# STATE-SELECTED PHOTOFRAGMENTS FROM TWO-PHOTON EXCITATION OF $H_2O_2$ AT 193 nm

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The UV photodissociation of $H_2O_2$ was studied at high laser fluences Hydrogen peroxide was photolyzed with an excimer laser at 193 (ArF) and 248 nm (KrF) The state distribution of nascent fragments, $OH(A\,^2\Sigma, v', N')$, has been obtained through spectrally resolved resonance transitions of the $OH(^2\Sigma^+ \rightarrow \,^2\Pi)$ fluorescence At 193 nm a strong fluorescence from $OH(A\,^2\Sigma^+)$ was observed, while at 248 nm no electronically excited $OH(A\,^2\Sigma^+)$ was found Measurement of the fluorescence intensity as a function of laser fluence, as well as the state-resolved internal distribution of the $OH(A\,^2\Sigma^+)$, indicate a two-photon process In this dissociation process rotationally hot OH photofragments in the $A\,^2\Sigma^+$ state are generated Only the vibrational states $v' = 0$ and $v' = 1$ of $OH(A\,^2\Sigma^+)$ are populated. At laser fluences of 16 $J/cm^2$ 68% of OH(A) are formed in $v' = 0$ and 32% in $v' = 1$. The rotational distributions can be described by Boltzmann distributions with $T_{v'=0} = 4450 \pm 180$ K and $T_{v'=1} = 3560 \pm 150$ K. The two spin components in the OH photofragment are populated statistically. The fragments must be formed with high translational energy.

## 1. Introduction

The single-photon excitation of hydrogen peroxide has been studied in detail recently [1,2]. These experiments probed the fate of the ejected nascent photofragments following optical preparation of the $H_2O_2$ excited electronic state. The results obtained from high-resolution studies of the energy partitioning in the OH photofragment give a deeper insight into the dynamics of this dissociation process. It could be shown [3] that at wavelengths below 172.2 nm $OH(A\,^2\Sigma^+)$ in the first electronic excited state is formed. By dispersing the $OH(A\,^2\Sigma^+ \rightarrow X\,^2\Pi)$ resonance fluorescence the internal state distribution of the photofragments could be obtained. At $H_2O_2$ excitation wavelength of 157.8 nm the vibrational excitation of $OH(^2\Sigma^+)$ is very low (<3%) whereas the rotational excitation is extremely high [2,4]. The single-photon photolysis of $H_2O_2$ at 193 and 248 nm, the strongest emissions from the excimer laser, shows no production of electronically excited OH [1]. Instead it was found that the excess energy must mainly be converted into kinetic energy of the dissociation products leaving the OH without

any detectable vibrational, and even with very low rotational, energy.

The investigation of high electronic excited and dissociative states of $H_2O_2$ would need laser radiation in the far VUV, even below the lithium cut-off wavelength. However, very powerful laser radiation induces two-photon transitions in the hydrogen peroxide and the photofragmentation of $H_2O_2$ in high electronic excited states can be studied by the use of light sources emitting light of lower quantum energy.

For this reason, an experiment was set up in which the radiation of an excimer laser at 193 nm and also at 248 nm was focused to increase the probability of a multiphoton process. As the molecules absorb at the single-photon energy this dissociation would result from a resonant sequential two-photon absorption for which a reasonable cross section is expected. Low resolved fluorescence light of the OH $A\,^2\Sigma \rightarrow X\,^2\Pi$ transition could be observed by 193 nm excitation of $H_2O_2$ [5].

The results of the experiment reported here is described in the following where the influence of laser fluence on the multiphoton process is studied. As the

rotational excitation of the OH radical can be fully resolved, a precise and careful discussion of the rotational state distribution is possible for the $OH(^2\Sigma^+)$ in $v'' = 0$, as well as in its first excited vibrational state which is produced in the same dissociation process.

