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The dynamics of the $\text{H} + \text{D}_2\text{O} \rightarrow \text{OD} + \text{HD}$ reaction at 2.5 eV: Experiment and theory

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The title reaction has been studied both experimentally and computationally at a mean collision energy of 2.48 eV. OD quantum state populations, rotational alignment parameters, rovibrational quantum state-resolved center-of-mass angular scattering distributions and HD co-product internal energy release distributions have been determined, along with OD quantum state averaged energy disposals. The experiments employ pulsed laser photolysis coupled with polarized Doppler-resolved laser induced fluorescence detection of the radical products. The OD angular scattering distributions show a preference for scattering in the forward direction, and are quite different from those observed previously at the lower collision energy of 1.4 eV. So too are the kinetic energy release distributions, which reveal that the HD co-products are born significantly more internally excited at 2.48 eV than at 1.4 eV. The HD internal energy distributions obtained from analysis of the Doppler resolved profiles are in reasonable accord with that derived from the direct HD population measurements performed by Zare and co-workers [J. Chem. Phys. **98**, 4636 (1993)] at collision energies around 2.7 eV. The data are compared in detail with the results of new quasi-classical trajectory (QCT) calculations employing two alternative potential energy surfaces (PESs), as well as with the results from previous QCT studies of the title reaction by other workers. Refinements to the most recent of the PESs employed here, that developed using the iterative methods of Collins and Zhang and co-workers [J. Chem. Phys. **115**, 174 (2001)], are also described. The theoretical results obtained using this refined PES agree very well with many of the experimental observables, and the surface appears to be a significant improvement on those previously developed. However, even with this new PES, the QCT calculations at 2.48 eV overestimate the internal excitation of the HD products.
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I. INTRODUCTION

The reaction

has played a key role in the development of reactive scattering theory. There are now several versions of the ground electronic state potential energy surface (PES) available,^{1–10} produced using a variety of semi-empirical or *ab initio* methods, and both quasi-classical trajectory (QCT)^{4,11–18} and quantum mechanical (QM) scattering calculations^{7,19–29} of ever-increasing sophistication have been performed on them. A large body of experimental data is also available with which to compare theoretical predictions. The majority of this experimental work has been devoted to measuring quantum state populations and reaction cross-sections (or rate coefficients) for the forward reaction between H atoms and either vibrationally cold^{30–35} or vibrationally excited^{35–37} water molecules. The molecular frame alignment of vibra-

tionally excited H_2O molecules generated by inelastic scattering between thermal water molecules and translationally excited H atoms has also been observed by Leone and co-workers.³⁸ Much of this experimental and theoretical material has been the subject of recent review.^{39–45}

In spite of all this activity, apart from reports from the work of Brouard *et al.* on the product $\text{OH}(\text{OD})$ quantum state-resolved scattering dynamics of the forward reaction between H and H_2O (Refs. 46 and 47) and $\text{H} + \text{D}_2\text{O}$ (Ref. 47) at collision energies close to 1.4 eV, there have been only two measurements of angular scattering and kinetic energy release distributions for this system. Both of these have focused on the reverse reaction between OH and D_2 at energies just above threshold. Casavecchia and co-workers employed the crossed-molecular beam method,^{48,49} while more recently Davis and co-workers⁵⁰ studied the same reaction using the D atom Rydberg tagging method. In the latter case, Davis and co-workers were able to obtain the angular scattering

distribution with HOD product vibrational quantum state resolution.⁵⁰

We focus here on the scattering dynamics of the isotopically substituted reaction

at collision energies close to 2.5 eV ($\equiv 240 \text{ kJ mol}^{-1}$), about 1.5 eV above the reaction barrier (the thermochemistry is based on a recent re-evaluation by Ruscic *et al.*⁵¹). This particular isotopic variant has been studied previously, principally by the group of Wolfrum and co-workers, who used hot H atom experiments similar to those presented here to determine reaction cross sections and OD rotational quantum state population distributions.³¹ Zare and co-workers have used resonantly enhanced multiphoton ionization (REMPI) techniques to provide a direct determination of the HD quantum state populations³⁴ at collision energies centered around 2.7 eV. They have also determined OD rotational distributions at a collision energy of 1.5 eV, both for the reaction with ground state D_2O , and with vibrationally excited D_2O .³⁵ As noted above, Brouard *et al.* have compared the scattering dynamics of reaction (2) with that of reaction (1) at a collision energy of 1.4 eV.⁴⁷ Much of the data from that study have been compared with the results from QCT calculations on several recently developed potential energy surfaces (PESs).^{4,13,15–18} Although these calculations account qualitatively for some features of the experimental results, to date none of them are able to reproduce all aspects of the experiments.

We will present both experimental and QCT calculated OD rotational quantum state population distributions, rotational angular momentum alignment parameters, and quantum state-resolved angular scattering and kinetic energy release distributions for reaction (2) at a collision energy close to 2.5 eV. The experimental data have been obtained using the photon-initiated reaction technique, coupled with polarized, Doppler-resolved laser induced fluorescence (LIF) detection.^{52,53} The QCT calculations have been performed on two different PESs, that by Ochoa and Clary (henceforth referred to as the OC PES),³ and a refined version of that developed using iterative methods by Yang, Zhang, Collins, and Lee (the YZCL2 PES).^{7,9,10} In Sec. II we outline the experimental, data analysis and computational procedures that have been employed. Refinements to the YZCL2 PES are also described. In Sec. III the results are presented and discussed in the light of the new QCT theoretical data, and in the light of previous experimental and theoretical work. In particular, where calculations are available,^{4,15,16} we also compare the experimental data with those predicted using the PES of Schatz and Harding and their co-workers (known as the WSLFH PES).⁴

