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The state-to-state photodissociation dynamics of HOD(A)

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HOD, rotationally state selected in the third and fourth OH stretching overtone ($|04\rangle$, $|05\rangle$) levels, has been photodissociated *via* the \tilde{A} state at $\lambda \approx 288$ nm. In accord with previous studies, H + OD is the dominant dissociation channel, with the yield of OH photofragments being below the detection limit in both sets of experiments. Model Franck-Condon calculations suggest that the OD photofragment rotational state distributions, determined by OD(A-X) laser induced fluorescence (LIF), reflect primarily the rotational and zero-point bending motions in the selected rovibrational state of HOD(\tilde{X}). However, in contrast to the state selected photodissociation of H₂O, the OD rotational distributions from HOD also reveal the influence of a small exit channel torque, which is enhanced in the photodissociation of the deuterated molecule by the shift in the OD centre-of-mass relative to that in OH. A modified Franck-Condon model, which accounts approximately for this modest impulsive torque, qualitatively reproduces the observed behaviour. © 1997 American Institute of Physics. [S0021-9606(97)00615-6]

I. INTRODUCTION

The study of state-to-state molecular photodissociation dynamics has for many years attracted much experimental effort and provides a direct and rigorous test of the theoretical understanding of the fragmentation process. The dependence of the photodissociation dynamics on reagent state has perhaps been most thoroughly explored, and understood, for the photodissociation of H₂O via its $A \leftarrow X$ transition. The fully state resolved experimental studies¹⁻⁷ provided by a number of researchers, show that the scalar (internal energy) and vectorial (momentum) disposals in the OH photofragments are profoundly influenced by the rotational and vibrational motions of the parent molecule in its ground electronic state, and are little affected by modest exit channel torques generated on the dissociative A state. Theoretical modelling of these observations, together with data from resonance Raman⁸ and one-photon photodissociation^{9,10} studies, have provided a very detailed understanding of the photodissociation dynamics.^{1,3,5,11–15}

A further chapter in understanding the photodissociation dynamics of water has been opened by study of its partially deuterated isotopomer, HOD. Photofragmentation from the \tilde{A} state potential energy surface, at total supplied energies $<60000 \text{ cm}^{-1}$, occurs *via* two distinguishable product channels, leading to:

$$\operatorname{HOD}(\widetilde{A}) \xrightarrow{\operatorname{D}({}^2\operatorname{S}) + \operatorname{OH}(\operatorname{X}{}^2\Pi)} \operatorname{HOD}(\operatorname{X}{}^2\Pi) + \operatorname{OD}(\operatorname{X}{}^2\Pi).$$

In the ground electronic state, the reduction in symmetry arising from substitution of a deuterium atom for a hydrogen atom lifts the degeneracy of the local mode stretching vibrational states $|nm\rangle$ and $|mn\rangle$ (for the state $|ab\rangle$, *a*, and *b*

refer to the number of quanta in the O-H and O-D local mode stretches, respectively), and the dynamical tunnelling effect, which produces the local mode doublets $|nm\rangle^{\pm}$ in $H_2O_1^{16,17}$ is destroyed.¹⁷ Excitation of either of the two stretching modes is localised and vibrationally mediated photodissociation (VMP) of HOD via the A state can result in selective cleavage of the vibrationally excited bond. In the light of this, the theoretical studies of Imre and co-workers¹⁸ and Schinke and co-workers, 19,20 and the state-selected experiments of Crim and co-workers^{20,21} (photodissociating HOD $(4\nu_{OH})$ at 218.5, 239.5 and 266 nm) and Rosenwaks and co-workers 22,23 (photodissociating HOD in the $1\,\nu_{OH},\,1$ $v_{\rm OD}$ and $3v_{\rm OD}$ modes at 193 nm), have focussed on the parent vibrational state and photon energy dependence of the H + OD/D + OH branching ratio. The theoretical predictions are in qualitative agreement with the experimentally observed trend: provided the supplied energy is less than that required for excitation above the D + OH \rightarrow H + OD reaction barrier on the A state surface, the selectivity of the dissociation process is enhanced by increased initial vibrational excitation in the bond to be cleaved. These results have been shown to be in accord with classical expectation.²⁰ When excitation occurs above the barrier (as in the case of the 218 nm photodissociation of HOD($4\nu_{OH}$), ^{20,21} the 193 nm photodissociation of HOD($3\nu_{OD}$) (Ref. 23), and the 157 nm direct photolysis experiments of Bersohn et al.²⁴), the branching ratios have been shown to be strongly dependent on quantal interferences arising from the overlap of the ground and excited state parent molecular wavefunctions, and classical mechanics provides only a very qualitative picture of the dissociation dynamics.²⁰ Except for the 193 nm photolysis of HOD($3\nu_{OD}$), ^{18,20,23,24} the measured and (quantum) calculated ratios in this energy regime are in near quantitative agreement.