## 2. Experimental

The apparatus used for the present experiment has been described in detail [2]. Briefly, the beam from a pulsed excimer laser at 193, and also 248 nm, was focused into an aluminum cell by using a quartz lense of 150 mm focal length. A mixture of $H_2O_2$ and $H_2O$ (86% $H_2O_2$) was pumped through the cell with a pumping speed sufficient to completely exchange the detection volume between two photolysis pulses. The average laser intensity was constant during each experimental run. The maximum laser output energy was held at 400 mJ per pulse.

Fluorescence from the $A\ ^2\Sigma^+ \rightarrow X\ ^2\Pi$ transition of the OH product was observed in a direction perpendicular to the laser beam. Dispersion of the emission spectrum was provided by the use of a 0.5 m monochromator (Minuteman). In contrast to the earlier apparatus [2], an optical multichannel analyser (OSMA, Spectroscopy Instruments) was used. With this fast detection system a complete spectrum that is either the 0−0 or the 1−0 band of the A−X transition could be registered within less than one minute with a good signal-to-noise ratio. This allowed a fast test of the reproducibility of the experimental conditions and an excellent check of the high-resolution data obtainable with the scanning device. The resolution obtained with the scanning monochromator was $\Delta\lambda/\lambda = 1 \times 10^{-4}$ whereas the maximum resolution with the OSMA was about three times less.

The dependence of the total fluorescence upon the energy density of the laser light in the cell was measured by setting the monochromator at the center of the 0−0 band with both slits fully opened, which permits more than 95% of the band emission to fall on the photomultiplier cathode. When using the OSMA the integration was carried out with the computer. Both systems gave the same results. The laser intensity was varied with the help of a 5 mm diameter baffle and a set of quartz filters placed in front without changing the power supply. This arrangement guaranteed repro-

ducibility of beam conditions, which is important when multiphoton processes are studied.

$H_2O_2$ (86% purity) was kindly supplied by DEGUSSA. It was kept in a Pyrex glass reservoir mounted under the reaction cell and was cooled to 0°C by ice. Two different probes were used during the measurements, and no influence on the spectra was observed; indicating the independence of the signal from possible impurities. All spectra at high resolution were recorded at a total pressure of $7 \times 10^{-3}$ mbar. The pressure in the cell was controlled with a MKS Baratron capacitance manometer. Measurements with the OSMA at pressures up to $8 \times 10^{-2}$ mbar did not show a pressure effect on the rotational distribution.

## 3. Results and discussion

The absorption of light at 193 and 248 nm does not result in the production of excited $OH(A\ ^2\Sigma^+)$ in a single-photon process [3]. However, if the light beam at 193 nm, emerging from the excimer laser, is focused with a lense of 15 cm focal length, then UV radiation around 300 nm can be observed. All observed lines of the spectrum can be assigned to the $A\ ^2\Sigma^+ \rightarrow X\ ^2\Pi$ transition of the OH photodissociation product. Thus, in order to obtain this radiation, more than one photon is absorbed in the elementary process. The fluorescence is observed when using the 193 nm radiation but not for laser radiation at 248 nm.

For single-photon absorption in a non-saturated transition the emission intensity of the OH fragment has to be linear with the laser energy. In the case of two-photon absorption a quadratic dependence is expected. In order to prove the mechanism of the photodissociation process the OH emission has been measured for different laser fluences. As the multiphoton absorption is very sensitive on the beam characteristics, a set of filters was used to change the laser fluence instead of changing the laser power output by varying the discharge voltage of the excimer laser. Fig. 1 shows the results of the experiment demonstrating clearly a quadratic dependence.

