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# Absolute reactive cross section for the reaction $H+D_2O \rightarrow OD+HD$: a comparison to the protonated case

A. Jacobs, H.R. Volpp and J. Wolfrum

*Physikalisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 253, W-6900 Heidelberg, Germany*

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Using translationally hot H atoms generated via the photolysis of HBr at 193 nm, we have investigated the dynamics of the reaction $H+D_2O \rightarrow OD+HD$ at a center-of-mass energy of $E_{c.m.}=2.53$ eV. The nascent OD ($v=0$) rotational distribution was probed by laser-induced fluorescence. We found that only a small fraction (2.3%) of the total available energy appears as rotational energy of the OD product molecule and within our detection limit no OD ($v=1$) could be found. The absolute reactive cross section $\sigma_R=0.11\pm0.02$ Å$^2$ at $E_{c.m.}=2.53$ eV was determined by means of a calibration method and was found to be 2.4 times smaller than the reactive cross section of the reaction $H+H_2O \rightarrow OH+H_2$ at a comparable center of mass energy of $E_{c.m.}=2.52$ eV.

## 1. Introduction

No absolute value of the reactive cross section for the hot H atom reaction

$$H+D_2O \rightarrow OD+HD \qquad (1)$$

has been measured up to now. However, for the protonated reaction

$$H+H_2O \rightarrow OH+H_2\,, \qquad (2)$$

absolute reactive cross sections and OH rotational product distributions have been measured at several center-of-mass energies [1–3] using translationally excited H atoms with $E_{c.m.}=1.48$, 1.5 and 2.52 eV and room temperature $H_2O$. In these studies it was found that only a small fraction of the total available energy is channeled into OH product rotation and in none of these studies vibrationally excited OH was detected although on the simple basis of energetic considerations OH ($v=1$) rotational levels could be populated. The results of those measurements are in good agreement with QCT calculations [4] on the ab initio Walch–Dunning/Schatz–Elgersma potential energy surface (WD/SE-PES) [5].

Studies on the influence of vibrational overtone excitation of the water molecule on the relative reactive cross section of reaction (2) have also been carried out [6] with thermal H atoms generated in a microwave discharge. The observed dependence of the reactive cross section on the bending and stretching quantum numbers agrees also well with the QCT calculations of Schatz et al. [4] and recent quantum reactive scattering calculations by Clary [7].

Furthermore mode and bond-selected experiments on the reactions

$$H+HOD \rightarrow OH+HD\,, \qquad (3a)$$

$$H+HOD \rightarrow OD+H_2 \qquad (3b)$$

have been performed using both thermal [8] and translationally excited H atoms [9]. The results clearly show that the reactivity of a single OH or OD bond in HOD could be selectively enhanced by deposition of one or more quanta of vibrational energy in the corresponding stretch mode of HOD. For reaction (3) quantum reactive scattering calculations have also been performed by Clary [10]. Because within the framework of the Born–Oppenheimer ap-

*Correspondence to* A. Jacobs, Physikalisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Field 253, W-6900 Heidelberg, Germany.

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proximation the PES is invariant with regard to isotopic substitution, studies on isotopic substituted reactions could serve as a test both for the accuracy of the PES and the calculation method. The investigation of reaction (1) therefore offers the opportunity to determine how mass effects and zero-point energies affect the reaction dynamics of reaction (2).