Less information is available on the effect of isotopic substitution on the OH/OD photofragment rovibrational dis-

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tributions. Crim and co-workers,²¹ photolysing HOD($4\nu_{OH}$) at 218.5, 239.5 and 266 nm, measured the relative yields of the OH and OD photofragments produced in v=0 and 1. Both fragments are produced predominately in their ground vibrational states, with the relative yield of vibrationally excited products exhibiting a dependence on the photon energy. Wavepacket propagation calculations²⁰ on an *ab initio* potential energy surface²⁵ reproduce these observations well. However, at supplied energies corresponding to excitation below the barrier on the A state surface, the calculations underestimate the yield of vibrationally excited fragments. The D + OH/H + OD branching ratio at these energies^{20,21,23} was also underestimated by these calculations,²⁰ and by the calculations of Imre and co-workers,¹⁸ which used the same *ab initio* surface, suggesting that some modification of the calculated A state surface is required, perhaps in the barrier height for the hydrogen/ deuterium exchange reaction. Discrepancy between the calculated and measured OH product vibrational distributions arising from H₂O photolysis *via* the A state would likewise suggest this to be necessary.^{9,10,13}

The OH rotational distributions generated in the state-tostate photodissociation of H_2O ,^{1–5} have been shown to be satisfactorily modelled using the Franck-Condon model of Balint-Kurti,¹¹ implying that final state interactions in the exit channel are of minor importance. Variations in the photofragment rotational distributions with increasing parent molecule vibrational excitation and decreasing photolysis wavelength have been shown to reflect changes in the bound state rotational-bending motion of water, arising from preferential dissociation from increasingly extended H-OH regions of the potential.⁵ Small differences in detail between the calculated and experimental OH distributions are probably the result of the neglect of exit-channel torques in the Franck-Condon calculations.^{1,5} The shift in the centre-ofmass arising from the substitution of a deuterium atom for a hydrogen atom in the water molecule should make the OD photofragment rotational distributions produced in HOD photolysis more sensitive indicators of these exit-channel effects. Resonance Raman spectra of HOD obtained by Sension and co-workers,8 exciting at 174.6, 171.4 and 160.0 nm (resonant with the A state), show no activity in the bending mode, and therefore indicate that the OD photofragment rotational population distributions should still be strongly influenced by the initial ro-vibrational motion of the bound state HOD molecule. A state-to-state study of HOD photodissociation should therefore provide detailed information on the sensitivity of the photofragment rotational distributions to the concerted influence of the motions of the parent molecule on both its ground and electronically excited state surfaces.

Presented in this article are the measurement and interpretation of the OD photofragment rotational distributions arising from the 288 nm photodissociation of HOD, initially prepared in the third and fourth OH stretching overtone levels. A branching ratio between the H + OD and D + OHdissociation channels has also been estimated from OD and OH LIF measurements. The OD fragment distributions are found to be only slightly dependent on the intermediate vibrational state, a result which contrasts with the analogous H_2O experiments⁵ (photolysing $H_2O(4\nu_{OH})$ and $(5\nu_{OH})$ at 282 nm) in which a strong dependence was observed. Calculations using a modified Franck-Condon model, which includes an approximate treatment of the small exit-channel torque, qualitatively reproduce the experimental data and provide an insight into the dynamics of parent molecule during the photodissociation.

II. EXPERIMENT

The apparatus employed has already been described in detail elsewhere.^{5,26} An excimer laser was used to pump two dye lasers, one to provide the overtone excitation radiation $(\lambda \simeq 720 \text{ and } 590 \text{ nm for HOD}(4\nu_{OH}) \text{ and } (5\nu_{OH}) \text{ respec-}$ tively) and the other to provide both the photolysis radiation $(\lambda \simeq 288 \text{ nm})$ and the OD/OH photofragment LIF probe radiation, using the 1-0 band of the OD/OH(A-X) transition. Both beams were counterpropagated into a reaction cell with their electric vectors parallel to the fluorescence detection axis, and the photofragment fluorescence signal was detected through a 310 nm interference filter (centered on the 1-1 OH/OD band) using a photomultiplier. The photomultipler signal was recorded on a boxcar integrator and transferred on a shot-by-shot basis to a PC for power normalisation and averaging. The HOD was produced with a 5:1 mixture of H₂O and D₂O (99.95% pure, Aldrich Chemical Ltd.), which was allowed to flow into the reaction cell at pressures of \sim 50 mTorr.

Similar to the previously reported study of the VMP of $H_2O(A)$ from this laboratory,⁵ the high intensity of the photolysis radiation used in this study was sufficient to saturate highly the photofragment LIF spectra. Therefore, no correction for the OH/OD rotational linestrengths or rotational alignment were made^{6,27,28} and rotational population distributions were determined from peak height measurements. The close agreement between the rotational distributions extracted from the main and satellite transitions, which probe the same product ground state level, substantiates the use of this procedure.