In a simple rate model, where $k_1$ and $k_2$ are the rates of dissociation from the first and second excited $H_2O_2$ state, $k_1$ and $k_2$ are greater than the pump rates $P\sigma_1$ and $P\sigma_2$, where $P$ represents the number of
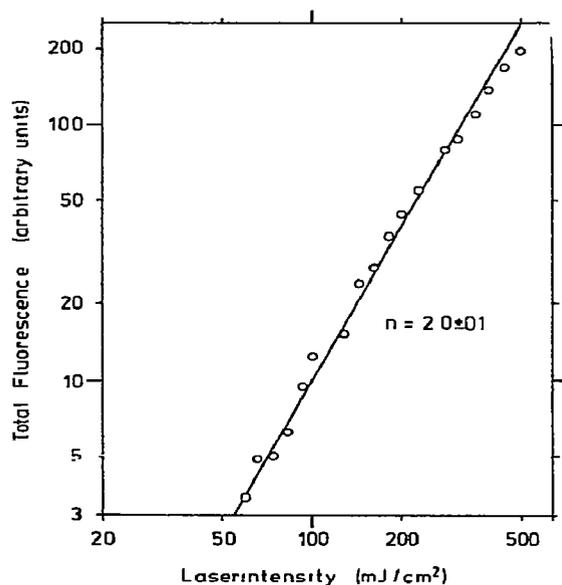
Fig. 1. Total $OH(A^2\Sigma^+ \to X^2\Pi)$ nascent photofragment emission at different laser fluences. The laser was varied by using a set of nonsaturable filters. The slope is $2.0 \pm 0.1$ as it is expected for a two-photon process. At higher fluences $H_2O_2$ is completely photolysed and the total fluorescence signal increases linear with laser fluence.

photons/$cm^2$ and $\sigma_1, \sigma_2$ the absorption cross section. The population of the two excited states $(N_1, N_2)$ of $H_2O_2$ are determined by the differential equations:

$$\dot{N}_1 = P\sigma_1 N_0 - k_1 N_1 - P\sigma_2 N_1,$$

$$\dot{N}_2 = P\sigma_2 N_1 - k_2 N_2. \tag{1}$$

The last term of $\dot{N}_1$ is very small and will be neglected in the following. During the duration of the pump pulse the change in population of $N_1$ and $N_2$ is determined by the dissociation rate. Therefore follows: $\dot{N}_1 \approx 0$ and $\dot{N}_2 \approx 0$,

$$N_2 = (\sigma_1 \sigma_2 / k_1 k_2) P^2 N_0(t). \tag{2}$$

$N_0(t)$ is the time dependent concentration of $H_2O_2$ in the ground state. The observed signal $S$ is proportional to the product $k_2 N_2$ integrated over the pulse duration $T$. If we introduce the fluence $I$ of the laser radiation by $I = PT$, then we obtain for the observed signal $S$.

$$S \propto \int_0^T k_2 N_2 \, dt$$

$$= (\sigma_1 \sigma_2 / k_1 T) P^2 \int_0^T [H_2O_2]_{t=0} \exp(-\sigma_1 Pt) \, dt, \tag{3}$$

$$S \propto [H_2O_2]_{t=0}(\sigma_2/k_1 T)I[1 - \exp(-\sigma_1 I)]. \tag{4}$$

At low laser fluences $(I < 1/\sigma_1)$ the exponential term in eq. (4) can be replaced by $(1 - \sigma_1 I)$. Thus we obtain a quadratic dependence for the signal.

$$S \propto [H_2O_2]_{t=0}(\sigma_1 \sigma_2 / k_1 T)I^2. \tag{5}$$

This quadratic dependence is only obtained at low fluences. At higher fluences $(I > 1/\sigma_1)$ the exponential term in eq. (4) vanishes and the amount of electronically excited $OH(A^2\Sigma^+)$ increases linearly with laser fluence:

$$S \propto [H_2O_2]_{t=0}(\sigma_2/k_1 T)I. \tag{6}$$

The physical reason for this behavior is that the laser light pulse photodissociates all $H_2O_2$ molecules. Between the two extreme cases represented by eqs. (5) and (6), that laser fluence $(I_S)$ for which only $1/e$ of the $H_2O_2$ molecules is left non-photolysed, is given by $\sigma_1 I_S = 1$. With the absorption cross section [6] of $6.5 \times 10^{-19} \, cm^2$ and a spot area of 2.4 $mm^2$ in the focus of the laser beam, a value $I_S = 1.5 \, J/cm^2$ or $E_S = 37$ mJ is obtained, which agrees with the experimental data.