II. METHOD

A. Experimental procedures

The experimental procedure has been described previously.^{46,47,54} Polarized laser photolysis of HBr at $\lambda \approx 193 \text{ nm}$ was used to generate translationally excited H atoms,

yielding a mean collision energy of $\langle E_t \rangle = 2.48 \text{ eV}$ (FWHM $\sim 0.21 \text{ eV}$), with a mean translational anisotropy parameter close to $\beta \approx -1.0$.^{55,56} The collision energy distribution is bimodal (with peaks at 2.11 eV and 2.55 eV), due to the spin-orbit splitting in the ground state of the Br atom, but the population in the excited spin-orbit state, which is responsible for the slower H atoms, is only 15%.^{55–57}

The HBr precursor and D_2O target molecule gases in a 1:1 ratio were flowed through separate inlets into the reaction chamber at a total pressure $p \leq 100 \text{ mTorr}$. The delay τ between the photolysis and probe laser pulses was $\sim 50 \text{ ns}$. These conditions yield pressure times time-delay values of $p \times \tau \sim 5 \text{ Torr ns}$, similar to those achieved in our previous studies,^{46,47} and sufficiently stringent to ensure single collision conditions. $\text{OD}(v' = 0)$ radicals were probed on the 0–0 band of the $A \leftarrow X$ transition using polarized, narrow-band radiation at wavelengths around 310 nm: the etalon narrowed dye laser bandwidth was determined to be $0.095 \pm 0.010 \text{ cm}^{-1}$ using procedures discussed in detail previously.⁵⁴ LIF signals were detected through a 310 nm interference filter with a ultraviolet (UV) sensitive photomultiplier, and transferred to a microcomputer for shot-to-shot normalization and signal averaging. To improve the signal-to-noise ratios, approximately 20 scans of the Doppler-resolved profiles were recorded in each of the laser pump–probe geometries A, B, and D.⁵⁸ Broad-band spectra were assigned and populations determined using output data from the program LIFBASE.⁵⁹ Great care was taken to avoid complications that might arise due to signal saturation, and the broad-band spectra were corrected for the transmission curve of the interference filter.

The method used to obtain the rotational angular momentum alignment data has also been described elsewhere.⁵⁴ The photolysis laser radiation was first polarized using a Rochon polarizer, after which it passed through a photoelastic modulator, which enabled the polarization to be switched on alternate laser shots. Broadband scans of isolated LIF transitions were performed with the photoelastic modulator switching between pump–probe geometries A and B.⁵⁸ The LAB frame rotational alignment parameters $A_0^2(\text{LAB})$ were determined from the ratio of integrated line-intensities obtained in the two geometries, using the line strength equations developed by Greene and Zare.^{60,61}

In the semiclassical limit, the LAB frame rotational alignment can be related approximately to the rotational alignment in the CM frame *via* the equation⁶²

$$A_0^2(\text{LAB}) = \frac{2}{5} \beta \langle P_2(\hat{\mathbf{v}}_{\text{H}} \cdot \hat{\mathbf{j}}') \rangle \approx \frac{2}{5} \beta \langle P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{j}}') \rangle = \frac{2}{5} \beta a_0^2, \quad (3)$$

where β is the translational anisotropy parameter characterizing the reactant H atom angular distribution,^{55,56} and $\mathbf{v}_{\text{H}}$ is the velocity vector of the hot H atom. Formally, the LAB frame rotational alignment is referenced to the H-atom velocity, $\mathbf{v}_{\text{H}}$, rather than to the relative velocity, $\mathbf{k}$. However, in the present system $v_{\text{H}} \gg v_{\text{D}_2\text{O}}$, such that $\mathbf{v}_{\text{H}} \approx \mathbf{k}$, and therefore Eq. (3), together with the knowledge that the translational anisotropy parameter for the photodissociation of HBr is -1.0 ,^{55,56} can be used to effect an approximate transformation from the LAB to the CM frame. Finally, additional rotational alignment data were obtained at a collision energy of

1.4 eV, using 225 nm photodissociation of H_2S as the source of hot H atoms, as described in detail in Refs. 46, 47, and 54.

B. Doppler profile analysis

Composite Doppler profiles, which depend separately on moments of the joint LAB velocity-polarization distribution, were constructed from linear combinations of sets of experimental data^{61,63} recorded using the counter-propagating (cases A and B) and mutually orthogonal (case D) excitation-detection geometries, and $Q\uparrow$ and $P/R\uparrow$ transitions.^{58,61} The composite Doppler line shapes (suitably convoluted with laser line-shape function) may be written as functions of the component of the product velocity along the probe laser propagation axis, v_p :⁶³

$$D_0^K(k_1, k_2; v_p) = \int_{v=v_p}^{\infty} \frac{1}{2v} \overline{\beta}_0^K(k_1, k_2; v) P_{k_1}\left(\frac{v_p}{v}\right) dv,$$

where $\overline{\beta}_0^K(k_1, k_2; v)$ are the rescaled laboratory frame bipolar moments,⁶³ averaged over the spread of atomic and molecular reagent velocities, and the P_{k_1} are Legendre polynomials.

The center-of-mass (CM) angular and kinetic energy release distributions were determined by a least-squares-fitting procedure to the LAB speed dependent composite profile,

$$D_0^0(0,0; v_p) = \int_{v=v_p}^{\infty} \frac{1}{2v} \overline{\beta}_0^0(0,0; v) P_0\left(\frac{v_p}{v}\right) dv,$$

and the LAB anisotropy dependent profile,

$$D_0^2(2,0; v_p) = \int_{v=v_p}^{\infty} \frac{1}{2v} \overline{\beta}_0^2(2,0; v) P_2\left(\frac{v_p}{v}\right) dv,$$

using a series of basis functions, as described in detail previously.^{46,54} The analysis yielded the moments, a_{nm} , of the joint CM distribution in scattering angle, θ_t , and fractional energy release into translation f_t

$$P(\theta_t, w) \equiv P(\theta_t, f_t) \left| \frac{df_t}{dw} \right| \\ = \frac{1}{4} \sum_{n,m} a_{nm} P_n(\cos \theta_t) P_m(f_t') \left| \frac{df_t'}{dw} \right|,$$

where w is the CM speed of OD, and

$$f_t' = (2f_t - 1),$$

$$\left| \frac{df_t'}{dw} \right| = 2M \frac{m_{\text{OD}}}{m_{\text{HD}}} \frac{w}{E_{t,\text{max}}'},$$

and $E_{t,\text{max}}'$, the maximum possible kinetic energy release, is given by

$$E_{t,\text{max}}' = -\Delta_r H_0^0 + E_t + E_{\text{D}_2\text{O}} - E_{\text{OD}}. \quad (4)$$