## 2. Experimental

The experimental apparatus is shown in fig. 1. The reaction was studied in a teflon-coated quartz reactor equipped with long sidearms acting as a baffle system to keep scattered light out of the fluorescence collecting optics. To photodissociate the HBr precursor molecules at a wavelength of 193 nm an ArF excimer laser (Lambda EMG 150 TMSC) with unstable resonator was used. the photolysis laser was operated in the broadband mode (with a bandwidth of about 80 $cm^{-1}$). A diaphragm with an aperture of 3 mm was used to skim off a homogenous irradiated part of the rectangular excimer profile to provide the photolysis beam. To minimize the OD background from $D_2O$ photolysis the photolysis energy was reduced to 3 mJ/pulse. The UV probe beam (bandwidth 0.4 $cm^{-1}$) in the wavelength region of 305–320 nm was provided by a frequency-doubled dye laser (Lambda FL 2002 EC) working with rhodamine B pumped by a XeCl excimer laser (Lambda EMG 201 MSC). To ensure a linear dependence of the OD fluorescence on the probe laser intensity the probe beam was attenuated and expanded with a telescope to a diameter of 15 mm. This beam was aligned to overlap the 3 mm diameter photolysis beam in the focus region of observation. Typically, the OD excitation was performed 80–150 ns after the photolysis pulse. The OD fluorescence emitted was collected by a lens perpendicular to the beams and projected upon the cathode of a photomultiplier. To reduce the influence of the scattered light from the photolysis pulse we used a filter (Schott UG 11) in front of the photomultiplier. The laser-induced fluorescence (LIF) signal from the photomultiplier as well as the photolysis and probe energy (both measured with photodiodes) were recorded with a 3-channel boxcar system (SRS 250) and transfered to a microcomputer (HP series 9000, model 320) via an analog-to-digital converter (SRS 235). The OD fluorescence signal was normalized to both laser energies. In order to obtain a satisfactory S/N ratio each point in the recorded spectra was averaged over 40 laser shots.

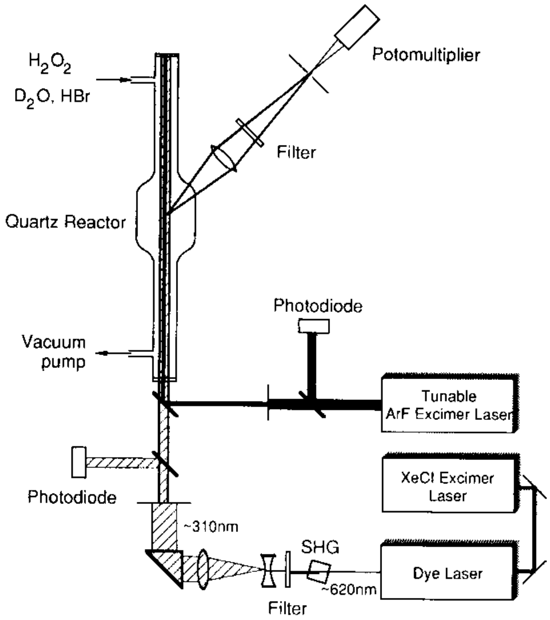

Fig. 1. Schematic diagram of the optical components of the experimental apparatus.

Room temperature $D_2O$ (99.75%, Merck for NMR spectroscopy) and HBr (99.8%) flowed through the reactor with flow rates high enough to ensure total renewal of the gas in the detection volume between two successive laser shots at a repetition rate of 20 Hz. The total pressure in the reactor, typically 70–120 mTorr, was measured with a MKS Baratron. Typical partial pressures of HBr were 5–20 mTorr. With these pressure values, and time delays between 80–150 ns, the recorded OD spectra are, within the experimental error, almost free from rotational relaxation effects. For the calibration measurements $H_2O_2$ (99.8%) could be pumped through the reactor, with typical pressures of 10 mTorr. OD LIF spectra were recorded between 306.5 nm and 320 nm, where most of the OD($A\,^2\Sigma^+$, $v'=0, 1 \leftarrow X\,^2\Pi$, $v''=0, 1$) transitions are located. Line positions and identifications of the OD(A–X) transitions were taken from ref. [11]. Relative number densities $n_i$ of the OD radicals in the absorbing rotational level $i$ were calculated using the following linear relationship:

$$I_{\mathrm{meas},ik} = C n_i B_{ik} \nu_{ik} I_{\mathrm{probe}} F(i,k)\,, \qquad (4)$$

where $B_{ik}$ is the Einstein coefficient of absorption (taken from ref. [12]) and $\nu_{ik}$ is the wavenumber for the transition $i \rightarrow k$. $I_{\mathrm{probe}}$ is the probe laser energy. The factor $C$ describes the effects of detector system like quantum efficiency, geometrical collection efficiency etc. on the measured LIF intensity. $I_{\mathrm{meas},ik}$ is determined by numerical integration of the corresponding spectral line profile $i \rightarrow k$ in the digitized LIF spectrum. Overlapping lines were deconvoluted by fitting separate Gaussian functions to the digitized LIF spectrum using a numerical least-squares fit procedure. For those branches where satellite and main lines overlap, the sum was determined and separated into components by the known ratio of the Einstein coefficients. $F(i,k)$ is a correction which had to be made because of the large rotational level dependent quenching cross section of $D_2O$ for $OD(A\,^2\Sigma^+)$ [13].