The results from the fluence dependence of the emission intensity strongly suggest that a two-photon absorption is the promoting step of the molecular dissociation. The emission cannot be due to secondary excitation of free OH radicals which are formed in the single-photon dissociation, because the excitation of OH by 193 nm radiation would result in high excitation of the molecule which could only populate the $A^2\Sigma^+$ $v' = 0, 1$ states through subsequent relaxation. But these very highly excited levels of the $OH(A^2\Sigma^+)$ state show an extremely strong predissociation [7]. In principle, the emission could also result from impurities; however, it should be mentioned that a linear response is observed between emission and sample pressure. In addition the distribution of product states is independent of the use of samples from different purification preparation cycles. The main impurity in

the present experiment is water and, even at the highest laser fluence of 16 $J/cm^2$, no detectable amounts of $OH(A^2\Sigma^+)$ are produced by irradiating $H_2O$ at 193 nm.

We therefore conclude that the emission is in fact from the subsequent two-photon absorption of the 193 nm radiation by the parent $H_2O_2$ molecule. This latter conclusion is supported by the very recently published result of McKendrick et al. [5] which appeared in the literature after completion of the present experiment. McKendrick et al. could observe low resolved $OH(A^2\Sigma \rightarrow X^2\Pi)$ emissions. The $OH(A^2\Sigma)$ produced by two-photon dissociation of $H_2O_2$ was used to determine the rate of quenching of $OH(A^2\Sigma)$ by $H_2O_2$.

The dispersed radiation of $OH(A^2\Sigma \rightarrow X^2\Pi)$ from the two-photon absorption of $H_2O_2$ is represented by the spectra which are shown in figs. 2 and 3. Whereas
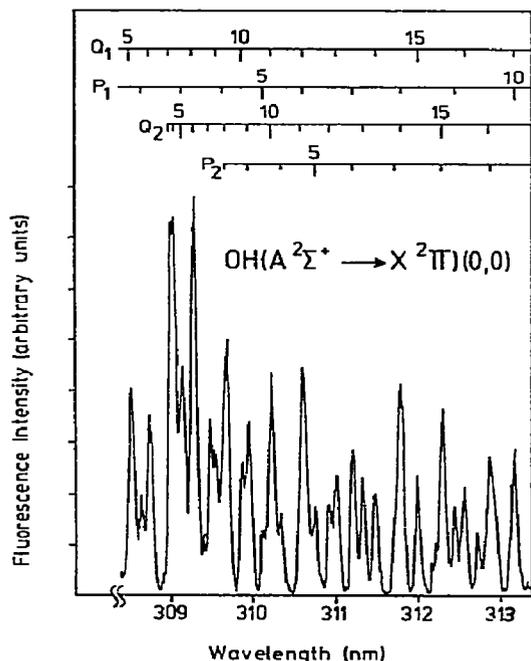


Fig. 2. $OH(A^2\Sigma^+ \rightarrow X^2\Pi)$ nascent photofragment emission spectrum from the two-photon dissociation of $H_2O_2$ at 193 nm Shown is a small section of the P and Q branches of the $v' = 0 \rightarrow v'' = 0$ band. The rotational transitions can be clearly resolved and the complete OH(A) product state distribution can be obtained. Experimental conditions: $7 \times 10^{-3}$ mbar $H_2O_2$ and a laser fluence of 8 $J/cm^2$.
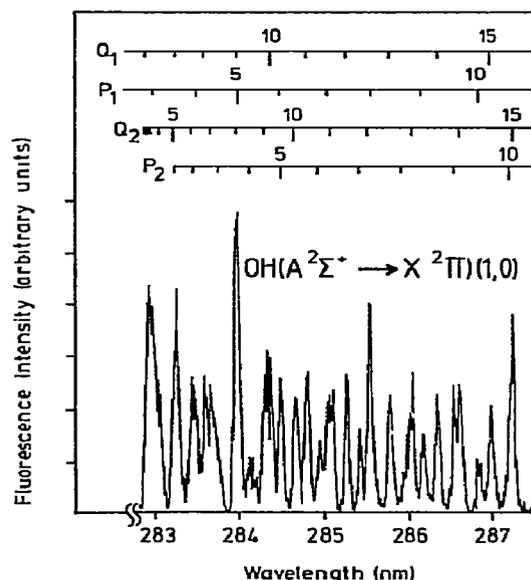