The HOD $(4\nu_{OH})$ and $(5\nu_{OH})$ overtone transitions were initially detected by recording the action spectra, detecting the OD photofragment LIF and scanning the overtone excitation radiation (Figure 1(c)). Rotational assignments were made on the basis of rigid asymmetric rotor simulations of the spectra^{30,31} (Figure 1(d)), assuming predominantly A-type rather than B-type character ($\sim 0.7:0.3$).^{32,33} Rotational transitions (P \uparrow , Q \uparrow and R \uparrow) up to J'' = 8 were unambiguously assigned in the $(4\nu_{OH})$ and $(5\nu_{OH})$ VMP OD action spectra recorded between 13706.1 and 13954.8 cm⁻¹ and 16730.8 and 17015.5 cm⁻¹, respectively.²⁹ The calculated rotational constants and the observed band origins are given in Table I, along with the corresponding wavenumbers of the ground and fundamental vibrational states.^{32,33} To ensure that only HOD molecules were state selected in the photodissociation experiments, a comparison was made between the photoacoustic overtone spectra of pure H₂O and of



FIG. 1. A segment of the rovibrational spectrum in the region of the third OH stretch overtone of HOD using (b) photoacoustic spectroscopy and (c) recording a VMP action spectrum, fixing the probe radiation on the A $^{2}\Sigma-X^{2}\Pi$ (1–0) Q₂₂(1) LIF transition of OD and scanning the overtone excitation radiation. Also shown are (a) the photoacoustic spectrum of pure H₂O in the same region and (d) a simulation of the HOD(4 ν_{OH}) band at 298 K.

a H₂O and HOD mixture (see Figures 1(a) and 1(b)). Only HOD transitions that were clearly unblended with H₂O resonances were used in the study. According to the simulations, the HOD(4 ν_{OH}) and (5 ν_{OH}) overtone transitions to J=0, $0_{00} \leftarrow 1_{01}$, were both overlapped with other HOD transitions, within the resolution of the laser radiation (~ 0.2 cm⁻¹), and thus no data were obtained for photodissociation of HOD(J = 0). (Throughout the text, the unprimed J_{Ka,Ka} no-

TABLE I. The band origin energies and rotational constants for selected O–H stretching vibrational states of HOD. The zero point energy of HOD is 4000.3 cm⁻¹. The rotational constants quoted for $(4\nu_{OH})$ and $(5\nu_{OH})$ reproduce the line positions of transitions to levels with J \leq 8 to an estimated accuracy of \pm 0.2 cm⁻¹.

Vibrational level	Band origin energies / cm^{-1}	Rotational constants cm ⁻¹			
$(\nu_{\rm OH}, \nu_{\rm bend}, \nu_{\rm OD})$		A	В	С	
(0,0,0) ^a	0	23.4139	9.1034	6.4063	
(1,0,0) ^b	3707	22.3549	9.0864	6.3183	
(4,0,0)	13844.8	19.465	9.042	6.092	
(5,0,0)	16911.8	18.467	9.022	6.020	

^aTaken from Ref. 32.

^bTaken from Ref. 33.



FIG. 2. A plot of the water ground state potential of Jensen and co-workers (Ref. 40) and the \tilde{A} state potential of Staemmler and Palma (Ref. 25) against the dissociation coordinate, R_{H-OD} . Excitation to the excited state potential in this study should preferentially occur from more extended H–OD configurations than in the previous studies of Crim and co-workers (Ref. 20,21) and Rosenwaks and co-workers (Ref. 22).

tation is reserved for the asymmetric rotor level in the upper vibrational level of HOD(\widetilde{X}).) The majority of the photofragment LIF spectra were recorded using R↑ overtone transitions, although the spectra were found to be insensitive to the choice of the branch employed.³⁴ The loss of information concerning the effect of parent rotational alignment on the photodissocation dynamics is attributed to the highly saturated condition of the photofragment LIF spectra.

III. (H + OD)/(D + OH) BRANCHING RATIO

The 288 nm photodissociation of HOD, initially excited into the third and fourth OH stretching overtone, provides ~8000 cm⁻¹ and ~11000 cm⁻¹ excess energy, respectively, for partitioning into the photofragments. This is considerably lower than that provided in the 218.5, 239.5 and 266 nm experiments of Crim and co-workers^{20,21} on HOD (4 ν_{OH}) and the 193 nm experiments of Rosenwaks and co-workers²² on HOD(1 ν_{OH}). Simple energy conservation arguments suggest that excitation to the \widetilde{A} state surface in the present experiments of the ground state than in previous studies (see Figure 2).

The OD(H) LIF spectra, obtained subsequent to the photolysis of HOD($5\nu_{OH}$) $J_{K_a,K_c}=4_{04}$ and shown in Figure 3, demonstrate that the relative yield of OH radicals is very low: from the total LIF signals collected, the branching ratio was estimated to be $\Phi(OD,v=0)/\Phi(OH,v=0)>23$. A similar result was found for the photodissociation of HOD



FIG. 3. (a) OD $A^2\Sigma - X^2\Pi$ (1–0) and (b) OH $A^2\Sigma - X^2\Pi$ (1–0) LIF spectra arising from the 288 nm photodissociation of HOD(5 ν_{OH}) $J_{K_a,K_a}=4_{04}$.

 $(4\nu_{\rm OH})$, but reduced signal-to-noise levels meant that the best estimate of the branching ratio was $\Phi({\rm OD}, v=0)/\Phi({\rm OH}, v=0)>12$. Compared with the values obtained by Crim and co-workers^{20,21} (~1, >15 and >15 for the 218.5, 239.5 and 266 nm photodissociation of $HOD(4\nu_{\rm OH})$), the data are consistent with an increasing preference for OD production with increasing photolysis wavelength and parent OH stretch excitation.

