Cross Section for the H + H_2O Abstraction Reaction: Experiment and Theory

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The absolute value of the cross section for the abstraction reaction between fast H atoms and H_2O has been determined experimentally at a mean collision energy of 2.46 eV. The OH population distribution at the same mean energy has also been determined. The new measurements are compared with state-of-the-art quantum mechanical and quasiclassical scattering calculations on the most recently developed potential energy surface.

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The abstraction and exchange reactions

$$H' + H_2O \rightarrow OH + HH' \quad (1)$$

$$\rightarrow H'OH + H \quad (2)$$

have played a key role in the development of reaction dynamics [1,2]. The numerous kinetic studies [3] of reaction (1) testify to its importance in influencing the overall rate of combustion of hydrogen and oxygen [4]. More recently, the mechanism of the reaction has become the subject of attention. It is the simplest reaction in which the dynamics can be influenced by both the kinetic energy of the reactants and the excitation of different vibrational modes of the polyatomic reactant [2]. Because the reactions involve three light atoms, high levels theory can be used to probe the dynamics and, consequently, studies of this system have been central to the development of a quantitative understanding of polyatomic chemical reactions.

In this Letter, we present a new determination of the cross section for reaction (1) and of OH quantum state populations at a mean collision energy of 2.46 eV. These data are compared with the results from five-dimensional (5D) quantum mechanical (QM) and quasiclassical trajectory (QCT) scattering calculations. The theoretical, computational, task involved is challenging, particularly at the high energies studied here. Chemical accuracy in the potential energy surface (PES), which demands a very high level of *ab initio* electronic structure calculation, is required over a broad range of molecular configurations. Because the abstraction reaction probability is very low, the QCT study must employ large ensembles of trajectories, while the QM scattering study is made difficult by the very many product states which become accessible at high energies. Although the reaction cross section provides a vital test of theory, the necessity to determine absolute product (OH or H_2) number densities makes it a difficult quantity to measure accurately. Pioneering work by Wolfrum and Kleinermanns and co-workers [5–8] overcame this problem by calibrating the OH product number density relative to that generated photolytically using a precursor with a known photodissociation cross section. However, the cross sections they obtained for reaction (1) [5–8] are significantly larger than current theoretical estimates [2,9,10], and a redetermination is therefore timely.

The new calculations employ the YZCL2 PES [11], determined using the iterative procedures developed by Collins and co-workers [12]. This surface appears to be the most accurate global PES available at present [9,13,14]. The 5D QM scattering calculations treat one OH bond as a spectator, and employ the initial state-selected time-dependent wave packet approach to state-to-state integral cross sections for four-atom reactions developed recently by Zhang and co-workers [10]. Full dimensionality QM scattering calculations for total angular momentum $J = 0$ and $J = 15$ performed up to a collision energy of 1.6 eV indicate that the OH bond can be treated satisfactorily as a spectator for the abstraction reaction, but not for exchange [15]. For partial waves with $J > 0$, the present calculations are performed without using the centrifugal sudden (CS) approximation, which has been shown recently to be unreliable for these reactions [16].

The QCT method employed has been described elsewhere [13,14,17,18]. Batches of 2×10^5 trajectories were run at $E_t = 2.45$ eV using a modified version of the VENUS96 program [19] in order to calculate v', j' state-resolved integral cross sections. Smaller batches were run at other collision energies to determine the total integral cross section with an uncertainty less than 0.004 Å^2. The maximum impact parameter was varied from 1.5 Å ($E_t \leq 2.20$ eV) to 1.7 Å for $E_t = 2.5$ eV. The initial distance from the H atom to the H_2O molecule was set to 8 Å and a time integration step of 0.025 fs was used, providing an energy conservation better than 1 in 10^5.

The experiments were of the laser pump-probe variety, employing room temperature mixtures of HBr and H_2O. HBr was photolyzed with excimer laser radiation at 193 nm to generate fast H atoms, and the OH products were probed after a short time delay by laser induced fluorescence (LIF) on the $A \leftarrow X$ transition. The cross-section measurements were performed using the calibration technique of Wolfrum and Kleinermanns [5]. However, unlike previous studies, we have employed the (*in situ*) photodissociation of the target H_2O molecule itself as an "internal" OH calibrant. This contrasts with the work of Wolfrum [5–7] and Kleinermanns [8] and coworkers, who used H_2O_2 or HNO_3 as calibrants, and performed the H-atom reaction and calibration experiments consecutively. In the present study, the OH LIF spectra have *two* components, one from photolysis of water at 193 nm, and the other from bimolecular reaction. These contributions were unravelled in the following way.

