LASER-INDUCED FLUORESCENCE STUDIES OF ROTATIONAL STATE POPULATIONS OF OH DESORBED IN THE OXIDATION OF HYDROGEN ON Pt

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The state-sensitive laser-induced fluorescence technique has been employed to study the rotational state population of OH radicals desorbed from a polycrystalline platinum foil in the $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ reaction. The experiments were performed at steady-state reaction conditions in the pressure (p) range 2-200 mTorr at a catalyst temperature of T = 1200 K. In the limit $p \rightarrow 0$ Boltzmann-type plots produce almost straight lines with a rotational temperature $T_{rot}/T = 0.81 \pm 0.03$ demonstrating the rotational cooling upon desorption previously observed by Hsu and Lin [J. Chem. Phys. 88 (1988) 432]. The rotational cooling is smaller for OD. For both molecules these results are compatible with desorption of thermally equilibrated molecules (on the surface), which loose one rotational quantum upon desorption. At higher pressures significant deviations from Boltzmann distributions and rotational cooling is observed due to gas-phase collisional processes.

1. Introduction

Studies of molecules desorbing from surfaces have to a large extent been performed using temperature-programmed desorption (TPD) or molecular beam scattering combined with time-of-flight mass spectrometry (TOF) [1,2]. This type of measurement has given valuable information about the kinetics and dynamics of desorption processes by determining the angular and velocity distributions of the desorbing species.

The access to laser spectroscopic techniques [3–5], as laser-induced fluorescence (LIF) and resonant enhanced multiphoton ionization (REMPI), has considerably advanced the studies of the dynamics of molecule-surface interactions by determining internal energy distributions as vibrational and rotational state populations.

In studies of desorption processes molecules can be supplied to the surface and made to leave the surface in different ways. Cavanagh, King and Mantell exposed Ru(100) [6] and Pt(111) [7] to NO molecules at low temperatures and studied the thermally desorbed molecules by LIF as the temperature of the sample was increased. Another approach was used by Kubiak and co-workers [8] and Zacharias and co-workers [9], who by use of REMPI studied the rotational and vibrational distributions of H_2 desorbed from Cu and Pd surfaces, respectively, after atomic permeation of hydrogen from the rear of the sample.

A third way of studying desorption processes is to probe molecules that desorb as products of a surface reaction. Mantell et al. [10] investigated by IR chemiluminescence the vibrational and rotational distributions of CO_2 , which desorbed as a final product produced in the oxidation of CO over Pt.

An interesting possibility in the case of surface reactions is that highly reactive (and thus shortlived) reaction intermediates can be detected and studied by use of lasers [3]. Such reaction intermediates can be studied by e.g. establishing a steady-state situation, where the intermediate species are desorbed from the surface at high temperatures before reacting to terminate the chain reaction. This approach has been used by Lin and co-workers [11–13] and by our group [14–17], to study the reaction intermediate OH produced in the oxidation of hydrogen on Pt. The technique is also used to study production and quenching of OH radicals in catalytic combustion [43].

In the case of intermediate reaction species desorbed in a surface chain reaction, the desorption is a branching channel prior to the termination of the chain. In the specific case, $H_2 + \frac{1}{2}O_2 \rightarrow$ H₂O, the OH species is formed by association of O and H atoms [16,18] that originate from H_2 and O₂ molecules that have adsorbed by dissociative sticking. Inspection of the enthalpy diagram [19,40] for the reaction shows that the most energetic steps are the H₂ and O₂ dissociative adsorption events. There is a possibility that intermediate OH desorption may be principally different than thermal desorption of stable molecules that have been adsorbed on the surface. The reason is the possibility of conversion of some fraction of the large chemical energy released in the reaction ($\sim 2.5 \text{ eV}$ per formed H_2O) to internal excitations of the OH molecule. Analysis of the rotational state populations of desorbed OH could reveal such processes.

The measured rotational energy distributions in the different types of experiments referred to above show various degrees of rotational cooling, i.e. "rotational temperatures" that are lower than the surface temperature. Many cases have shown a Boltzmann-like distribution independent of whether the species have been scattered from a beam, preadsorbed and desorbed, or produced in a catalytic reaction. For recent reviews, see Comsa and David [1], Barker and Auerbach [2], Lin and Ertl [3], Zacharias [4] and King and Cavanagh [5].

