FLUORESCENCE ANALYSIS OF LASER PRODUCED RADICALS AND ATOMS

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#### SUMMARY

The IR-MPD of  $C_2^{+}H_4$  and  $C_2^{+}H_5^{-}CL$  leads to  $C_2^{-}$ radicals in electronic excited states  $(0^3 \ \mbox{m}\ g)$  and electronic ground state  $(a^3 \ \mbox{m}\ u)$ . Treating the measured fluorescence of the  $C_2^{-}$ radicals in the visible range as a measure for the radical concentration, we have found that the radical concentration depends quadratically on the laser fluence and with the power of 2 on the parent gas pressure. The addition of buffer gas Xe leads to an enhancement of the radical concentration due to rotational relaxation. By UV-photolysis of Mo(CO)<sub>6</sub> neutral Mo-atoms are produced (at 308 nm as well as 248 nm). The intensity dependences of the fluorescence of the excited Moatoms indicate direct 2-photon absorption at 248 nm and 3-or 4 photon absorption at 308 nm. An upper limit of the dissociation energy is estimated to be  $E_{diss} = 5.6 \text{ eV}$ .

#### 1. INTRODUCTION

With the development of the  $CO_2$ -Laser, espescially the TEA-CO $_2$ laser the idea of inducing chemical reactions was born. /l/ On the basis of infrared multiphoton excitation and dissociation of polyatomic moleculs reaction products like radicals, atoms and ions are obtained depending on the excitation process. /2/ We are espescially interested in the C2-radical generation from carbon hydrogen molecules, e. g.  $C_2H_4$  and  $C_2H_5Cl$ . The  $C_2$ -radicals are produced in the electronic ground state as well as in electronic excited states. Thats why it is possible to detect them by means of fluorescence spectroscopic measurements in the visible region. In the last years in an extented way, also UV-excimer laser are used to dissociate molecules via multiphoton absorption processes. We are interested in the photolytic decomposition of organometallic compounds in the gas phase, e. g.  $Mo(CO)_6$ . The linear absorption cross section of the hexacarbonyls(Mo(CO)<sub>6</sub>, Cr(CO)<sub>6</sub>, W(CO)<sub>6</sub>) at the different laser wavelengths (308 nm, 248 nm) are well known. /3/ Focusing the laser beam into the cell, filled with the Mo(CO), at vapour pressure, a fluorescence is observed. The investigation of this fluorescence shows that neutral Mo atoms are produced in electronic excited states.

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## 2. EXPERIMENTAL SETUP

The Laser (a TEA-CO<sub>2</sub>-laser, E = 800 mJ/pulse for IRMPD-experiments, a Lambda Physics 1003i excimerlaser for UV-photolysis) is focused by a lens with f  $\sim$  80 mm into the reaction cell. The fluorescence signal in the focal region is detected perpendiculary to the laser beam by meams of monochromator and multiplier. A suitable diaphragm in front of the monochromator is used to select the focal volume where the fluorescence is detected.

The reaction cell was evacuated down to  $10^{-3}$  Pa and filled with  $C_2H_5Cl$  or  $C_2H_4$  (up to 10 kPa) in the case of IRMPD or with Mo(CD)<sub>6</sub> vapour pressure (about 12 Pa) at room temperature.

## 3. FLUORESCENCE MEASUREMENTS AND INTERPRETATION

# 3.1. IR-Excitation

In the case of  $C_2H_4$  many efforts had been made to study the mpd process and the radical production in the collisionless manner. /e. g. 4/ We investigate the MPD of  $C_2H_4$  and  $C_2H_5Cl$  and  $C_2H_5Cl$  with the intention of  $C_2$ -radical production at higher pressures (p  $\sim$  10 kPa). The upper limit of the pressure is given by the appearance of the laser spark depending on the laser fluence  $\oint$ . We identify the  $C_2$ -radicals by detection of Swan-band in the spontaneous emission spectrum.

Because of the nature of the mpd process starting with resonant absorption steps and climbing the vibrational ladder and the energy level structure of the moleculs (anharmonicity) the wavelength dependence of the dissociation process was investigated in the range of the  $CO_2$ -laser emission spectrum. Some laser lines (IOP(10) for  $C_2H_4$ , IOR(6) for  $C_2H_5CI$ ) are favoured in the dissociation process, leading to the maximum of  $C_2$ -fluorescence.