The absorption cross-section for the $(5\nu_{OH})$ band, $\sigma_{(5\nu_{\rm OH})}$, is approximately an order of magnitude lower than that of $(4\nu_{OH})$.³⁵ However, the overall VMP cross-section, which is a product of $\sigma_{\rm (5\,\nu_{OH})}$ and $\sigma_{\rm elec}$ (the state specific photodissociation cross-section), was estimated to be approximately twice as large as that for the VMP of HOD $(4\nu_{OH})$, based on an analysis of both the total LIF signals and the observed signal-to-noise ratios. This would suggest that, at $\lambda \sim 288$ nm, the overlap between the A state continuum and $(5\nu_{OH})$ overtone wavefunctions is approximately 20 times larger than that of the $(4\nu_{OH})$ state. As is shown in Figure 2, on purely energetic grounds, 288 nm excitation from the $(4\nu_{OH})$ overtone to the A state should occur preferentially from a classically forbidden region of the bound state potential, where the vibrational wavefunction drops off exponentially from a peak close to the classical turning point. In contrast, excitation from $(5\nu_{OH})$ should occur from near the maximum amplitude of the vibrational wavefunction, close to the outer turning point. This may well be the primary cause for the differing VMP cross-sections, and will be discussed further in Section V.



FIG. 4. The OD(${}^{2}\Pi_{3}$) photofragment rotational distributions, for both lambda doublet states $A'(\bullet)$ and $A''(\bigcirc)$, arising from the 288 nm photodissociation of HOD($4\nu_{OH}$) J_{K_a,K_c= 3_{13} (a), 4_{04} (b) and 5_{05} (c). The data (shown on the left) are compared with the distributions obtained in the 282 nm photodissociation of H₂O($4\nu_{OH}$) (Ref. 5).}

IV. $OD(X^2\Pi)$ ROTATIONAL DISTRIBUTIONS

A. The 288 nm photodissociation of HOD($4\nu_{OH}$)

The OD($X^2\Pi_{\frac{3}{2}}$) photofragment rotational distributions are shown in Figure 4 (plotted as a function of N, the total angular momentum quantum number excluding spin), for both lambda doublet states A' and A", arising from the dissociation of HOD($4\nu_{OH}$) J_{K_a,K_c}= 3_{13} (a), 4_{04} (b) and 5_{05} (c). For comparison, the corresponding data arising from the near isoenergetic 282 nm photolysis of H₂O($4\nu_{OH}$)⁵ are also included. Clearly the OD distributions are very sensitive to the rotational state selected in the HOD intermediate overtone level.

B. The 288 nm photodissociation of HOD($5\nu_{OH}$)

The increased OD LIF signal-to-noise levels resulting from the initial excitation of the fourth compared with those from the third overtone meant that a more detailed study of the 288 nm photodissociation of HOD(5 ν_{OH}) was undertaken. The resulting OD rotational distributions are summarised in Figures 5(a)-5(e) for a range of parent rotational states $(J_{K_a,K_c}=3_{13} (a), 4_{04} (b), 5_{05} (c), 5_{15} (d) and 6_{06} (e)).$ The oscillations in the lambda doublet population distributions are clearly quite different from the corresponding OH distributions obtained in the H₂O(5 ν_{OH}) VMP study.^{5,34} Comparing the OD distributions obtained from the photodissociation of HOD(4 ν_{OH}) and (5 ν_{OH}) (i.e. those shown in Figures 4(a)-4(c) with those in 5(a)-5(c), there are small but noticeable differences in parts of the oscillatory structure, although the general forms of the lambda-doublet resolved distributions remain very much the same. This contrasts with



FIG. 5. The OD(${}^{2}\Pi_{3}$) rotational population distributions in the A' (\bullet) and A" (\odot) lambda doublet levels generated via the 288 nm photodissociation of the J_{K_a,K_c=3₁₃ (a), 4₀₄ (b), 5₀₅ (c), 5₁₅ (d) and 6₀₆ (e) rotational states of HOD(5 ν_{OH}). The data (shown on the left) are compared with the distributions obtained in the 282 nm photodissociation of H₂O(5 ν_{OH}) (Ref. 5).}

the VMP of H_2O , where excitation from the $(4\nu_{OH})$ and $(5\nu_{OH})$ overtone states⁵ yield dramatically different oscillatory structure in the OH photofragment rotational distributions. Given the similar energetics of the HOD and H_2O experiments, the contrasting behaviours of the two molecules must be associated with the differing nuclear motions on the ground and excited surfaces accessed in the VMP processes.

Within the experimental errors, the OD spin-orbit population ratios are approximately statistical. Averaging over the lambda-doublet populations, for a given initial parent rotational state, removes the oscillatory structure and yields OD spin-orbit state-resolved population distributions which could be characterized well by a Boltzmann distribution employing a single "rotational temperature". (Slight deviations from Boltzmann behaviour at high N values may reflect the modest preference for the A" lambda doublet state observed at high N.) The photofragment rotational temperatures obtained in this study, and from the previous isoenergetic H₂O study,⁵ are summarised in Table II. Comparing the values for the isoenergetic pairs (HOD(4 ν_{OH}) + 288 nm with

TABLE II. OD photofragment rotational temperatures, calculated from Boltzmann plots of the lambda doublet averaged rotational distributions, generated via the 288 nm photodissociation of HOD($4\nu_{OH}$) and ($5\nu_{OH}$) J_{K_a,K_c} (J = 3-7). Also shown are the corresponding OH product temperatures arising from the 282 nm photolysis of H₂O($4\nu_{OH}$) and ($5\nu_{OH}$) (Ref. 34).