Fig. 3. $OH(A^2\Sigma^+ \rightarrow X^2\Pi)$ nascent emission spectrum Shown is a small section of the P and Q branches of the weaker $v' = 1 \rightarrow v'' = 0$ band. Experimental conditions: $7 \times 10^{-3}$ mbar $H_2O_2$ and a laser fluence of 8 $J/cm^2$

fig. 2 is part of the emission of the 0–0 band the emission spectrum in fig. 3 represents part of the 1–0 band demonstrating that also $v' = 1$ of the $A^2\Sigma^+$ state of the OH is populated. The two figures show only a small section of the completely observed band spectra and demonstrate that a fully resolved rotational spectrum was obtained for both bands and even for transitions from low rotational levels. The rotational structure of the two bands could also be observed with the use of an optical spectrum multichannel analyser (OSMA). In this case the information could be obtained with only a few laser shots thus reducing errors introduced by a possible change of gas flow or laser intensity. But because of the relatively large size of the diodes the resolution was only $\frac{1}{3}$ of that obtained with the scanning monochromator. Therefore, the results from the OSMA were used to prove the reproducibility of the spectral observations. In addition, the OSMA results were used to prove the pressure dependence of the emission and the sensitivity of the rotational distribution on collisions.

Earlier measurements [2] indicate that, at a total pressure of 100 mTorr, the nascent state distribution of the radiating $OH(^2\Sigma^+)$ does not show a pressure

effect with the present experimental apparatus demonstrating that collision free conditions obtained. In addition to the total intensity, the OSMA provides us with the rotational band contour. Therefore, pressure effects on this contour can easily and sensitively be measured. As a result of this observation, we found that for all pressures used in the course of the experiment the same rotational and vibrational distribution was obtained. The relative rotational populations $P(N')$ were determined from the P and Q branches [8]. From plotting $\ln[P(N')/2J + 1]$ versus the energy of the molecular state [9] a straight line was obtained; thus, the energy of the molecular state can be described by a temperature. The temperatures which were obtained for $v' = 0$ and for $v' = 1$ of the excited OH($^2\Sigma^+$) are $T_{v'=0} = 4450 \pm 180$ K and $T_{v'=1} = 3560 \pm 150$ K, respectively. The straight-line behaviour has been checked for rotational states $N'$ from 2 to 23. The results further show that there is no indication of bimodal distribution which strongly supports the suggestion that the emission is from only one of the two dissociation products although the total energy (104070 cm$^{-1}$) available to the fragments is high enough to excite electronically the second OH radical as well. The absence of any deviation from a temperature behavior of the rotational distribution is, therefore, a strong hint for a dissociation process that leaves one of the two products in its electronic ground state.

The transitions from both spin systems in OH($^2\Sigma^+$) could be analyzed. Both spin systems show a similar distribution among the different rotational states. Thus the available energy is partitioned statistically between the two spin components. From the intensity of the 1−0 band and the transition probabilities of the observed two vibrational bands [10] the relative yield for the $v' = 1$ formation is calculated to be 0.32 for $v' = 1$ and 0.68 for $v' = 0$ formation [*]. Because of the relatively low internal excitation of the products OH(X) + OH(A), the main part of the available energy

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[*] Very recently a value of 0.25 has been obtained for $v' = 1$ [5].

must be transferred into OH translation.

The results obtained in the present experiment are also of great interest with regard to the dynamics of the dissociation process. The intermediate state in the subsequent two-photon absorption is repulsive; thus on a time scale comparable to the dissociation time, the second photon inducing the molecular transition will probe different Franck—Condon regimes depending on the time lag between the absorption of the two photons. A change in the energy partitioning of the dissociation products should be the result of a dissociative intermediate state. An effect is therefore expected which shows a change in the energy partitioning for the two fragments as a function of laser fluence. This result has been actually observed and will be discussed in a later paper.

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