The type of results emerging from these desorption and scattering experiments have also received considerable theoretical interest. Tully and coworkers [20,21] and Polanyi and Wolf [22] have used the classical trajectory approach to study the desorption of NO from Ag(111) and Pt(111). They found an overall colder-than-thermal rotational energy distribution after desorption due to rotational to translational energy conversion. Bowman and Gossage [23] have calculated rotational state distributions by subtracting a certain constant energy loss from the rotational energy of each desorbing molecule. A different mechanism is proposed by Gadzuk et al. [24]. They projected the hindered-rotor rotational states of the adsorbed molecule onto the rotational states of a free rotor and found a rotational heating as a consequence of the desorption process. However, by taking into account that the zero-point energy of the adsorbed molecule is split between free rotations and translations at desorption they argue for a rotational cooling.

We have in our earlier investigations [15,16] studied the kinetics of the oxidation of hydrogen on Pt by measuring the rate of H₂O production (via the dissipated chemical energy) in parallel with LIF measurements of the total desorption yield of OH. Both the H₂O and OH yields have been determined as functions of catalyst temperature, total pressure, and relative hydrogen concentration, $\alpha (\alpha = p_{H_2}/(p_{H_2} + p_{O_2}))$, where p_{H_2} and p_{O_2} are the partial pressures of H₂ and O₂). The measurements have also recently been extended to studies of the temperature dependence of the rate of OH desorption, I_{OH} , to determine the "true" desorption energy E_{OH}^{d} [17]. These experimental results have been combined with kinetic modelling of the reaction channels for the OH and H₂O production on Pt [16,40].

In this work we have studied the rotational state populations of desorbed OH molecules both in the collision-free limit and at higher pressures where collisional quenching processes influence the measurements. The results in the collision-free limit are compared with previously reported data by Hsu and Lin [13]. The data in the regime where gas-phase collisions occur and influence the results are not of explicit surface science concern. However, it is of utmost importance to understand and keep control over such effects for correct data interpretation. Therefore, data from the gas collision regime are also shortly presented and discussed.

2. Experimental set-up

A detailed description of the experimental setup used for the LIF studies of thermally desorbed OH has been presented in earlier papers [14,16]. A schematic diagram of the experimental arrangement is shown in fig. 1. The vacuum system is turbo-pumped with a typical base pressure of 10^{-7} Torr. H₂ and O₂ gases are mixed before entering the vacuum system as described before [16] and continuously flown over the catalyst from below.



Fig. 1. Schematic overview of the experimental set-up.

The total pressures used in the experiments were in the range 2–200 mTorr. In order to avoid concentration gradients at higher pressures we occasionally used a Roots pump offering an increased pumping speed at 100 mTorr by a factor of ~ 30. Inside the chamber the catalyst which is a high-purity polycrystalline Pt foil (MRC, 99.95%, size 20 mm \times 2 mm \times 0.025 mm), is mounted horizontally on a manipulator. The foil is heated resistively and the temperature is determined by a four-point probe measurement technique [27], which allows simultaneous recording of the current passing the foil and the voltage drop over it. This gives the resistance of the sample at any heating current through the relation:

$$R(T) = R_{300} \left[1 + \alpha_{300} (T - 300) + \beta_{300} (T - 300)^2 \right],$$
(1)

where the temperature coefficients α_{300} and β_{300} are given in ref. [28]. The values for platinum are $\alpha_{300} = 3.57 \times 10^{-3}$ and $\beta_{300} = -5.25 \times 10^{-7}$. R_{300} , i.e. the resistance at 300 K, is obtained by using a sufficiently small heating current through the foil and measuring the voltage. The temperature is as seen from eq. (1) a function of four variables $T = T(\alpha_{300}, \beta_{300}, R_{300}, R)$. The error in the determination of the temperature is estimated to be $\Delta T \approx 10$ K at the temperatures used. The largest part of this error (~70%) is due to the uncertainty in the determination of the room-temperature resistivity of Pt.