	3 ₀₃	313	404	5 ₀₅
HOD $(4\nu_{OH})$ + 288 nm ^a		135 ± 30 K	160 ± 40 K	222±40 K
$HOD(5\nu_{OH}) + 288 \text{ nm}^{b}$	162 ± 40 K	173 ± 40 K	200 ± 30 K	241 ± 50 K
$H_2O(4\nu_{OH}) + 282 \text{ nm}^{a,c}$		192 ± 20 K	$200\pm20~{\rm K}$	244±30 K
$H_2O(5\nu_{OH}) + 282 \text{ nm}^{b,c}$		$208\!\pm\!20~\mathrm{K}$	210 ± 20 K	259±30 K
	5 ₁₅	6 ₀₆	616	7 ₀₇
	233 ± 50 K	250 ± 40 K	280 ± 60 K	292±60 K
	$246\!\pm\!20~\mathrm{K}$			
	$259\!\pm\!30~K$	$292\!\pm\!20~K$		355 ± 20 K

^aAvailable energy for the photofragments $\sim 8000 \text{ cm}^{-1}$.

^bAvailable energy $\sim 11000 \text{ cm}^{-1}$.

^cTaken from Ref. 34.

 $H_2O(4\nu_{OH})$ + 282 nm and $HOD(5\nu_{OH})$ + 288 nm with $H_2O(5\nu_{OH})$ + 282 nm) clearly reveals a slight cooling of the OD photofragment rotational distributions from HOD compared with those of OH arising from H_2O photodissociation.

V. FRANCK-CONDON CALCULATIONS

The OH photofragment lambda doublet population distributions arising from the VMP of H_2O via the A state¹⁻⁵ have been successfully simulated using a simple Franck-Condon model derived by Balint-Kurti.¹¹ The model makes the same basic assumptions as the earlier work of Beswick and Gelbart³⁶ and Morse and Freed,³⁷ that exit-channel effects can be neglected and the transition dipole moment function is independent of the nuclear coordinates, but also takes into account the open shell character of the OH $(X^2\Pi)$ and $H(^2S)$ photofragments.¹¹ In the previous study,⁵ it was demonstrated that application of this model to VMP experiments employing high intermediate stretching vibration overtone levels and low energy photolysis photons, requires the use of extended values of the dissociation coordinate R (throughout this paper, the Jacobi coordinates R, rand γ will be used to describe the geometry of parent molecule - see Figure 6(a)). To simulate the OD rotational distributions observed in this study, the model (more specifically, Eq. (75) of Ref. 11) has been applied by fixing r at its equilibrium value in free OD, r = 0.970 Å, and varying R from 0.970 to ~ 1.5 Å. The ground state water potential function of Jensen and co-workers⁴⁰ was used throughout the calculations. By freezing r and R, the HOD ground state Hamiltonian becomes that of a "rigid bender":

$$\hat{H} = \frac{\mathbf{l}^2}{2\mu R^2} + \frac{\mathbf{j}^2}{2\mu_{\text{OH}}r^2} + \mathbf{V}(R, r, \gamma)$$
(1)

for which the bound state rotational-bend wavefunctions are expanded in terms of an orthonormal set of parity adapted angular basis functions, ^{11,38,39}

$$\Psi^{\rm JM}(R,r,E) = \sum_{j\lambda} C^{\rm Jp}_{j\lambda} Y^{\rm JMp}_{j\lambda}(\gamma,\underline{\Omega}), \qquad (2)$$



FIG. 6. The centre of mass body-fixed coordinate system used in the Franck-Condon model calculations. The Jacobi coordinates are shown in (a). The body-fixed axes used in this study and by Reisler and co-workers (Ref. 41) are shown in (b) and (c) respectively.

where

$$Y_{j\lambda}^{JMp}(\gamma,\underline{\Omega}) = \frac{1}{\sqrt{2(1+\delta_{\lambda 0})}} [Y_{j\lambda}^{JM}(\gamma,\underline{\Omega}) + (-)^{J+p} Y_{j-\lambda}^{JM}(\gamma,\underline{\Omega})], \qquad (3)$$

and 38

$$\mathbf{Y}_{j\lambda}^{\mathrm{JM}}(\boldsymbol{\gamma},\underline{\boldsymbol{\Omega}}) \!=\! \left(\frac{2\mathbf{J}+1}{4\,\pi}\right)^{\frac{1}{2}} \! \mathbf{Y}_{j\lambda}(\boldsymbol{\gamma},\!0) \mathbf{D}_{\lambda \mathrm{M}}^{\mathrm{J}}(\underline{\boldsymbol{\Omega}})$$