M in these equations is the total mass, and $E_{\text{D}_2\text{O}}$ and E_{OD} , appearing in the final expression, are the average internal

energy of the thermal D_2O precursor and the *fixed* internal energy of the probed OD level, respectively. As in the QCT calculations (see below), the CM scattering angle θ_t is defined so that rebound dynamics corresponds to backward scattered OD products. The moments of the CM distribution were assumed to be independent of the comparatively narrow spread of reactant relative speeds, v_r . As noted in our previous reports,^{46,47} satisfactory fits to the data could be obtained assuming a joint CM distribution of separable form, for which the a_{nm} coefficients may be set equal to $a_n \times b_m$. Converged fits to the data were obtained with three moments in $\cos \theta_t$ and four moments in f_t . Finally, the error limits on $P(\cos \theta_t)$ and $P(f_t)$ were determined using a Monte Carlo technique, described in detail elsewhere⁵⁴ (see also discussion in Sec. III).

C. Potential energy surface

The YZCL2 PES¹⁰ is given by a weighted, w_i , average of second order Taylor expansions, T_i , centered at data points scattered throughout the configuration space of the system,⁶⁴⁻⁶⁷

$$V = \sum_{g \in G} \sum_{i=1}^{N_{\text{data}}} w_{g \circ i} T_{g \circ i}. \quad (5)$$

Here, G denotes the symmetry group of the molecule, the complete nuclear permutation inversion (CNPI) group, and $g \circ i$ denotes that the i th data point is transformed by the group element g . The sum over $g \in G$ means that all permutationally equivalent data points are included in the data set, so that the PES of Eq. (5) exhibits the full molecular symmetry. In this context, the H and D atoms are indistinguishable. The data which defines the YZCL2 PES was constructed using an established iterative procedure^{64,65} that selects data geometries from molecular configurations encountered in classical trajectory simulations of the reactions. These simulations were originally carried out at a range of translational energies no higher than 2.1 eV. Therefore, to improve the accuracy of this PES at configurations appropriate to the present experiments, the iterative construction of the PES was recommenced with simulations of $\text{H} + \text{H}_2\text{O}$ collisions carried out at a relative translational energy of 2.45 eV. The H_2O molecule was given a microcanonical distribution of vibrational energy approximately equal to the zero point energy (0.57 eV), with no rotational angular momentum. Using the standard iterative method, 122 new data points were added, giving a total of 2037 data points (the modified PES is available on request). The additional data points were initially constructed for the YZCL1 surface using the QCISD(T)/6-311++G(3df,2pd) level of theory for the electronic energy, and first and second derivatives of the energy. The energy (only) of each data point was then replaced by the more reliable value obtained at the UCCSD(T)/aug-cc-pVQZ level of theory, which defines the data set of the YZCL2 PES. The new data points have energies mostly in the range between 1.0 eV and 2.5 eV above the zero point energy of $\text{H} + \text{H}_2\text{O}$. Classical trajectory calculations show that this modification of the PES appears to have only a very

small effect on the integral cross section for the abstraction reaction, even at high energy. However, the cross section for exchange in $\text{H} + \text{H}_2\text{O}$ is increased by about 20% at 2.48 eV.

D. Computational method

The QCT methods employed here have been described previously in detail in Refs. 17, 18, and 68. Batches of 25 000 trajectories were propagated for each collision energy in the range 0.9 to 2.2 eV. At $E_i = 2.48$ eV a batch of 400 000 trajectories was run using the YZCL2 PES and 150 000 using the OC PES. A total of about 1700 reactive trajectories were found in both batches at this collision energy. The maximum impact parameter was set at 1.5 Å, and the initial distance from the H atom to the D_2O molecule was 8 Å. The ground vibrational state of the rotationless D_2O reagent was determined by means of a vibrational action calculation,⁶⁹ where actions were converged to $0.05 \hbar$. Integration of the equations of motion was carried out using a modified version of the VENUS96 program,⁷⁰ A time step of 0.025 fs was employed, which gave a conservation of energy better than 1 in 10^5 . The pseudoquantization of the final diatomic products has been performed by equating the modulus of the classical rotational angular momentum to $\sqrt{j'(j'+1)}\hbar$. With the (real) j' value so obtained, the vibrational quantum number v' was found by equating the internal energy of the molecule to a rovibrational Dunham expansion in $(v'+1/2)$ and $j'(j'+1)$, whose coefficients were calculated by fitting the semiclassical or quantum rovibrational energies given by the asymptotic diatomic potentials of the PES. The integral cross sections, product quantum state distributions and differential cross sections for the $\text{H} + \text{D}_2\text{O}$ reaction have been calculated without considering energy constraints imposed either on the OD or HD diatoms;¹⁵ that is, trajectories yielding a diatom with an internal energy smaller than the zero point vibrational energy have not been discarded. We have observed that the present results do not change within the statistical uncertainty by imposing such energy constraint on the HD product molecule. Interestingly, we have found that the OD vibrational action is not conserved for most of the trajectories leading to $\text{OD}(v'=0)$. Thus, the standard binning method described above may yield integral cross sections higher than those obtained by quantum mechanical methods. It would be interesting to test the weighted binning approach proposed by Bonnet and Rayez⁷¹ on the $\text{H} + \text{D}_2\text{O}$ and $\text{H} + \text{H}_2\text{O}$ reactions.⁷²

The scattering angle has been defined^{17,18} as that formed between the incoming D_2O and the outgoing OD molecule. Differential cross sections (DCSs) were calculated using the Legendre moment expansion method,⁶⁸ with the implementation of the Smirnov–Kolmogorov statistical test to decide when to truncate the series. Significance levels higher than 90% were achieved using 3–4 moments, ensuring good convergence, such that the inclusion of more terms did not produce a significant change. The rotational angular momentum alignment a_0^2 of OD rotational states has been calculated using the method presented elsewhere.^{17,73} Finally, the $P(f_i)$ distributions have been simulated using the procedure indicated in Ref. 17 (see also Sec. III F).