The foils used here were cleaned as described by Kasemo, Keck and Högberg [27] and occasionally analyzed by Auger electron spectroscopy (AES) in a separate chamber for detection of impurities. No other impurities than a low carbon contamination (most probably deposited during the transport to the AES equipment) was observed [16]. The foils were also analysed by scanning electron microscopy (SEM) after removal from the system. The SEM pictures showed that during the reaction the polycrystalline foils had recrystallized to grains of a few up to ~ 100 μ m in size. These grains are probably dominated by the close-packed (111) surface [30].

The laser system consists of an excimer laser (Lambda Physik EMG 102E), which by the XeCl line (308 nm) pumps a dye laser (Lambda Physik FL 2002E) with the dye rhodamine B. The fundamental wavelength is frequency-doubled with a

SHG crystal to lie in the region 306.3-307.5 nm, i.e. within the absorption band of OH ($A^2\Sigma(v=0)$) $\leftarrow X^2 \Pi(v=0)$). The repetition frequency of this pulsed-laser system was in the present experiments 10-20 Hz and the pulse length 22 ns. The polarization of the laser light is horizontal, and achieved by an air-spaced polarizer inside the dye laser which enhances the conversion efficiency of the frequency doubling. The energy in each pulse is 150 μ J and its band width 0.2 cm⁻¹. To avoid saturation of the optical transitions the light is attenuated through a variable attenuator (Newport Model 935-10) to about 50 µJ corresponding to 7.5×10^{13} photons/pulse measured by a headon photomultiplier (Hamamatsu 1P28) after passing through the vacuum system. The scanning of the dye laser is carried out automatically by a microcomputer (Lambda Physik FL 582) with a scan-step of 8×10^{-4} nm.

The volume in which OH molecules are laser excited and thus the volume from which the fluorescence light is collected has the shape of a cylinder 1 mm in diameter (the laser beam diameter) and 11 mm long. It is located ~ 2 mm below the horizontal foil as is shown in fig. 2. The fluorescence light is collected at 90° with respect to the laser beam through $0.01 \times 4\pi$ steradians by a quartz lens system and imaged onto a photomultiplier tube (Hamamatsu R943-02) cooled by a thermoelectrically refrigerated chamber (Products for Research TE-206 TSRF). Blackbody radiation from the heated Pt foil is eliminated with a bandpass filter (Schott UV-M-Al) centered at 305 nm with a band width of 20 nm well covering the fluorescence light from OH $(X^2\Pi(v=0) \leftarrow A^2\Sigma(v=0))$. The fluorescence signal is detected with a boxcar averager (Stanford Research SR250). The boxcar gate is 0.9 μ s long, i.e. approximately 1.5 times the lifetime of the excited OH molecules [31] and delayed 0.1 μ s with respect to the laser pulse to avoid detection of scattered laser light. The output from the boxcar averager is stored in a microcomputer (IBM AT) using the software, SR265, provided by Stanford Research Systems, Inc.

3. The LIF technique and data analysis

A schematic overview of the experimental arrangement for the excitation of OH molecules in the region probed outside the sample and the detection of the resulting fluorescence light is shown in fig. 2. When the laser light with intensity $I_0(\nu)$ is scanned through a certain transition with the absorption cross section $\sigma(\nu)$, the absorbed light intensity can be expressed as [32]

$$I_{A}(\nu) = I_{0}(\nu)n_{i}\sigma(\nu) \Delta x$$
$$= I_{0}(\nu)n_{i}\frac{h\nu}{c}B_{ik}g(\nu) \Delta x, \qquad (2)$$

where B_{ik} is the Einstein coefficient of induced absorption for the transition from *i* to *k* and $g(\nu)$ is the corresponding line-shape function. B_{ik} is related to the corresponding Einstein coefficient for spontaneous emission, A_{ki} , which in the case of electric dipole radiation can be given as a



Fig. 2. Schematic overview of the geometry of the probed volume, exciting laser light and fluorescence detection.

function of the line strength, S_{ki} . By using the Franck-Condon principle one can write

$$S_{ki} = \sum \sum |R_{ki}|^{2} = |\mu_{el}(R_{e})|^{2} F_{vib} H_{rot}, \qquad (3)$$

where R_{ki} is the matrix element of the dipole operator and the first factor in the second equality is the electronic transition probability (R_e is the equilibrium distance between the nuclei), the second factor is the vibrational transition probability called the Franck-Condon factor and the third factor the rotational transition probability called the Hönl-London factor. When evaluating the matrix element R_{ki} in a limited wavelength region it is normally sufficient to consider the selection rules for the Hönl-London factors, i.e. the electronic and vibrational transition moments are kept constant. The OH molecule is however rather unusual since the electronic transition probabilities strongly depend on the rotational levels [33]. Therefore the dependence on all these factors must be considered in the case of OH. When polarized light is used to detect randomly oriented molecules, the polarization characteristics of the transitions involved influence the amount of fluorescence light detected in a certain direction even if the detection is non-polarized [34].