Neglecting the electronic fine-structure of the photofragments, the Franck-Condon expression for the (closed-shell) rotational probabilities is then given by

$$P_{j}^{Jp} \propto \sum_{\lambda} |C_{j\lambda}^{Jp}|^{2}$$

$$\tag{4}$$

in which $C_{i\lambda}^{Jp}$ are the expansion coefficients of the parent ground state rotational-bend wavefunction. To make a comparison with the experimental measurements, the electronic and spin degrees of freedom of the photofragments are included within the model.¹¹ A proper treatment of the symmetry and coupling of the electronic spin, s, and orbital angular momentum, l, to the rotational angular momentum, j, produces a more complicated, but analogous expression for the (open-shell) rotational probabilities.¹¹

Within the Franck-Condon framework, the photofragment rotational population distributions, characterized by the expansion coefficients $C^{Jp}_{j\lambda}$, simply reflect the bound state rotational and bending motions of the parent molecule. Franck-Condon calculated $OD(^{2}\Pi \frac{3}{2})$ lambda doublet population distributions for HOD $J_{K_a,K_c} = 6_{06}$, calculated at increasing values of R, are compared in Figure 7 (middle) with the corresponding experimental distribution (left). A poor fit to the experimental data can only be achieved by fixing both bondlengths at their equilibrium values. The same is also true for other initial parent molecule rotational states, but the agreement is considerably worse than that shown in Figure 7, with only the phase of the oscillatory structure in the rotational populations, for selected values of N, being correctly predicted. Furthermore, the values of R returned by such an analysis, are unrealistically small compared with those expected based on energetic considerations (see Figure 2). The failure of the Franck-Condon model to reproduce the experimental OD distributions from HOD photolysis, but its comparative success in accounting for those of OH from H₂O, is likely to have its origins in the increased influence of the excited state potential energy surface in the HOD photodissociation dynamics, arising from the shift in the centre-ofmass of the OD moiety further away from the oxygen atom, as demonstrated below.

Reisler and co-workers⁴¹ have shown that for a fast dissociation with a modest exit-channel torque, the final photofragment rotational distribution may still reflect, in part, the angular momentum distribution inherent in the parent molecule bound-state wavefunction. For such a system, they developed a modified form of the semiclassical (closed-shell) Franck-Condon model of Morse and Freed³⁷ for parent molecules with J=0, which includes an approximate treatment of the small exit channel torque generated on the excited potential surface.⁴¹ Using the body-fixed axes shown in Figure 6(c), the semiclassical expression for the product rotational distribution³⁷ for a non-rotating parent molecule can be written as⁴¹

$$\mathbf{P}_{j}^{n} \sim (|\mathbf{C}_{+j}^{n}|^{2} + |\mathbf{C}_{-j}^{n}|^{2}) + \text{interference terms},$$
(5)

where n is the reagent (bending) quantum state. (This expression is analogous to Equation 4, which, however, uses the body-fixed axes defined in Figure 6(b).) Equation 5 can be interpreted in terms of the bound-state bending motion in the parent molecule providing an equal source of clockwise $(m_i = -j)$ and counter-clockwise $(m_i = +j)$ rotation of the diatomic fragment (caused by opening and closing of the bending angle, respectively).⁴¹ The interference of these motions can be understood as the cause of oscillatory structure in the product rotational distributions. The exit-channel torque is treated in a time-dependent fashion and the resulting change in the parent molecule equilibrium bending angle during dissociation generates a time dependent, unidirectional angular momentum $J_{ta}(t)$, superimposed on the product angular momenta derived from the parent bending motion. Calculating $J_{ta}(t)$ at a time T when the Franck-Condon expansion is carried out, Reisler and co-workers rewrite Equation 5 as⁴¹

$$P_{j}^{n} \sim F[j - J_{tq}(T)] + F[-j - J_{tq}(T)] + \text{interference terms}$$
(6)

with

$$\mathbf{F}(\mathbf{x}) = |\mathbf{C}_{\mathbf{x}}^{n}|^{2}.$$

A similar approach has been taken to modify the open shell Franck-Condon model of Balint-Kurti,¹¹ for parent rotational states $J \ge 0$. The measured dissociation time for water in the A state is between ~ 20 fs (Ref. 10) and ~ 40 fs (Ref. 6) and it is assumed that the torque may be treated as impulsive. Nearly all the available energy in the 288 nm photolysis of $HOD(4\nu_{OH})$ and $(5\nu_{OH})$ (~8000 and ~11000 cm⁻¹ respec-



FIG. 7. The calculated $OD({}^{2}\Pi_{\frac{3}{2}})$ population distributions, for both lambda doublets A' (\bullet) and A" (\bigcirc), for HOD $J_{K_a,K_c}=6_{06}$, as a function of *R*, using the original Franck-Condon model (middle) and the modified model (right) which includes an added impulsive torque. Also shown in the left of the figure is the corresponding experimental distribution, photolysing HOD(5 ν_{OH}) at 288 nm.

tively) is channelled into translational excitation of the photofragments, and a simple classical estimate suggests that an additional ~ 1.1 and ~ 1.3 units of angular momentum are generated in the OD fragment by the impulsive bond rupture, for HOD($4\nu_{OH}$) and ($5\nu_{OH}$), respectively. In the simulations that follow, J_{tq} is assigned a value of 1 (indeed, the modified model only allows the "addition" of integral angular momenta) and is chosen to lie in a direction specified by the direction of the torque, which decreases the bending angle (i.e. a counter-clockwise rotation).