LIF spectra in the region of the R↑ branch head were recorded as a function of time delay, $\Delta\tau$, and HBr concentration, [HBr]. $\Delta\tau$ was varied between 50 and 150 ns, and total pressures (of varying HBr:H_2O composition) were maintained between 10 and 200 mTorr. These raw spectra were used to determine OH(v', N') quantum state populations using known Einstein absorption coefficient data [20]. For both reaction and photolysis, only OH fragments born in the $v' = 0$ vibrational level were observed. At the short pump-probe time delays employed, the *relative* signal from bimolecular reaction, x (i.e., the LIF signal from reaction divided by the signal from photolysis), can be written [5]

$$x = a\Delta\tau[\mathrm{HBr}], \tag{3}$$

where the constant a is given by

$$a = \left(\frac{\sigma_{\mathrm{HBr}}}{\sigma_{\mathrm{H_2O}}}\right) v_{\mathrm{rel}} \sigma_{\mathrm{r}}.$$

σ_r is the abstraction reaction cross section of interest, v_{rel} is the relative velocity, and the term in brackets is the ratio of photodissociation cross sections for HBr [21–23] and H_2O [21,24] at 193 nm. These cross sections [$\sigma_{\mathrm{HBr}} = (1.79 \pm 0.36) \times 10^{-18}$ cm^2, $\sigma_{\mathrm{H_2O}} = (1.75 \pm 0.26) \times 10^{-21}$ cm^2] are known quite precisely [21–24]. Because the rotational distribution obtained from the photolysis of water at 193 nm, $P_{\mathrm{ph}}(N')$ (N' is the total OH angular momentum quantum number apart from electron spin), is very cold [25] compared with that generated by reaction (1) at 2.5 eV [6], the relative yield of OH from reaction, x, and the reactive population distribution $P_{\mathrm{r}}(N')$ could be determined by fitting the observed rotational population distributions, $P_{\mathrm{obs}}(N')$, using the equation

$$P_{\mathrm{obs}}(N') = fP_{\mathrm{r}}(N') + (1 - f)P_{\mathrm{ph}}(N'),$$

where $f = x/(1 + x)$ is the fraction of the signal arising from reaction. A global fit to over 30 separate population distributions was performed, in which the populations $P_{\mathrm{ph}}(N')$ were constrained to the values determined in scans without HBr present, and parameter a in Eq. (2) and the reaction populations $P_{\mathrm{r}}(N')$ were optimized.

In Fig. 1, we compare raw OH rotational quantum state population data $P_{\mathrm{obs}}(N')$ obtained under conditions of low [HBr] and high [HBr], together with the fits to the data using the above procedure. Also shown are the separate contributions to the signal from reaction and photolysis derived from the fits. At low [HBr], the majority of the OH signal comes from photolysis of water, and leads to a cold rotational quantum state population distribution, while high [HBr] ensures that the majority of the OH signal is generated by reaction, and the OH populations are found to be considerably hotter. Note that the OH rotational quantum state populations observed here for the photodissociation of pure H_2O agree very well with the previous measurements of Andresen and co-workers [25].

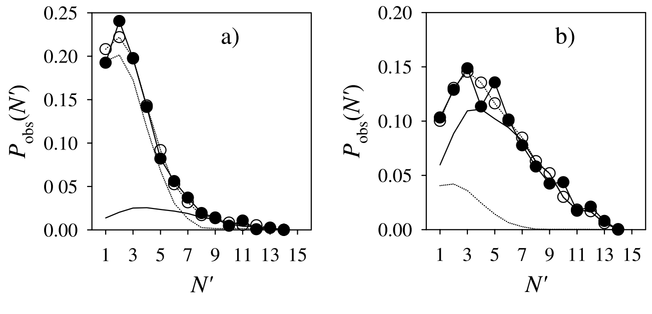

FIG. 1. Observed OH($^2\Pi_{3/2}$) rotational population distributions (●). In (a) the partial pressure of HBr was $p_{\mathrm{HBr}} = 22$ mTorr, with $\Delta\tau = 50$ ns, while in (b) $p_{\mathrm{HBr}} = 100$ mTorr and $\Delta\tau = 125$ ns. Also shown are the global fits to the complete population data set (○), and the contributions from reaction (solid line) and photodissociation (dotted line) returned by the analysis.

The experimental OH population distribution for reaction (1) is shown in Fig. 2. Good agreement is obtained with the distribution determined previously by Wolfrum and co-workers [6]. The population data are compared with the results of the QM and QCT calculations in Figs. 2(a) and 2(b), respectively. In these plots, we have used the equivalence $j' = N'$, where j' is the (closed shell) OH rotational quantum number used in the calculations. This correspondence works well for all but the lowest N' values, where OH approaches the Hund's case A limit [14,26]. The agreement between experiment and both QCT and QM scattering theory is excellent.

The results of the cross-section measurements at 2.46 eV are presented in Table I and Fig. 3. Separate analysis of the experimental data obtained at short and long delay times gave very similar values for the cross section, well within the experimental uncertainties. Our measurement is about a factor of 6 smaller than the previous determination by Wolfrum's group at the same collision energy [5,6], and is also smaller than might be expected based on the cross sections measured at lower collision energies by Kleinermanns [8] and Wolfrum [7] and their co-workers. While we have taken special care to eliminate possible sources of error in our experiments, perhaps the most convincing evidence in support of the present data is that competitive photodissociation of H_2O was also observed in the second set of experiments at 193 nm reported by Wolfrum and co-workers [6]. This observation, similar to our own, places a constraint on the abstraction reaction cross section relative to the absorption cross section of H_2O. Given that it is unlikely that the absorption cross section of the H_2O calibrant is in error by a factor of 6 [21,24], our conclusion is that difficulties may have arisen in the previous abstraction cross-section measurements [5–8] due to the use of separate photolytic calibrants with absorption cross sections between 10 and 500 times that of water at 193 nm.