The optical spectra resulting from transitions between the two lowest-lying electronic states of OH are well known from the work of Dieke and Crosswhite [35]. The electronic ground state is assigned $X^2\Pi$ while the first excited state is $A^2\Sigma$ (located at about 33000 cm⁻¹). In order to evaluate state population distributions from LIF measurements of OH, a computer program has been written [36]. This program calculates, for given molecular constants, the energies for the ground and excited states and simulates a fluorescence spectrum for a given rotational distribution. Examples of such simulated spectra have been presented before [37].

3.1. Procedure for determination of the absolute OH desorption rate

If the intensity of the laser light is kept constant over the wavelength region considered and if the quenching probability (i.e. the probability for radiationless transitions from the excited to the ground state) is low or approximately independent of the excited state we can write

$$n_i \propto (I_{\rm fl}/S_{ki}). \tag{4}$$

Measurements of relative fluorescence intensities of different peaks, I_{fl} , and normalization with respect to their corresponding line strengths, S_{ki} , will then give the relative population, n_i . To determine the absolute number of OH molecules in the detection volume from a LIF scan we need to know the relative distribution among rotational levels as well as the absolute number of molecules populating one of the levels.

The absorbed light intensity is equal to the fluorescence light intensity only under collisionfree conditions. At pressures where collisions occur on the time scale of excitation + radiation, molecules that are excited by the laser can undergo radiationless transitions to the ground state, so-called quenching, via (bi)molecular collisions [38]. If we define a quenching factor q = Q/(A + Q), where A is the inverse of the natural lifetime and Q is the quenching rate, the fluorescence light intensity can be expressed as $I_{\rm fl}(\nu) = (1 - q)I_{\rm A}(\nu)$.

This fluorescence light is detected through an optical system and imaged onto the cathode of a photomultiplier tube. The output (anode) current from the photomultiplier I_{ph} can be written

$$I_{\rm ph} = erk_{\rm ph}\eta_{\rm ph}\eta_{\rm m}(\Omega/4\pi)I_{\rm fl}, \qquad (5)$$

where e is the electron charge, r is the repetition frequency of the laser, $k_{\rm ph}$ is the gain and $\eta_{\rm ph}$ the quantum efficiency of the photomultiplier, $\eta_{\rm m}$ is the transmission through mirrors, baffles, etc., and Ω is the solid angle for collection of the fluorescence light. The fluorescence light intensity is given as the number of fluorescence photons/laser pulse.

Since the absorbing molecules are distributed over many rotational levels we need to know the fraction, b_i , of the total number of molecules/ volume, n_{tot} that is in the probed level. This can be achieved by probing all occupied levels. If the molecules are distributed according to a Boltzmann expression, b_i can be written

$$b_{i} = \frac{g_{i} \exp\left(-E_{i}/k_{\mathrm{B}}T_{\mathrm{rot}}\right)}{\sum_{j} g_{j} \exp\left(-E_{j}/k_{\mathrm{B}}T_{\mathrm{rot}}\right)},$$
(6)

where T_{rot} is the rotational temperature and E_j and g_j are the rotational energies and the degeneracies, respectively, of level *j*. An example of an evaluation of this factor is presented in section 4.2.

The number of molecules/volume, n_{tot} can now be calculated:

$$n_{\rm tot} = \frac{1}{b_i} \frac{1}{1-q} \frac{1}{I_0(\nu_0) * \sigma(\nu_0)} \frac{I_{\rm ph}}{C_{\rm exp}}, \qquad (7)$$

where $C_{\exp} = erk_{ph}\eta_{ph}\eta_{m}(\Omega/4\pi)\Delta x$. $(I_0(\nu_0) * \sigma(\nu_0))$ denotes the convolution of the laser light and the cross section of the transition at the resonance frequency, ν_0 . If the laser light and the transition both are Gaussian-broadened this convolution can be written

$$I_{0}(\nu_{0}) * \sigma(\nu_{0}) = I_{0}^{\text{tot}} \sigma^{\text{tot}} \frac{1}{\sqrt{(\Delta \nu_{I_{0}})^{2} + (\Delta \nu_{\sigma})^{2}}}, \quad (8)$$

where I_0^{tot} and σ^{tot} are the integrated quantities over the line shapes and $\Delta \nu_{I_0}$ and $\Delta \nu_{\sigma}$ the corresponding widths.

