results obtained from measurements at the intense NO lines in the head of the P_{11} branch (fig. 3). The slight deviation from linearity at pressures higher than 5×10^{-6} bar is partly caused by the beginning of saturation of the pulse counting system. When less intense NO lines were used linear dependence was observed up to about 10^{-5} bar.

Fig. 5 shows the CO_2-laser fluence dependence of the NO production for two different CO_2-laser lines. Both curves show saturation and the "threshold" seems to be lower for the 1046.8 cm^{-1} line. As mentioned above, for this line the energy defect for VIS + 2 IR photon-dissociation is smaller, so almost the whole thermal NO_2 distribution can in principle be dissociated by 1 VIS + 2 IR photons, whereas in the case of the 944.2 cm^{-1} line a considerable part of the thermal rotational distribution needs 1 VIS + 3 IR photons for dissociation.

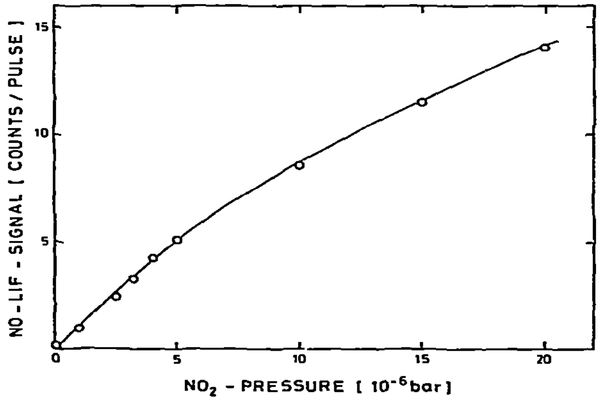

Fig. 4. NO_2 pressure dependence of the NO dissociation yield, measured by the LIF intensity of NO excited in the P_{11} band head. Visible excitation at 435 7 nm, CO_2-laser line 1046 8 cm^{-1}.

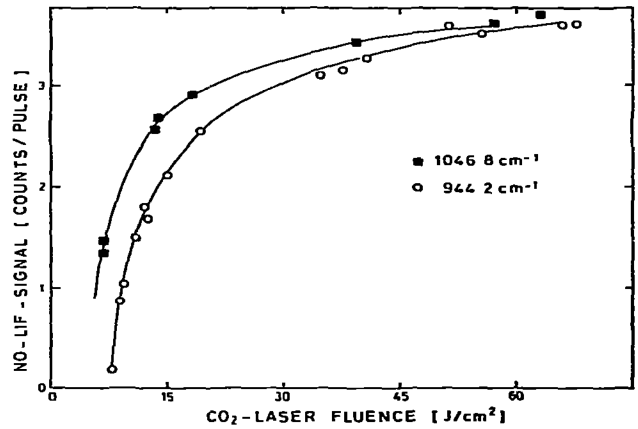

Fig. 5 CO_2-laser fluence dependence of the NO dissociation yield measured as under fig. 4. Visible excitation at 435.7 nm (22952 cm^{-1}), CO_2-laser lines at 1046.8 cm^{-1} and 944 2 cm^{-1}.

The dissociation by 1 VIS + (2–3) IR photons shows the same saturation character as the blue-shifted fluorescence after 532 nm excitation, described above (fig. 2)

532 nm. The dissociation yield with 532 nm excitation was found to be smaller than with 435.7 nm by about a factor of 20. In order to observe NO at this smaller density the background spectrum level of NO had to be lowered to reach higher sensitivity This was achieved by reducing the spot size of the probing laser beam and by more precise alignment of the detection system with respect to the effective fluorescence volume, so that NO fluorescence originating from outside this volume was more effectively eliminated.

Fig. 6 shows the CO_2-laser energy dependence of the NO yield for the two CO_2-laser lines. As with 435.7 nm the IR line with the higher photon energy is again more efficient than that with the lower energy. This behaviour is opposite to that observed for fluorescence excitation (fig. 1). A pronounced difference is observed in the slopes of the fluence dependence for the two visible excitation lines. Before speculating about the cause, more systematic measurements are needed.

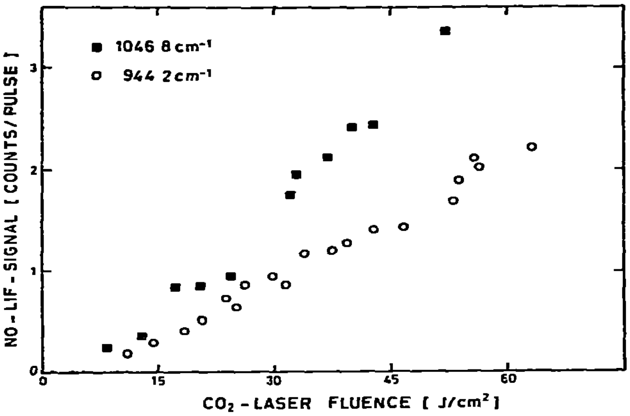

Fig. 6 CO_2-laser fluence dependence of the NO dissociation yield, measured as under fig. 4. Visible excitation at 532 nm (18797 cm^{-1}), CO_2-laser lines at 1046.8 cm^{-1} and 944.2 cm^{-1}.

The pressure dependence measured with a CO_2-laser energy of 1 J/pulse was again found to be linear up to 10^{-5} bar of NO_2. Also the dependence of the NO yield on the intensity of the 532 nm radiation was measured to increase linearly up to an energy of 5 mJ/pulse, which for a beam diameter of 3 mm^2 and 8 ns pulse duration corresponds to an intensity of about 20 MW/cm^2. When the 532 nm intensity was increased by focusing to a spot size of less than 1 mm^2 NO_2 dissociation into NO + O by two-photon absorption was observed.

4. Conclusions

Experimental evidence is presented that NO_2 excited by 532 nm radiation can absorb up to six or seven IR CO_2-laser photons.

From the rotational and vibrational distribution of the NO produced by (1 VIS + 2 IR) dissociation of NO_2 one can conclude that the dissociation process is very fast.

The method of preparing molecules in excited states, before multiple IR photon dissociation starts, offers some advantages for a more detailed study of IR excitation and dissociation: (a) One can follow the way of excitation by observing visible fluorescence. (b) By choosing the proper wavelengths of the visible radiation one can change the minimum number of IR photons necessary for dissociation.

References

[1] K L. Kompa and S.D. Smith, eds., Laser-induced processes in molecules (Springer, Berlin, 1979).
[2] D.K. Hsu, D L. Monts and R.N. Zare, Spectral atlas of nitrogen dioxide, 5530 A to 6480 A (Academic Press, New York, 1978).
[3] K H. Becker, W. Groth and D. Thran, Chem. Phys. Letters 15 (1972) 215.
[4] R. Schmiedl, R. Böttner, H Zacharias, U. Meier and K.H. Welge, Opt. Commun. 31 (1979) 329.
[5] M. Geilhaupt, Diplomarbeit, Bielefeld (1979).
[6] V. Wilke and W. Schmidt, Appl. Phys. 16 (1978) 151; 18 (1979) 177.
[7] H. Zacharias, A. Anders, J.B. Halpern and K.H. Welge, Opt. Commun. 19 (1976) 116.
[8] A E. Douglas and K P. Huber, Can. J. Phys. 43 (1965) 74.
[9] I P. Herman, A. Javan and R.W. Field, J. Chem. Phys. 68 (1978) 2398.
[10] H. Gaedtke, H. Hippler and J. Troe, Chem. Phys. Letters 16 (1972) 177.