FIG. 1. (a) Absolute cross sections (in $\text{\AA}^2$) for the $\text{H} + \text{D}_2\text{O} \rightarrow \text{D} + \text{HOD}$ exchange reaction: ●, Wolfrum and co-workers (Ref. 31); ○, present QCT results on YZCL2 PES; —, QM results on the ZCL PES (Refs. 9 and 10). (b) Absolute cross-sections (in $\text{\AA}^2$) for the $\text{H} + \text{D}_2\text{O} \rightarrow \text{OD} + \text{HD}$ abstraction reaction: ●, Wolfrum and co-workers (Ref. 31); ○, present QCT results on YZCL2 PES; ▼, QCT results obtained using the WSLFH PES reproduced from Ref. 15.

III. RESULTS AND DISCUSSION

A. Integral cross sections

Figure 1(a) shows the present QCT calculated integral cross sections (ICSSs) on the YZCL2 PES as a function of collision energy (i.e., the excitation function) for the $\text{H} + \text{D}_2\text{O} \rightarrow \text{HOD} + \text{D}$ hydrogen exchange reaction. As can be seen the QCT ICSSs at 1.5 eV and 2.2 eV slightly overestimate the experimental values measured by Wolfrum and co-workers³¹ but fall within the error bars. The QM excitation function calculated by Zhang *et al.*⁹ using the YZCL1 PES is always below the QCT excitation function although the agreement is fairly good. In contrast, the QCT calculations by Castillo and Santamaria¹⁷ using the OC PES yielded ICSSs much larger than the present ones and the QM ICSSs on the YZCL1 PES at $E_i < 1.5$ eV. The large discrepancy between the excitation functions obtained with the OC PES and the YZCL1 and YZCL2 PES is to be expected because the

OC PES describes the exchange reaction path quite poorly due to the lack of *ab initio* points around this region.³

In Fig. 1(b) the QCT excitation function on the YZCL2 PES for the $\text{H} + \text{D}_2\text{O} \rightarrow \text{OD} + \text{HD}$ abstraction reaction is compared with the experimental determinations by Wolfrum *et al.*,³¹ the QM wavepacket calculations on the YZCL1 PES by Zhang and co-workers⁹ and the QCT calculations by Troya *et al.* using the WSLFH PES.¹⁵ In this case, all the theoretical ICSs are in clear disagreement with the experimental ones by almost a factor of 10. The same lack of agreement has been found for the $\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$ reaction in the most recent QCT and QM calculations.^{9,15,17,18} In any case, the theoretical and experimental excitation functions have a fairly small slope indicating that translational energy does not promote the reaction effectively.

B. OD quantum state populations

The $\text{OD}(v'=0)$ rotational population distribution generated *via* the hot H atom reaction with D_2O at 2.48 eV is shown in Fig. 2(a). $\text{OD}(v'=1)$ fragments could not be detected under the conditions described in Sec. II. The rotational population data have been averaged over OD spin-orbit and Λ -doublet levels. These fine-structure state averaged populations are in excellent accord with those determined under similar conditions by Wolfrum and co-workers³¹ [see Fig. 2(a)], although the present measurements extend the earlier ones to somewhat higher N' . We have previously demonstrated that a simple Franck-Condon model can be used to account almost quantitatively for the OH and OD rotational population distributions observed at collision energies close to 1.4 eV.⁴⁷ By contrast, the OD rotational distribution determined here at 2.48 eV is significantly hotter than that reported previously,⁴⁷ suggesting some momentum transfer between the highly energetic H atoms and the DOD moiety at these high collision energies.

Figure 2(b) and Fig. 2(c) show the Λ -doublet and spin-orbit population ratios for the OD products of reaction (2). The spin-orbit data have been corrected for differences in the degeneracies of the two sets of levels: apart from the very lowest levels, the spin-orbit ratios are close to statistical. By contrast, the reaction leads to preferential population of the A' Λ -doublet level [see Fig. 2(b)], behavior which mirrors that found previously for the reaction (2) at 1.5 eV,³⁵ and the $\text{H} + \text{H}_2\text{O}$ reaction.³⁰ Enhanced population of the A' over the A'' level would be consistent with the conservation of electronic A' symmetry during reaction, and a reaction mechanism in which torques exerted on the departing OD moiety are confined preferentially to the DOD plane. The behavior is very similar to that observed in the photodissociation of H_2O (D_2O) *via* the $\tilde{A}$ state, although in that case the electronic symmetry is A'' , and it is the OH(OD) A'' Λ -doublet level which is overpopulated.⁷⁴

In Figs. 3(a)–3(c) we compare the experimental OD quantum state populations (averaged over the fine-structure state) with those derived from the present QCT calculations on the OC and YZCL2 PESs, discussed in Sec. I, and with previous QCT results obtained by Schatz and co-workers employing the WSLFH PES.^{4,15,16} (Note that the latter cal-