The QCT and QM calculated abstraction cross sections (shown in Table I and Fig. 3) are found to agree well, perhaps not surprisingly in light of previous theoretical work on the $H + H_2$ reaction [27]. However, the calculated cross sections are about a factor of 2 larger than the present experimental value. There are several potential reasons for the discrepancy, apart from experimental error. It is possible that the PES is insufficiently accurate in the high energy region relevant to the abstraction reaction. However, QCT calculations by Schatz and coworkers [28], employing the WSLFH PES [29], yield a cross section of 0.09 Å^2 at 2.5 eV, in excellent accord with the present calculations, reducing the likelihood that errors in the ground state PES are responsible for the discrepancy. A further complication to the dynamics is that an excited electronic state may play a role at the energies sampled by the experiments: High level *ab initio* calculations [QCISD(T)/aug-cc-pVTZ] show that, at the saddle point configuration for reaction (1), the lowest excited state has an electronic energy only ~2 eV above the equilibrium energy of the reactants. Therefore, it is possible that this excited state could influence the reaction cross section at 2.46 eV.

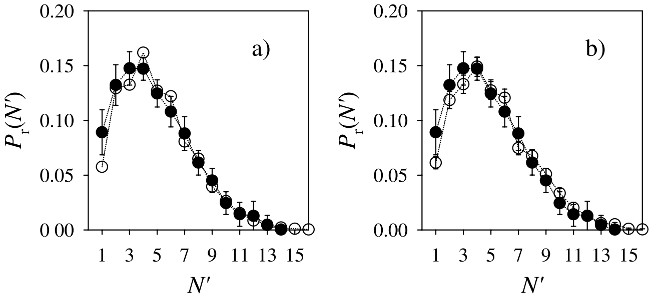

FIG. 2. Comparison between the experimental OH rotational distributions determined here (●) for the $H + H_2O$ abstraction reaction with those predicted (○) by (a) the 5D QM and (b) QCT calculations.

TABLE I. Cross sections (in Å^2) for the reaction (1) at collision energies close to 2.46 eV (see also Fig. 3).

Experiment	This work	0.041 ± 0.018
Experiment	Wolfrum and co-workers [6]	0.26 ± 0.09
QM 5D theory	This work	0.10
QCT theory	This work	0.089 ± 0.002

The QM dynamical calculations are also approximate. While freezing one of the OH bonds appears to be an excellent assumption up to energies around 1.5 eV [15], it may be less reliable at the high energy employed here.

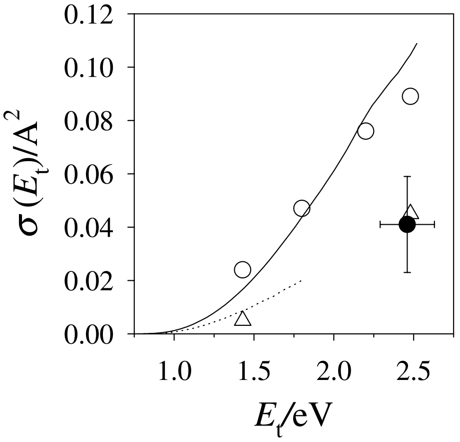

FIG. 3. Comparison between the experimental abstraction reaction cross section (solid point with error bars), and the 5D QM calculations (solid line). The "error bar" in E_t on the experimental cross section allows for the possibility of translational cooling at high values of $p \times \tau$. The 6D QM cross sections (dotted line) [9], which employed the CS approximation, and the QCT data using normal (○) and Gaussian (△) binning procedures are also shown.

Interestingly, the QCT calculations reveal that most trajectories emerge with the OH vibrational action below $1/2 h\nu$. If trajectories are weighted with a Gaussian function centered on the OH quantum mechanical vibrational action, rather than binned in the conventional way, the reaction cross section is reduced to 0.045 Å^2, in much better agreement with experiment (see Fig. 3). By contrast, Gaussian binning for the H_2 fragment has little effect on the cross section. A further assumption in the dynamical calculations is the neglect of rotation in the H_2O reactant. It has been found classically for this reaction that including reagent rotation increases the reaction cross section [14,28,29], but at 300 K only by a modest amount. Quantum mechanically, the effect of H_2O rotation would have to be in the opposite sense to, and significantly more pronounced than, that predicted classically to bring theory and experiment into better agreement.

In summary, we have presented state-of-the-art 5D QM and QCT scattering calculations for the title reaction using the YZCL2 PES. Calculated absolute cross sections and OH rotational distributions are compared with new experimental results obtained at a mean collision energy of 2.46 eV. Although the new theoretical and experimental data agree better than previous studies, there remains a factor of 2 discrepancy in the abstraction reaction cross section. Further work is required to identify the origin of this difference.

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