To modify the Balint-Kurti model, a new set of expansion coefficients, $C_{j'\lambda}^{Jp}$, were generated from the original coefficients, $C_{j\lambda}^{Jp}$ (defined in Equation 2 and calculated using the parent bound state Hamiltonian), using

$$C_{j'\lambda}^{Jp} = \sum_{j} (j\lambda J_{tq}0|j'\lambda)C_{j\lambda}^{Jp}$$
⁽⁷⁾

and (...|...) are Clebsch-Gordon coefficients.⁴² Thus, within this modified Franck-Condon treatment, the effects of the small exit channel torque are accounted for simply by coupling the angular momenta generated on the bound and dissociative electronic potential energy surfaces. Inserting the new values of the coefficients into the expression for the rotational population distribution (Equation 75 in Ref. 11), which contains the remaining terms needed to couple j' with

s and l, the spin and orbital angular momentum of the photofragments, yields the exit-torque modified OD rotational distributions. We note in passing that, for parent molecules with J=0, calculating the closed shell OD rotational distribution using Equation 4, with the new set of coefficients, yields the same results as obtained from the work of Reisler and co-workers,⁴¹ employing Equation 6.

Modified Franck-Condon calculated OD(${}^{2}\Pi \frac{3}{2}$) rotational population distributions obtained at three values of R for HOD $J_{K_a,K_c} = 6_{06}$ are shown on the right hand side of Figure 7. Comparison of these distributions with those calculated using the original Franck-Condon model, reveals that the exit channel torque has a marked effect on the oscillatory structure of the lambda-doublet resolved populations. More importantly, good agreement between experiment and the modified theory is obtained using energetically realistic values of R. A selection of experimental and their corresponding "best-fit" (modified) Franck-Condon calculated OD photofragment distributions are shown in Figure 8 for HOD $J_{K_a,K_c} = 3_{13}$ (a), 4_{04} (b), 5_{05} (c), 5_{15} (d) and 6_{16} (e). The level of agreement between the experimentally measured and calculated distributions is the same for both OD lambda-doublet states, but for clarity only the A" lambda-doublet is shown. Of particular note from this figure is that the differences observed experimentally between the OD distributions aris-



FIG. 8. The modified Franck-Condon model calculated OD ${}^{2}\Pi \frac{3}{2}(A'')$ rotational distributions (shown on the left) obtained at the values of *R* indicated for $J_{K_{n},K_{n}}=3_{13}$ (a), 4_{04} (b), 5_{05} (c), 5_{15} (d) and 6_{16} (e). On the right hand side are the experimental distributions.

ing from HOD(4 ν_{OH}) and (5 ν_{OH}) J_{K_a,K_c} = 5₀₅ [Figure 8(c)] can be reproduced by the model only if a *larger* value of *R* is used for the *lower* overtone experiment.

These results are further summarised in Tables III and IV, in which are presented the reagent rotational statespecific and the averaged values of R at which experiment and theory are in reasonable accord. Also shown in Table IV are estimates of the values of R at which preferential excitation to the \tilde{A} state is expected to occur, R_{exp} , based purely on simple energetic considerations. (The ground state potential of Jensen and co-workers⁴⁰ and the excited state surface of Staemmler and Palma²⁵ were used to make these estimates.) These tables serve to highlight two key points. Firstly, the results are consistent with the Franck-Condon simulations of the VMP of H₂O,⁵ in which experiments conducted at lower photolysis photon energies or *via* higher intermediate overtone levels tend to yield fragment rotational distributions in good agreement with those from the calculations employing more extended values of *R*. Secondly, the values of *R* given in the Tables III and IV appear sensible. The outer maximum of the HOD(5 ν_{OH}) vibrational wavefunction occurs at $R \sim$ 1.35 Å and at $R \sim$ 1.30 Å for HOD(4 ν_{OH}).^{18,20} However, the $\widetilde{A}-\widetilde{X}$ transition moment function, which may be assumed the same as that for H₂O,¹⁵ decreases significantly with bond extension. Excitation from HOD(5 ν_{OH}) appears to occur preferentially at *R* values very close to the maximum in the bound state vibrational wavefunction, the position of which is little affected by the decaying transition moment function

TABLE III. The parent rotational state-specific approximate values of *R* required in the modified Franck-Condon model in order for the calculated OD distributions to be in accord with the experimental measurements. The length *r* is fixed at its equilibrium value for free OD of 0.97 Å.

HOD state			Par	ent Rotatio	nal State J _k	K _a ,K _c		
a	303	313	4 ₀₄	5 ₀₅	5 ₁₅	6 ₀₆	6 ₁₆	7 ₀₇
$(4\nu_{\rm OH})$ + 288 nm		1.48 ± 0.05	1.40 ± 0.05	1.34 ±0.05				
$(5\nu_{\rm OH})$ + 288 nm	$\begin{array}{c} 1.43 \\ \pm 0.05 \end{array}$	1.48 ± 0.05	1.40 ± 0.05	1.31 ± 0.05	$\begin{array}{c} 1.43 \\ \pm 0.05 \end{array}$	1.29 ±0.05	1.29 ± 0.05	1.29 ±0.05

^aThe parent molecule intermediate vibrational state and the dissociation wavelength.