FIG. 2. (a) $\text{OD}(v'=0, N')$ rotational population distribution for the $\text{H} + \text{D}_2\text{O}$ reaction, averaged over OD fine-structure states, determined at a mean collision energy of 2.48 eV. ●, this work; ○, Wolfrum and co-workers (Ref. 31). (b) The OD Λ -doublet propensities determined under the same conditions. The filled and open circles refer to the $\Pi_{3/2}$ and $\Pi_{1/2}$ states of OD. (c) The spin-orbit population ratios for the A' Λ -doublet levels of OD.

culations were performed with D_2O in $j=2$,¹⁵ unlike the present calculations in which rotationless D_2O was employed.) In making the comparisons with the new calculations we have used the assignment $N'=j'$, where N' is the

FIG. 3. (a) Comparison between the experimental and QCT calculated rotational quantum state distribution for the title reaction at 2.48 eV. The QCT data employ the YZCL2 PES, and we have made the quantum number assignment $N'=j'$ where j' is the classical rotational angular momentum, and N' is the total $\text{OD}(^2\Pi)$ angular momentum, apart from electron spin (see text for details). (b) As in (a), except that the QCT calculations employ the WSLFH PES, and have been read off Fig. 6(a) of Reference 15. (c) As in (a), except that the QCT calculations employ the OC PES. Note the change in x-axis scale compared with (a) and (b).

total angular momentum apart from electron spin, and j' is the rotational angular momentum employed in the QCT calculations which treat OD as a closed shell species. As discussed in Ref. 18, the assignment $N'=j'$ is justifiable on the

basis of a comparison of rotational energies for $N'\geq 5$. While the QCT calculations on all the surfaces agree qualitatively with experiment, the OC PES overestimates the OD rotational excitation, and, as noted previously,¹⁵ it is somewhat underestimated on the WSLFH PES. It should be borne in mind that the OC PES also predicts unrealistically high levels of OD vibrational excitation,¹⁷ which are not observed experimentally (a fact which is evident in the energy disposal data to be presented below). The YZCL2 PES provides almost quantitative agreement with the experiment. Small discrepancies between experiment and QCT prediction for low N' values are perhaps not surprising, given the neglect of the open-shell nature of the electronic structure of OD.¹⁸

C. Rotational angular momentum alignment

Rotational alignment data (transformed into the center-of-mass frame as described in Sec. II) obtained at a mean collision energy of 2.48 eV are presented in Fig. 4 as a function of $\text{OD}(v'=0)$ quantum number N' . Figure 5 shows analogous alignment parameters for the $\text{H}+\text{D}_2\text{O}$ reaction at a collision energy of 1.4 eV. At both energies the OD products are born with near zero rotational alignment. In making these measurements we have employed the A'' Λ -doublet level to determine the alignment probed *via* the $Q_1\uparrow$ branch, which is the most sensitive branch to rotational alignment effects. However, separate experiments, in which we have probed the rotational alignment of the OH products generated by the $\text{H}+\text{H}_2\text{O}$ reaction at 1.4 eV, suggest that the alignment parameters are relatively insensitive to the Λ -doublet level probed.⁷⁵

Several factors might be responsible for the low rotational alignment observed experimentally. It is worthwhile considering first what one would expect if OD behaved as a pure spectator during reaction. In the room temperature bulb experiments, the angular momentum as well as the spatial orientation of the D_2O molecule is isotropically distributed. In the pure spectator limit, OD product rotation would come exclusively from the zero point bending and overall rotational motion of the reactant D_2O molecule, and would be aligned with respect to the D_2O plane. Let us suppose the reaction probability to be independent of the alignment of the D_2O target molecule with respect to the reactant relative velocity vector. Under these conditions of zero *reagent* stereoselectivity, transfer of angular momentum from the D_2O reactant to the OD product would generate negligible OD rotational alignment, since the distribution of reactive D_2O planes would be isotropic.

Under the present high collision energy conditions, the OD rotational excitation observed in Fig. 2(a) is significantly greater than that predicted in the spectator limit⁴⁷ (see preceding section). OD product rotational angular momentum does not result purely from thermal or zero-point motion of the parent molecule: some momentum transfer occurs between the H atom and the D_2O target molecule. However, even in the absence of spectator dynamics, it seems reasonable to suppose that the rotational alignment of the OD product will be correlated with the plane of the reactive D_2O target molecule, since torques exerted on the departing OD moiety are likely to be confined to the DOD plane. Thus, if

FIG. 4. (a) ●, rotational alignment parameters, a_0^2 (equivalent to $\langle P_2(\mathbf{k} \cdot \mathbf{j}') \rangle$) in the high- J limit) for the OD products of the H + D₂O reaction at a mean collision energy of 2.48 eV. All data are for the A'' Λ -doublet level. ○, QCT calculated rotational alignment parameters for the title reaction at 2.48 eV employing the YZCL2 PES. (b) As in (a), except that the QCT calculations employ the OC PES. Both QCT calculations employ rotationless D₂O reactants.

the reaction probability were again independent of the alignment of the D₂O target molecule (as discussed above), this would be sufficient to generate near-zero OD alignment, since on average the torque exerted on the OD moiety would be isotropic.