In our case we are interested in the number of molecules desorbing per unit time from the catalyst surface. Geometrically only a fraction f of these molecules enters into the detected volume. Assuming that the molecules leave the surface with a velocity v we get the number of desorbing molecules per unit time and unit area, n_{des} , as

$$n_{\rm des} = (n_{\rm tot} v/f). \tag{9}$$

From intensity versus pressure measurements of the fluorescence light after excitation of the $R_1(2)$ transition we found, at T = 1100 K, $\alpha = 0.05$ and $p_{tot} = 10$ mTorr a photocurrent of $I_{ph} = 6 \times 10^{-10}$ A at a gain of $k_{ph} = 10^7$. At this pressure the mean-free-path of the desorbed OH molecules is about 10 mm, i.e. very few collisions occur before detection, so eq. (9) can be used. Typical experimental factors were: r = 10 Hz, $\eta_{ph} = 0.25$, $\eta_m = 0.15$, $(\Omega/4\pi) = 0.008$, $\Delta x = 11$ mm, $I_0^{tot} = 7 \times 10^{13}$ photons/laser pulse and $\Delta \nu_{I_0} = 10^{10}$ s⁻¹. The factors associated with the $R_1(2)$ transition were: $\sigma^{tot} = 7 \times 10^{-10}$ m²/s, $\Delta \nu_{\sigma} = 5 \times 10^9$ s⁻¹, $b_i = 0.17$ and q = 0.16. The quenching rate was experimentally determined as $Q \approx 2.7 \times 10^5$ s⁻¹ (at these partial pressures) [41], which agrees with measurements by Crosley [38], whereas $A \approx 1.4 \times 10^6 \text{ s}^{-1}$ for the level excited by the $R_1(2)$ transition. From the measured value of $I_{\rm ph}$ we estimate the absolute number of molecules/volume as $n_{\rm tot} = 2 \times 10^{7\pm1} \text{ cm}^{-3}$. The molecules desorbing from the surface have approximately a $\cos \theta$ angular distribution as measured by a diode array detector [42]. From the geometry of the detection we get the fraction of the molecules desorbing from the surface that enters into the detection volume as f = 0.15. By estimating $v \approx 10^3 \text{ m/s}$ (corresponding to a translational temperature of approximately 500 K) we obtain from eq. (9) $n_{\rm des} = 1 \times 10^{13\pm1} \text{ cm}^{-2} \text{ s}^{-1}$ at $T_{\rm cat} = 1100 \text{ K}$ and $p_{\rm tot} = 0.1 \text{ Torr.}$

4. Results and discussion

Fig. 3 shows a typical LIF scan recorded in the wavelength region 306.4–307.6 nm, which corresponds to a fraction of the $0 \rightarrow 0$ vibrational band with the R₁, R₂₁ and R₂ branches. The temperature of the catalyst was T = 1200 K and the relative H₂ concentration was $\alpha = 0.05$ ($\alpha = p_{H_2}/(p_{H_2} + p_{O_2})$) which is the H₂/O₂ mixture where the OH yield is maximum at this temperature [16].

The major goal was to determine the rotational distribution in the limit of zero pressure (i.e. under collision-free conditions) in order to obtain information about the OH desorption process. A second goal was to investigate when and to what extent gas-phase collisions started to influence the measurements as the pressure was increased. This was achieved by determining the rotational distribution at several different total pressures (extending from 2–200 mTorr) and then extrapolating these results to zero pressure. This procedure produced better accuracy in the low-pressure limit than by use of data recorded at one single pressure ≤ 1 mTorr, where the signal-to-noise ratio is poor.