## 3. Results and discussion

The photodissociation of HBr at 193 nm produces two classes of H atoms. Because of the fine structure splitting ($^2P_{1/2}$–$^2P_{3/2}$) of the Br atom, these two groups have slightly different average translational energies according to energy conservation in the photodissociation process. The spread of each translational energy distribution is due to the thermal motion of the HBr precursor molecules and the reactant molecules. Using the formulas given in ref. [14] we obtained the following average center-of-mass collision energies $E_1 = 2.10 \pm 0.10$ eV ($f_1 = 0.15$) and $E_2 = 2.53 \pm 0.11$ eV ($f_2 = 0.85$). $f_1$ and $f_2$ are the relative quantum yields of the two possible dissociation channels of HBr at 193 nm [15].

Fig. 2 shows a part of the OD LIF spectrum measured under typical experimental conditions. In fig. 3 the measured OD ($v = 0$) rotational fine structure distribution from reaction (1) is shown. As in our earlier measurements on reaction (2) where no LIF signals from OH ($v = 1$) could be detected, in our new measurements no LIF signals from OD($v = 1$) were found. From the S/N ratio which is about a factor of 2 less than in our earlier measurements on reaction (2), we estimated the OD vibrational excitation to be OD($v = 1$)/OD($v = 0$) < 0.2. To measure the absolute reactive cross section of reaction (1) we used the method described in detail in ref. [16]. By calibrating the absolute LIF signals $S(i, \mathrm{R})$ in the rotational level $i$ of the unknown OD concentrations from the reaction against the absolute LIF signals $S(i, \mathrm{Cal})$ in the same rotational level i from well-defined OH concentrations from the $H_2O_2$ photolysis we calculated the absolute reactive cross section using the following formula:

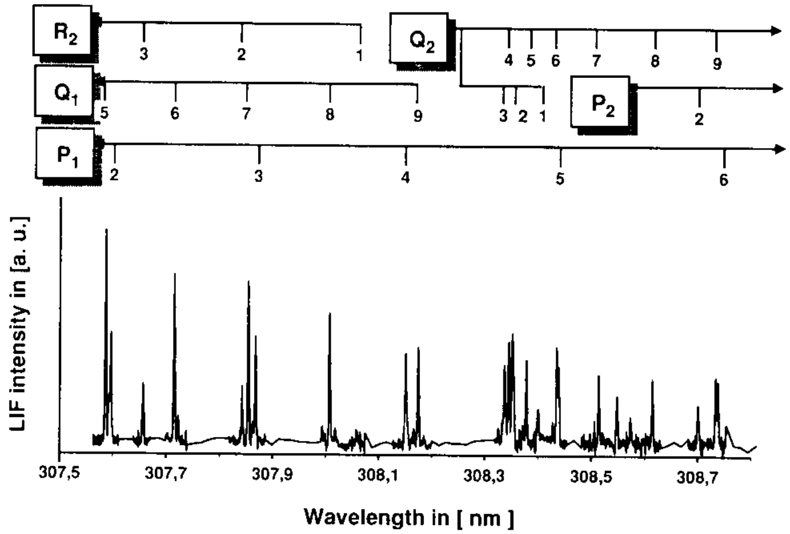

Fig. 2. Part of the OD($A\,^2\Sigma^+$, $v' = 0 \leftarrow X\,^2\Pi$, $v'' = 0$) LIF spectrum.