In Figs. 4(a) and 4(b) we compare the experimentally measured alignments with those derived from the QCT calculations at 2.48 eV on the YZCL2, and OC PESs, while in Fig. 5 the results at 1.4 eV are compared with the previous calculations by Schatz and co-workers¹⁶ using the WSLFH PES.⁴ In contrast with the latter work, the present calculations on the YZCL2 and OC PESs do not include the thermal rotational excitation in the target D₂O molecule. Inclusion of this motion is likely to reduce the magnitude of the calculated OD alignment from that shown for the YZCL2 and OC PESs in Fig. 4, but as seen from the calculations on the WSLFH PES¹⁶ (reproduced in Fig. 5), it is unlikely to wash

FIG. 5. ●, As Fig. 4, but the rotational alignment parameters are for the OD products of the H + D₂O reaction at a mean collision energy of 1.44 eV. ○, QCT calculated rotational alignment parameters for the title reaction at 1.4 eV employing the WSLFH PES (Ref. 16) (the data have been read off Fig. 2 of Ref. 16). Note that the calculations of Schatz and co-workers employ D₂O with initial angular momentum $j = 3$ (Ref. 16).

out the alignment completely, particularly at high N' . The OC and YZCL2 surfaces predict quite distinct alignment behavior: the OC PES probably performs worst in comparison with experiment, perhaps not surprisingly in the light of its deficiencies in accounting for the OD rotational excitation (see preceding section). The alignment parameters predicted using the WSLFH PES at 1.4 eV have been discussed previously by Schatz and co-workers,¹⁶ who found that the increasingly negative alignment values observed with increasing N' could be ascribed to the increasing importance of a rebound mechanism.¹⁶ Such a mechanism might also be responsible for the large negative alignment seen on the OC PES. It is tempting to speculate that the slight positive alignment generated on the YZCL2 PES reflects the fact that out-of-plane (i.e., the DOD plane) collisions are more reactive on this PES compared with the other two PESs. Such out-of-plane collisions could provide a mechanism whereby $\mathbf{j}'$ was aligned preferentially parallel to $\mathbf{k}$.

D. OD quantum state-resolved angular scattering distributions

Composite Doppler profile data are shown in Fig. 6, together with the fits and the residuals to the data obtained using the procedures outlined in Sec. II. Although the residuals to the anisotropy dependent profiles (shown in the right-hand panels) retain some very slight structure, the latter becomes almost undetectable when plotted on the same scale as the speed dependent composite profiles (shown in the left-hand panels). While the general features of the CM distributions derived from the analysis (shown below) were unaltered by inclusion of extra fitting parameters, better fits could be obtained by further increasing the size of the basis set. We have erred on the side of caution, and employed the smallest basis set which gives a satisfactory fit to the data.

FIG. 6. Experimental composite Doppler resolved profiles for (a) the $\text{OD}(\Pi_{1/2}, v'=0, N'=1, A')$ and (b) $\text{OD}(\Pi_{3/2}, v'=0, N'=6, A'')$ products of the $\text{H} + \text{D}_2\text{O}$ reaction at a mean collision energy of 2.48 eV. The data on the left are the LAB speed dependent composite profiles, and on the right are the LAB translation anisotropy dependent profiles. The smooth lines through the data are the fits obtained using the basis function methods described in Sec. II.

The CM angular scattering distributions derived from the fits to Doppler profile data for reaction (2) are shown in Figs. 7 and 8. For clarity of presentation, the Monte Carlo determined errors in these distributions have been shown only at selected values of $\cos \theta_t$.⁵⁴ Figure 7 shows the angular scattering distribution for the $\text{OD}(\Pi_{1/2}, v'=0, N'=1, A')$ products of the title reaction, while Fig. 8 shows the corresponding distribution for the $\text{OD}(\Pi_{3/2}, v'=0, N'=6, A'')$ products. In both cases the angular distributions are peaked preferentially in the forward direction, but also have significant components in the sideways direction.

In the same figures the angular distributions are compared with QCT calculated data on the YZCL2 and OC PESs. The QCT results in Figs. 7 and 8 represent averages over trajectories leading to OD in levels $0 \leq j' \leq 2$ and $5 \leq j' \leq 7$, respectively. Although the QCT calculations on neither PES predicts forward peaking angular distributions, those calculated on the YZCL2 PES more closely resemble the experimental data, particularly for the more highly probable OD channel generating ($v'=0, N'=6$) fragments. For this channel the agreement is nearly perfect, apart from in the extreme forward scattering direction. The agreement with the $N'=1$ data is poorer than for $N'=6$, but it should be noted that the former channel is a fairly minor one at these collision energies. [It should also not be forgotten that the experiments for $\text{OD}(v'=0, N'=1)$ probe the upper $\Pi_{1/2}$ spin-orbit state, while those for $N'=6$ probe the lower $\Pi_{3/2}$ spin-orbit state. Spin-orbit effects are of course neglected in the

FIG. 7. (a) Comparison between the experimental and QCT calculated angular scattering distribution for the $\text{OD}(\Pi_{1/2}, v'=0, N'=1, A')$ products of the title reaction at a mean collision energy of 2.48 eV. The QCT data employ the YZCL2 PES for reaction yielding $\text{OD}(v'=0, 0 \leq j' \leq 2)$. (b) As in (a), except that the QCT calculations employ the OC PES. The experimental error bars represent 2σ .

calculations, but OH spin-orbit state dependent differential cross sections have been observed for the reaction $\text{H} + \text{CO}_2$,⁷⁶ and cannot be ruled out in the present system.] The OC PES predicts predominantly backward scattering, at variance with experimental observation. There is a tendency for the dynamics on both PESs to become slightly more rebound in character as the rotational angular momentum of the OD increases, behavior noted previously by Schatz and co-workers on the WSLFH PES.¹⁶ This trend in scattering behavior has been observed previously in our experiments performed at the lower collision energy of 1.4 eV for both $\text{H} + \text{H}_2\text{O}$ and $\text{H} + \text{D}_2\text{O}$,^{46,47} but the current experimental data for $\text{H} + \text{D}_2\text{O}$ at 2.48 eV show no convincing trend with N' within the combined errors of the measurements.