Both molecules dissociate into  $C_2$ -radicals /5/ in the case of  $C_2H_5C1$  the stable products HC1 and  $C_2H_4$  are formed. /6/ For the fluence dependence of the radical concentration we found from low up to high (300 J/cm<sup>2</sup>) fluence.

$$C_2 \sim \oint 2 \dots 2, 3 \tag{1}$$

For very low pressures (p < 30 Pa) the C<sub>2</sub>-production process takes place without collissions for C<sub>2</sub>H<sub>4</sub> /7/ and also for C<sub>2</sub>H<sub>5</sub>Cl. Higher pressures lead to increasing C<sub>2</sub>-concentration in the form

$$C_2 \sim p^2$$
 (30 Pa  $\langle p \langle 8 k Pa \rangle$  (2)

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Fig. 1: Intensity dependence of the spontaneous fluorescence on laser fluence at different pressures of  $\rm C_2H_5Cl$ 



Fig. 2: Pressure dependence of the  $C_2(d^3 \pi g)$  concentration (spontaneous fluorescence) for dissociation of  $C_2H_4$ (10P(10)  $CO_2$ -laser line) and for dissociation of  $C_2H_5Cl$ (10R(6)  $CO_2$ -laser line)

The quadratic behaviour has its reason at first in the  $increasin_g$  number of molecules (as the pressure increases) and second in the effect of the rotational relaxation process. This process leads to an increasing number of molecules taking part in the excitation process because of better resonance conditions after changing the

energy state. The rotational relaxion process takes part between the  $C_2H_4$  or  $C_2H_5Cl$  molecules and is also effected by buffer gases like Xe. Hence the addition of buffergas leads to a higher  $C_2$ production, too. As maximum deposition rate of carbon 0,1 Å/pulse is achieved. (laser fokus in parallel adjustment to substrate)

# 3.2. UV-Excitation

Irradiating  $Mo(CO)_6$  vapour by focused excimer laser (XeCl, KrF) a fluorescence in the visible spectral range exists. We studied the fluorescence spectrum in the laser focus.



Fig. 3: Spectrum of spontaneous fluorescence of Mo(CO)<sub>6</sub> dissociation at 248 nm (Insert: Assigned Mo I transitions according to /10/)

Despite of the moderate spectral resolution the main lines of the two characteristic groups at 550 nm and 425 nm can be assigned unambigiously as lines of neutral Mo-atoms. The energy dependence of the fluorescence signal at 425 nm is given in fig. 4

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Fig. 4: Fluorescence intensity at 425 nm as a function of the laser energy E<sub>F</sub> (or the intensity I<sub>F</sub>) in the laser focus at different distances x from the laser focus

In the unsaturated region the slope 2 indicates the process characteristic, i. e. two photons have enough energy to dissociate the  $Mo(CO)_{6}$  completely and to form the Mo-atoms in electronic excited states. The saturation of the fluorescence starts at different laser energies depending on the beam diameter determined by the distance x between the locally probed fluorescence region and the focus centre.

At 550 nm a analogous curve with slope 2 for the fluorescence signal has been obtained, too.

The addition of buffer gas (He,  $N_2$ ) doesn't quench the fluorescence at 425 nm and has only a small influence on the fluorescence signal. So we conclude a direct two-photon absorption mechanism for the production of the excited Mo-atoms. Otherwise intermediate states should give rise to a fluorescence quenching by collisions with buffer gas.

Taking into acount the spectra of the excited Mo-atoms we are able to estimate an upper limit for the dissociation energy  $E_{diss}$ (complete dissociation). The energy of the excited Mo-atoms is about  $E_{ex} \sim 4.4$  eV, the excited Mo-atoms are formed after absorption of 2 photons of 248 nm wavelength (h $v \sim 5$  eV). The energy balance gives an energy value of  $E_{diss} < 2$  h $v - E_{ex} =$ 5.6 eV. This value is far below 218 kcal/mol for Mo(CO)<sub>6</sub> /8/ and somewhat below the corresponding energy of 6.45 eV for  $Cr(CO)_6$ /9/. At 308 nm excitation we found that a 3 or 4-photon process leads to dissociation of Mo(CO)\_6. The maximum deposition rates on quartz substrate are 0.2 Å/pulse and 1 Å/pulse at 308 nm and 248 nm respectively. (laser focus perpendicular to substrat)

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