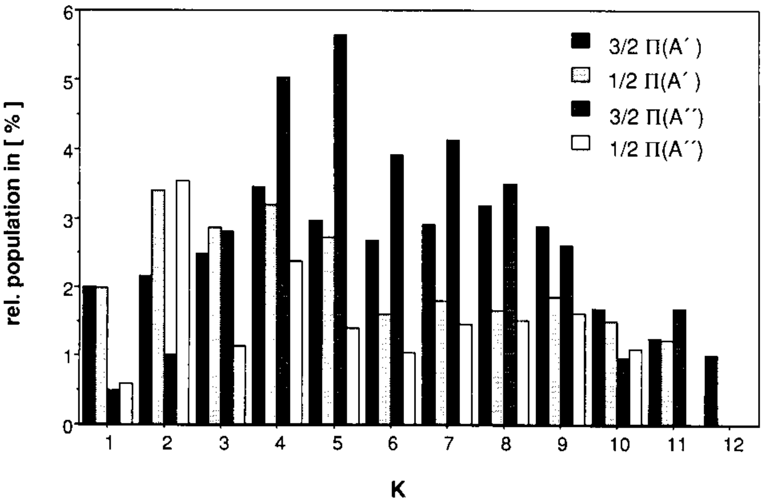

Fig. 3. Fine structure rotational population distribution of OD($v$=0) from reaction (1).

$$\sigma_R = \{S(i,\mathrm{R}) f(i,\mathrm{Cal}) B(i,\mathrm{Cal})\,[\mathrm{H_2O_2}]\,\sigma^{\mathrm{H_2O_2}}\}$$
$$\times \{S(i,\mathrm{Cal}) f(i,\mathrm{R}) B(i,\mathrm{R})$$
$$\times [\mathrm{H_2O}][\mathrm{HBr}]\,\sigma^{\mathrm{HBr}} v_{\mathrm{rel}}\, t\}^{-1}\,. \qquad (5)$$

Here $[x]$ denotes the concentration of species $x$, $v_{\mathrm{rel}}$ is the average relative H atom velocity (22000 m/s) and $t$ is the delay time between the photolysis and probe laser pulse. $f(i, \mathrm{R})$ and $f(i, \mathrm{Cal})$ at the relative populations of the OD rotational level $i$ from reaction and the relative populations of the OH rotational level $i$ from $H_2O_2$ photolysis, respectively. The values for $f(i, \mathrm{Cal})$ were taken from ref. [17]. $B(i, \mathrm{Cal})$ and $B(i, \mathrm{P})$ are the relative Einstein coefficients of the corresponding OH and OD spectral lines which were used in the calibration measurement. $\sigma^{\mathrm{HBr}}$ and $\sigma^{\mathrm{H_2O_2}}$ are the absorption cross sections of HBr and $H_2O_2$ as listed in ref. [16]. With formula (5) we obtained an absolute value of

$$\sigma_R(2.53\ \mathrm{eV}) = 0.11 \pm 0.02\ \text{Å}^2 \qquad (6)$$

for the reaction cross section of reaction (1). The total error given above represents two standard deviations calculated from 7 independent measurements of $\sigma_R$ using different Q and R lines for the calibration measurement. Our measured value of the absolute reactive cross section for reaction (1) is therefore about a factor of 2.4 lower than the value reported for reaction (2) at a comparable center of mass energy of 2.53 eV [3]. Our measurements are in agreement with previous studies of reaction (1) and (2) at a center of mass energy of 1.5 eV carried out by Honda et al. [18]. They found that the OH LIF signals from reaction (2) were a few times higher than the OD LIF signals from reaction (1) [19]. This large isotope effect in the reactive cross section, which seems not to be predicted from simple transition state theory [20], shows that a full quantum mechanical treatment of reaction (1) and (2) is clearly needed.

In fig. 4 the measured total OD rotational distribution is plotted versus the rotational energy and compared to the total OH rotational distribution from reaction (2) at $E_{\mathrm{c.m.}}=2.52$ eV taken from ref. [3]. As one can see the average rotational energy of the OH radicals from reaction (2) at $E_{\mathrm{c.m.}}=2.52$ eV is markedly higher than the average rotational energy of the OD radicals from reaction (1) at $E_{\mathrm{c.m.}}=2.53$ eV. In ref. [1] a simple impulsive model is used to explain the cold rotational distribution obtained from reaction (2) at $E_{\mathrm{c.m.}}=2.52$ eV. In this model it is assumed that the impulse along the reaction bond is responsible for the OH product rotational excitation. The small mass of the $H_2$ molecule and the short distance between the O atom and the center of mass in the OH molecule restrict how much torque could be exerted, i.e. how much of the angular momentum can appear as OH rotation.