4.1. Rotational distribution in the collision-free limit

In fig. 4 LIF scans from 306.8 to 306.9 nm for four different pressures, 2, 10, 25 and 100 mTorr, are shown in order to demonstrate how the relative intensities of the peaks (and thus the rota-



Fig. 3. Typical scan of the fluorescence intensity versus laser wavelength at a catalyst temperature of 1200 K and a total pressure of 5 mTorr. Assignments of the peaks are made according to Dieke and Crosswhite [35] using a simulated spectrum [37].

tional distribution) changes with pressure due to collisional redistribution among the rotational levels. As the pressure is increased the peaks originating from rotational levels with high quantum numbers, i.e. levels with high rotational energy, are becoming comparatively weaker in comparison with the peaks from low quantum number levels, i.e. levels with low rotational energy. The improved signal-to-noise ratio as p is increased is due to the almost linear increase in the desorption rate of OH with increasing pressure [16,40].

It is common to analyse the distribution among rotational levels by assuming that the molecules are Boltzmann-distributed, i.e that the distribution can be described by a temperature representing molecules in thermal equilibrium:

$$n_i \propto g_i \exp(-E_i/k_{\rm B}T_{\rm rot}), \qquad (10)$$

where n_i is the number of molecules in a certain rotational level, g_i the level degeneracy, E_i its rotational energy, k_B Boltzmann's constant, and T_{rot} the rotational temperature.





Fig. 4. Scans of the fluorescence intensity from OH for the wavelength region 306.8-306.9 nm for four different total pressures. These recordings have been taken as single scans with an average of three laser shots for each wavelength step. Notice the relative variation of the intensity between the different peaks when the pressure is changed.

Fig. 5. Boltzmann plots (relative rotational populations versus rotational energy) for three different total pressures. The R_1 , R_{21} and R_2 branches are shown by the squares, crosses and plus signs, respectively. An increasing curvature appears as the pressure is increased indicating non-Boltzmann distributions.

To explore if this kind of analysis is useful in the present case and to possibly obtain a rotational temperature we plot $\ln(n_i/g_i)$ as a function of E_i for various pressures. A rotational temperature would appear as the slope of a straight line in such plots. In fig. 5 such Boltzmann plots are shown for three of the pressures used in fig. 4 using wavelength scans of the kind shown in fig. 3. Experimental data are presented for three different rotational branches: R_1 , R_{21} and R_2 . We notice that there is no significant difference between the branches implying that the "spin-orbit temperature" is the same as the "rotational temperature", since the R_1 , R_{21} and R_2 branches probe different spin-orbit components [37].

We see further from fig. 5 that only for low pressures can the data be fitted to a straight line and a rotational temperature be defined. The curvature at higher pressures is due to inelastic collisions between the OH molecules and surrounding molecules, causing rotational redistributions which will be further discussed in section 4.2.

To determine the rotational population distribution in the limit $p \rightarrow 0$, the relative populations of every occupied rotational level were calculated from LIF spectra measured at different pressures. The result of this procedure is shown in fig. 6 for four rotational levels probed by the indicated transitions. An enlargement of the low-pressure region ≤ 10 mTorr is shown in fig. 7, where the



Fig. 6. Relative populations in four of the rotational levels probed by the R_1 branch ($R_1(2)$, $R_1(4)$, $R_1(6)$ and $R_1(9)$, for total pressures extending from 2 to 100 mTorr.



Fig. 7. Relative populations in four of the rotational levels probed by the R_1 branch for 2, 3, 5 and 10 mTorr. The relative populations at zero pressure are determined by fitting of polynomials of second degree.

relative populations are given for the pressures 10, 5, 3 and 2 mTorr. Polynomials of second order are then fitted to these experimental data points and used for extrapolation of the relative populations to zero pressure. The extrapolated values are shown by the four points on the vertical axis at pressure p = 0. The mean-free-path of the OH molecules is approximately 1 cm at 10 mTorr and 5 cm at 2 mTorr (at a gas temperature of T = 500K). Since the OH molecules are probed at a dis-



Fig. 8. Boltzmann plot of the relative populations at zero pressure as determined in fig. 7 when the pressure is extrapolated to zero. The rotational levels probed by the R_1 , R_{21} and R_2 branches, respectively, are shown by the crosses and squares, respectively. From the slope of the curve we estimate $T_{rot} = 976 \pm 25$ K.