E. HD quantum state populations

QCT calculated HD vibrational and rotational populations are presented in Table I and Fig. 9, respectively. HD

FIG. 8. (a) Comparison between the experimental and QCT calculated angular scattering distribution for the $\text{OD}(\Pi_{3/2}, v'=0, N'=6, A'')$ products of the title reaction at a mean collision energy of 2.48 eV. The QCT data employ the YZCL2 PES for reaction yielding $\text{OD}(v'=0, 5 \leq j' \leq 7)$. (b) As in (a), except that the QCT calculations employ the OC PES.

populations have not been determined directly experimentally in the present work, but as discussed in the next section, analysis of the Doppler-resolved profiles allows the kinetic energy release distribution to be determined, which by energy conservation reflects the internal energy disposal in the

TABLE I. Comparison between the QCT calculated HD vibrational population distributions determined on the YZCL2 and the OC PESs at a collision energy of 2.48 eV. Note that at collision energies centered around 2.7 eV Zare and co-workers determined the HD vibrational populations for $v'=0:1:2$ of 0.47:0.45:0.08 (Ref. 34). Statistical errors are typically less than ± 0.02 . Also included for comparison are QCT results on the WSLFH PES (Ref. 15), which have been taken from Fig. 4 of Ref. 15.

PES	$v'=0$	$v'=1$	$v'=2$	$v'=3$
YZCL2 (this work)	0.49	0.37	0.13	0.01
OC (this work)	0.61	0.28	0.09	0.02
WSLFH (Ref. 15)	0.44	0.51	0.05	0.00

FIG. 9. $\text{HD}(v'=2)$ rotational population distributions generated on the (a) YZCL2, (b) WSLFH (Ref. 15), and (c) OC PESs at a collision energy of 2.48 eV. The solid line in each figure is the $\text{HD}(v'=2)$ rotational distribution determined by Zare and co-workers (Ref. 34) at collision energies centered around 2.5 eV. The data for the WSLFH PES have been read off Fig. 5(c) of Ref. 15, for which the initial conditions also include a minor 30% contribution from slow H atoms with a collision energy of 1.55 eV (Ref. 15).

HD co-product. Direct comparison of the QCT results can be made with the HD population measurements of Zare and co-workers,³⁴ who used REMPI techniques to probe the HD products. As described in detail both in the original paper by

FIG. 10. (a) Comparison between the $\text{OD}(\Pi_{1/2}, v'=0, N'=1, A')$ kinetic energy release distribution determined here at a mean collision energy of 2.48 eV, with that derived from the $\text{HD}(v', j')$ quantum state populations determined by Zare and co-workers (Ref. 34) (which are averaged over all OD quantum states). Note that the latter one-color experiments sampled a range of collision energies, centered around 2.70 eV. See text for details. The sticks at the top of the figure mark the fractional kinetic energy releases for HD products born in $j'=0$ and $v'=0, 1, 2$, and 3 . (b) As for (a) except for $\text{OD}(\Pi_{3/2}, v'=0, N'=6, A'')$.

Zare and co-workers,³⁴ and by Schatz and co-workers,¹⁵ who undertook extensive QCT calculations to model the Stanford experiments, the one color REMPI study sampled a range of collision energies. However, the experimental rotational population data for $v'=2$ were acquired under conditions which approximate quite closely the 2.48 eV fixed collision energy conditions of the present QCT calculations. In Fig. 9 the $\text{HD}(v'=2)$ rotational populations computed for the YZCL2 and OC PESs are compared with the experimental results of Zare and co-workers.³⁴ Also shown are QCT data for the WSLFH PES, which have been read from Fig. 5 of Ref. 15. As noted in the more detailed comparison performed by Schatz and co-workers over all populated HD vibrational states,¹⁵ the WSLFH PES tends to overestimate the $\text{HD}(v'=2)$ rotational excitation,¹⁵ whereas it is underestimated slightly by the OC PES. The YZCL2 PES predicts rotational excitation somewhere between the two other PES, but the rotational distribution derived from this PES is also slightly hotter than observed experimentally.

The HD vibrational quantum state distributions predicted

FIG. 11. (a) Comparison between the experimental and QCT calculated kinetic energy release distribution for the $\text{OD}(\Pi_{3/2}, v'=0, N'=6, A'')$ products of the title reaction at a mean collision energy of 2.48 eV. The QCT data employ the YZCL2 PES. (b) As in (a), except that the QCT calculations employ the OC PES. In each figure, the kinetic energy release distribution has been derived from the $\text{HD}(v', j')$ quantum state populations determined in the QCT calculations, using the method described in the text.

on the OC and YZCL2 PESs are shown in Table I, where they are compared with the previously calculated populations derived on the WSLFH PES.¹⁵ In contrast with the HD rotational excitation, the predictions using the WSLFH and YZCL2 PESs are in reasonable agreement with respect to the HD vibrational excitation. Both PESs also yield vibrational populations which seem reasonably consistent with those determined experimentally by Zare and co-workers³⁴ at collision energies centered around 2.7 eV. This conclusion is supported by the more detailed analysis performed on the WSLFH PES by Schatz and co-workers.¹⁵ The OC PES predicts a significantly colder vibrational distribution than observed on the more recently developed YZCL2 and WSLFH PESs.

F. Kinetic energy release distributions, and energy balance

Analysis of the composite Doppler profile data as described in Sec. II yields OD quantum state-resolved kinetic energy release distributions, which by energy conservation reflect the distributions over internal energies in the unob-

TABLE II. Experimental and QCT calculated energy disposal data for the H+D₂O abstraction reaction at the mean collision energies quoted. The data on the WSLFH PES are taken from Table VIII of Ref. 15.