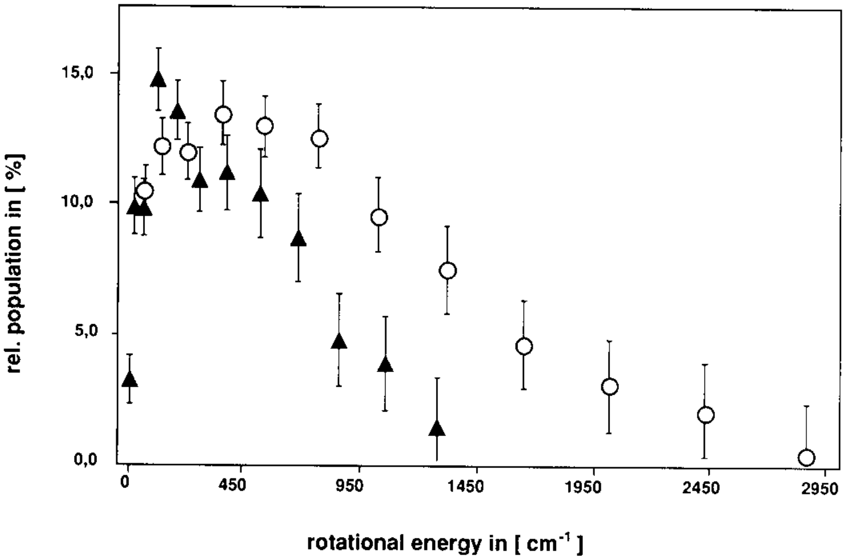

Fig. 4. Comparison between (▲) the total OD ($v=0$) rotational distribution from reaction (1) and (○) the total OH ($v=0$) rotational distribution from reaction (2).

Within this model the much hotter rotational distribution [21] of the reaction $H+O_2 \rightarrow OH+O$ at $E_{c.m.}=2.75$ eV could be explained and was attributed to the higher mass of the departing fragment.

From the rotational distributions shown in fig. 4 we calculated the corresponding average rotational energy $\langle E_{rot}\rangle^{OD}=0.04\pm0.01$ eV and $\langle E_{rot}\rangle^{OH}=0.07\pm0.02$ eV. In the impulsive model the rotational excitation of the OH/OD fragment comes from the torque which is exerted by the repulsion between the $H_2$/HD and the O atom along the O–$H_2$/HD direction. If one takes into consideration that the center of mass of the OD is about twice as far from the O atom as in case of OH, one would expect that the OD radicals from reaction (1) should have a higher degree of rotational excition than the OH radicals from reaction (2). So our experimental results are clearly in disagreement with predictions of the impulsive model.

In ref. [4] Schatz et al. found in a QCT study that the rotational excitation is due to a direct stripping mechanism, wherein the final OH rotational angular momentum comes from the $H_2O$ zero-point bending motion which becomes a free rotational motion after the reaction. It was shown that if the O atom is assumed as infinitely heavy, the final average OH rotational energy which comes from the $H_2O$ zero-point bending motion is approximately $\langle E_{rot}\rangle^{OH}=\frac{1}{4}\hbar\omega_{bend}$ in the harmonic oscillator model, so the ratio $\langle E_{rot}\rangle^{OH}/\langle E_{rot}\rangle^{OD}$ should be given by the ratio of the $H_2O$ and $D_2O$ bending frequencies. Taking the values from ref. [22] the ratio $\langle E_{rot}\rangle^{OH}/\langle E_{rot}\rangle^{OD}$ is about 1.4, which is in reasonable agreement with our experimental value of $1.7\pm0.7$. In ref. [23] Clary has carried out systematic quantum scattering studies on the influence of the bending excitation of $H_2O$ on the OH rotational product state distribution from reaction (2). His results clearly show that an increase of the bending quantum number of $H_2O$ leads to an increase in the most likely rotational state K of the OH product molecules. However no direct quantum scattering calculations for reaction (1) have been carried out, the theoretical results obtained for reaction (2) support our measurements which show that the amount of rotational energy in the OD/OH products from reaction (1) and (2), respectively, is correlated with the bending vibration zero-point energy of the $D_2O/H_2O$ molecule. Experiments to determine the observed isotope effect in the reactive cross section of reaction (1) and (2) as a function of the translational energy are currently under way.

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