Fig. 9. Rotational populations as a function of the rotational energy for distributions corresponding to $T_{\rm rot} = 1200$ K and $T_{\rm rot} = 976$ K together with the rotational distribution determined from the extrapolation procedure described in the text. The distributions are normalized to one at their highest points.

tance of ~ 2 mm from the surface we are confident that these extrapolated values represent the rotational population distribution of the OH molecules leaving the catalyst surface, and that the resulting distribution is unaffected by gas-phase collisions.

A Boltzmann plot of the extrapolated data points is shown in fig. 8. An almost straight line, but with a slight upward curvature, is obtained. The average slope corresponds to a rotational temperature $T_{\rm rot} = 976 \pm 25$ K at a surface temperature of $T = 1200 \pm 10$ K, which corresponds to a ratio $T_{\rm rot}/T = 0.81 \pm 0.03$, where the uncertainty in the determination of the catalyst temperature is taken into account. To more clearly see the difference between the surface temperature Tand the rotational temperature T_{rot} the experimental data are plotted in fig. 9 as relative rotational population versus rotational energy in a linear plot, together with corresponding theoretical Boltzmann plots at 1200 and 976 K. It is clearly seen that the rotational distribution is colder than a distribution corresponding to the surface temperature. Our result is in good qualitative and quantitative agreement with the experiments by Hsu and Lin [13]. They determined rotational temperatures for different mixtures of hydrogen and oxygen and different surface temperatures in the range T = 1206-1427 K. They found an average value of $T_{rot}/T = 0.86 \pm 0.05$.

Preliminary experiments were also performed with D₂. The desorbed OD molecules were detected by exciting the $A^2\Sigma(v=0) \leftarrow X^2\Pi(v=0)$ absorption band. OD has a smaller rotational constant than OH which results in a higher density of rotational states. Using a similar but not so elaborate extrapolation procedure as for OH, $T_{\rm rot}$ = 1248 K at T = 1300 K and $T_{\rm rot} = 1152$ K at T = 1200 K were obtained. This corresponds to a ratio $T_{\rm rot}/T \approx 0.96$ at both temperatures. These results are also in accordance with the results by Hsu and Lin [13] who found $T_{\rm rot}/T = 0.96 \pm 0.04$ as an average value for OD.

The proximity of T_{rot} and T indicates that the desorbing OH molecules are in thermodynamic equilibrium before desorption and loose a small fraction of their rotational energy in the desorption process (the latter is discussed in somewhat more detail later). This observation seems to rule out the possibility discussed in the introduction of significant transfer of the large reaction energy in the H₂ + O₂ reaction to internal OH excitation. At least the desorbed OH molecules carry no "memory" of such excitations.

It has been shown by stochastic trajectory calculations [20-22] that the sticking probability decreases with increasing rotational energy for NO molecules scattered on Ag(111) and Pt(111) surfaces. The reason for this decrease is the orientational dependence of the potential energy surface for this system [21]. It is more difficult for a molecule rotating with a high rotational energy to orient into the most favorable position for sticking to occur. By invoking detailed balance [20], one may conclude that there is a decreasing probability for desorption of molecules with higher rotational energy, where the rotational energy is the one for the molecule outside the surface after desorption, i.e. for the free molecule. This says little, however, about the rotational energy the molecule had on the surface before desorbing. According to Muhlhausen et al. [21] molecules with high (frustrated) rotational energy on the surface may desorb with lower rotational energy

by conversion of rotational energy into translational energy. Such a mechanism can explain an observed lower rotational temperature of desorbed species than the surface temperature.