$\langle f_t \rangle$	$\langle f_r^{\text{OD}} \rangle$	$\langle f_v^{\text{OD}} \rangle$	$\langle f_{\text{int}}^{\text{HD}} \rangle$	$\langle f_v^{\text{HD}} \rangle$	$\langle f_r^{\text{HD}} \rangle$	E_t/eV	Ref.
0.80 ± 0.10	0.07 ± 0.01	0.00 ± 0.02	0.13	≤ 0.05		1.44	47
0.66 ± 0.05	0.05 ± 0.01	0.00 ± 0.02	0.29			2.48	This work
			0.35	0.13 ± 0.03	0.22 ± 0.05	~ 2.7	34
0.60 ± 0.02	0.04 ± 0.001	0.003 ± 0.001	0.36	0.13 ± 0.004	0.23 ± 0.01	2.48	YZCL2
0.56 ± 0.02	0.10 ± 0.01	0.11 ± 0.01	0.23	0.11 ± 0.01	0.12 ± 0.01	2.48	OC
0.35 ± 0.01	0.03 ± 0.02	0.0	0.62	0.17 ± 0.02	0.45 ± 0.05	2.45	WSLFH (Ref. 15)

served HD co-product. These are shown in Fig. 10 for the two quantum states probed here. The distributions are very similar in each case, and vary little with OD quantum state. As noted previously,⁴⁷ the experimental error bars in the kinetic energy release distributions tend to become larger at high f_t values. We believe this to be an inherent feature of the experimental technique: fast moving products have large Doppler shifts, and therefore contribute less to the *amplitude* of the LIF signal. This effect is implicitly accounted for in the Monte Carlo error analysis procedures.⁵⁴ The combs shown in Fig. 10(a) indicate approximately the f_t values of the HD vibrational states for $j_{\text{HD}}=0$.

Given that the HD rovibrational quantum state populations have been determined directly using REMPI at collision energies quite close to those used here, it is important to establish that our own indirect measurements are consistent with this previous work.³⁴ To this end we have simulated the kinetic energy release distribution based on the population measurements of Zare and co-workers.³⁴ The procedure follows that adopted previously, and is described fully in Ref. 17. For each HD quantum state, the value of f_t is evaluated (see below), and the plot of quantum state population versus f_t is then convoluted with a Gaussian with a width chosen to mimic approximately the experimental energy resolution. In evaluating f_t we have accounted for the range of collision energies in the REMPI study³⁴ by assuming that HD products born in $v'=0, 1$ and 2 arise from collision energies of 2.85 eV, 2.65 eV, and 2.48 eV, respectively.^{15,34} We have neglected a minor 10–30% contribution from slow H-atoms (which are generated in conjunction with spin–orbit excited I^* atoms in the photolysis of the HI precursor employed in the Stanford experiments³⁴), since their contribution will be further diminished by the reduction in the relative velocity, and the lowering of the reaction cross-section with decreasing collision energy.³⁴

The simulated kinetic energy release distribution is shown as the dashed curve in Figs. 10(a) and 10(b). The agreement with the present measurements can be considered excellent, given the different initial conditions sampled in the two experiments. The $P(f_t)$ distribution derived from the HD populations of Zare and co-workers is slightly colder translationally (i.e., it peaks at somewhat lower f_t values) than the distributions measured here, but this we believe is consistent with the fact that the average collision energy of the REMPI experiments (~ 2.7 eV) is significantly higher than that used in the present study (2.48 eV). Comparison between the present results at 2.48 eV and those published previously,^{46,47} which sample a collision energy close to 1.4

eV, suggests that the HD internal excitation increases quite dramatically with increasing collision energy. The comparison between the present measurements and the direct experiments of Zare and co-workers³⁴ are entirely consistent with this observation.

In Fig. 11 we compare the experimental kinetic energy release distribution for OD($v'=0, N'=6$) with those derived via QCT methods on the OC and YZCL2 PESs. Unlike the other data we have shown, here the agreement with theory is best with the OC PES (recall that this is the same PES that provides particularly *poor* energy disposal data for the OD product). Although the problems with the QCT calculations on the YZCL2 PES are most likely to be associated with defects in the PES, particularly at these high energies, it is possible that quantum effects significantly influence the HD vibrational quantum state populations. It should be noted that quite small shifts in the HD rovibrational populations (similar to those predicted by the different PESs shown in Fig. 9) can have a significant effect on the $P(f_t)$ distributions, because of the wide rovibrational energy level spacing in HD.

The kinetic energy release data have been used to calculate the mean energy disposal in reaction (2). The averaging over OD internal quantum states is approximate because in the experiments the translational energy releases have only been determined for two OD quantum states. However, given that the kinetic energy release distributions are fairly insensitive to OD quantum state (see Fig. 10), we believe that the OD quantum state averaged energy disposal data should be reliable. The data are shown in Table II. The experiments indicate that at a mean collision energy of 2.48 eV around 66% of the available energy is channeled into product translational excitation. The table serves as a convenient summary of the strengths and weaknesses of the QCT calculations on the various available PESs (note that the data for the WSLFH PES is taken from Ref. 15). Consistent with previous findings,^{15,17} the OC PES significantly overestimates the OD excitation, while the WSLFH PES overestimates the HD rotational excitation.¹⁵ Once more the YZCL2 PES provides the best global fit to the experimental data.

IV. CONCLUSIONS

We have presented fully quantum state-resolved OD angular scattering and kinetic energy release distributions for the hot H atom reaction with D₂O at a mean collision energy of 2.48 eV. OD quantum state population distributions and rotational alignment parameters, as well as quantum state-averaged internal energy disposals have also been reported

under the same conditions. The experimental data provide a stringent test for QCT scattering calculations, and of the potential energy surfaces they employ. Detailed comparisons have been made with the results of QCT calculations on the OC PES,³ on the present version of the YZCL2 PES, and with previous QCT calculations from the group of Schatz and co-workers,^{15,16} who employed the WSLFH PES.⁴ Refinements to the YZCL2 PES which increase its accuracy at high collision energies $E_i \leq 2.5$ eV are also described. Overall the experimental findings are accounted for best by the most recent YZCL2 PES. Apart from the kinetic energy release distribution, the agreement with the data for this PES are nearly quantitative. It will be of interest to see whether QM scattering calculations^{7,24–28} on the most recent PESs^{3,4,9,10} can resolve some of the remaining areas of disagreement between experiment and theory. Further experimental work, particularly to define more precisely the $\text{HD}(\text{H}_2)$ quantum state populations as a function of collision energy, would also be desirable.

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