We performed a simple quantitative estimation of the observed rotational cooling effect by using a Boltzmann rotational distribution at the surface temperature and then subtracting from each level an energy corresponding to the decrease of one Jquantum number. This mimics a process where OH molecules, originally in thermal equilibrium with the surface, on the average loose one rotational quantum upon desorption. The new distribution produces a Boltzmann plot quite similar to the experimentally measured ones in the collision-free limit, $p \rightarrow 0$. The slight upward curvature for lower J values seen in the experimental plot of fig. 8 is also seen in the simulated distribution. Using the same evaluation procedure for the simulated as for the experimental data to obtain a rotational temperature, the former produces an average rotational temperature of $T_{\rm rot}/T$ = 0.85 to be compared with $T_{\rm rot}/T = 0.81 \pm 0.03$ from the experiment. For OD the simulated temperature quotient is 0.89 while the experiment gave the ratio 0.96 with larger error bars than for OH. We thus find that the difference between the rotational temperatures for OH and OD and their absolute values are compatible with the desorption of thermally equilibrated molecules on the surface which on the average loose one rotational quantum upon desorption. Our observations and interpretation are in qualitative agreement with the previous work of Tully and co-workers [20,21] and Bowman and Gossage [23] who also attributed the rotational cooling to rotational-to-translational energy transfer. However Bowman and Gossage subtracted a certain constant energy loss from the rotational energy of each molecule, while we subtracted an energy corresponding to the decrease of one J quantum number. i.e. in our case more highly excited molecules lost on the average more rotational energy to the translational degree of freedom upon desorption than in the work of Bowman and Gossage.

4.2. Rotational distribution as a function of pressure

A direct illustration of how the rotational distribution of the OH molecules changes with pressure is obtained by making Boltzmann plots of the experimental data and define an "effective" rotational temperature, " T_{rot} " from the average slope. We see in fig. 10 that " T_{rot} " approaches a value of " $T_{\rm rot}$ " ~ 1000 K in the limit of zero pressure (to be compared with the more accurate determination 976 K in section 4.1) and approaches " $T_{\rm rot}$ " ≈ 500 K at high pressures. This latter value is reflecting the temperature of the reactant gases in the detection volume, which are heated by the catalyst foil. Thus the fall off of " T_{rot} " with increasing pressure in fig. 10 illustrates the rotational cooling of OH molecules as they move from the surface with an initial " T_{rot} " = 976 K and then cool down rotationally by inelastic collisions with "colder" molecules before they are laser-excited 2 mm from the surface. This cooling effect of course increases with increasing pressure because the number of collisions before excitation increases. The effect has been studied in more detail by imaging of the OH fluorescence outside the catalyst by a diode array detector [42].

In order to investigate in more detail how the relative population of rotational levels changes with pressure, relative populations were evaluated



Fig. 10. Plot of an evaluated "effective" rotational temperature, " T_{rot} ", from the fluorescence scan of OH as a function of total pressure. " T_{rot} " is defined as the rotational temperature obtained from the slope of a least-squares fit of the experimental data.

for different pressures below 100 mTorr. Since the total OH yield is different for different pressures, the rotational fluorescence intensities from individual transitions have to be normalized with respect to the corresponding total OH yield for each pressure to obtain relative populations. In order to get a relative number of the total OH yield for each pressure we first normalize the measured fluorescence intensities at each pressure with respect to the corresponding transition probabilities. We then sum up the normalized fluorescence intensities from all rotational levels in the ground state up to N = 13, where the relative population is less than 0.004. This truncation introduces a small error in the relative population which has to be taken into account. The intensities from the levels that have not been measured are obtained from graphs as in fig. 5 by extrapolating the curve to energies corresponding to the rotational levels not probed.

In fig. 6 relative populations as a function of total pressure are plotted for four rotational levels probed by the R_1 branch. We notice that towards higher pressures the populations in low-N states are increasing while high-N states are depleted. Fig. 6 also shows that the relative populations in the low-N states change more rapidly than the relative populations in the high-N states when the pressure is increased. This is in accordance with the work by Polanyi and Woodall [39] who studied this type of processes for gas-phase reactions. Their best fit to their experimental data with different initial populations was obtained with a transition probability proportional to $e^{-\Delta E}$, where ΔE is the energy difference between two adjacent rotational levels. This means that the low-N states are more affected by collisions than the high-N states, because the rotational energy is proportional to N^2 .

5. Conclusions

Rotational energy distributions of desorbed OH molecules show a strong pressure dependence due to gas-phase collisional processes. The extrapolation of the rotational energy distributions to zero pressure gives almost but not quite straight lines in Boltzmann plots, with a rotational temperature which is $\sim 81\%$ of the surface temperature for OH

and ~96% for OD. The non-linearity of the Boltzmann plots, the difference between the rotational temperatures for OH and OD and their absolute values are compatible with desorption of molecules that are thermally equilibrated on the surface before desorption and then loose on the average one rotational quantum number upon desorption.

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