TABLE IV. As in Table III but showing the state averaged approximate values of R, $\langle R \rangle$, for which the modified Franck-Condon model described in the text yields OD distributions in reasonable accord with experiment. The length r is fixed at its equilibrium value in free OD of 0.97 Å. Also shown are the energetically expected values of R, R_{exp} , where excitation to the \widetilde{A} state surface should preferentially occur from. These were estimated using the ground state potential of Jensen and co-workers (Ref. 40) and the excited state surface of Staemmler and Palma (Ref. 25).

HOD State	$\langle R \rangle$ (Å)	$R_{\rm exp}$ (Å)
$(4\nu_{\rm OH})$ + 288 nm	1.41 ± 0.05	~ 1.49
$(5\nu_{\rm OH})$ + 288 nm	1.36 ± 0.05	~ 1.40

with bond extension.¹⁵ For HOD($4\nu_{OH}$), in contrast, energetic considerations alone suggest that excitation occurs from regions well beyond the outer maximum in the bound state wavefunction, ie. in the classical forbidden region, where the decreasing dipole moment function with bond extension is expected to have its greatest influence:¹⁵ excitation to the \tilde{A} state, in this case, therefore occurs at slightly smaller values of R than would be expected purely on the basis of energetic considerations. Note, furthermore, that the values of R required to obtain agreement between the modified Franck-Condon calculated and experimental rotational distributions (see Table IV) are also consistent with the experimental observation that the VMP cross-section for HOD ($5\nu_{OH}$) + 288 nm is approximately 20 times larger than that for HOD($4\nu_{OH}$) + 288 nm.

More detailed inspection of the data presented in Table III, reveals that the returned estimates of R, required to fit the modified Franck-Condon product state distributions to those of the experiment, decrease with increasing parent rotational state. As mentioned further below, the data may suggest that coupling between the H—OD stretching and rotational-bending degrees of freedom, not accommodated within the Franck-Condon Model, also influences the OD product rotational state distributions.

VI. DISCUSSION

Prevous Franck-Condon simulations⁵ of the OH distributions arising from the VMP of $H_2O(A)$ (Refs. 1,2,4,5) have demonstrated that increasing values of R must be used in the model calculations to reproduce the data from experiments employing increasing vibrational excitation in the dissociating bond and/or decreasing energy of the photolysis photon.⁵ The origin of the variations in the oscillatory structure of the product lambda-doublet resolved rotational population distributions is rationalised by the effect that changing R has on the inertial properties of the ground state parent molecule. These effects are illustrated schematically for H₂O in Figure 9(a) and 9(b). As R is increased, the a-inertial axis tends to lie increasingly parallel with the vector **R**, and the equilibrium bond angle, γ , becomes closer to 90°. As a consequence, at large R (~ 1.5 Å), the calculated OH distributions arising from levels with different J, but the same value of K_a (and parity p), resemble those for J = 0, but are shifted



FIG. 9. The change in the direction of the *a*-inertial axis of the ground state parent molecule with respect to **R**, as *R* is increased for H₂O, (a) and (b), and HOD, (c) and (d).

by the component of J about the *a*-inertial axis.⁵ For HOD, a corresponding change in the direction of the *a*-axis [Figures 9(c) and 9(d)] requires a much larger extension of *R* than for H₂O, because of the shift in the centre-of-mass in OD relative to OH. The OD photofragment rotational state distributions predicted by the model are thus less sensitive to bond extension than are those of OH arising from H₂O photodissociation.

This rationale is supported by inspection of the boundstate Hamiltonian for the rotational-bending motion of the parent molecule.⁵ The centrifugal and Coriolis coupling matrix elements arising from $\hat{\mathbf{l}}^2$, which depend on J and λ (the component of J (and j) about **R**), vary with $1/R^2$ and switch off as *R* increases. The remaining potential matrix elements and those arising from $\hat{\mathbf{j}}^2$ are both independent of J, but the former do depend on λ . As *R* increases, the overall rotational motion of the ground state parent becomes more prolate-top in character and the photofragment rotational distributions reflect the zero-point bending motion in the intermediate bound vibrational state together with the component of J about the *a*-inertial axis, K_a, which, at large *R*, approximately equals λ .

The present study provides an additional insight into the factors which affect the product state distributions and their variation with increasing R (that is, with increasing OH stretching quanta in the intermediate overtone level and/or decreasing photon energy). Accounting approximately for the effects of the small torque applied by the departing H atom on the OD photofragment on the A state surface, brings the predictions of the modified Franck-Condon model into qualitative accord with the experimental distributions, employing energetically realistic values of R for all of the initial parent rotational states studied. The simulations suggest that the phase and shape of the oscillatory structure in the lambda-doublet population distributions primarily reflects the ground state rotational-bending motion of the parent molecule (described above), perturbed by the influence of a small final-state interaction. This result also helps provide a rationale for the values of R required in the (original) Franck-Condon model to simulate the OH distributions ob-tained in the VMP of H_2O ,^{1,2,4,5} which were found to be

TABLE V. H₂O rotational state averaged approximate values of *R*, $\langle R \rangle_{\rm H_2O}$, for with the (original) Franck-Condon model yields OH distributions in reasonal accord with experimental distributions obtained in the VMP of H₂O *via* the \tilde{A} state (Refs. 1,2,4,5). Also shown are the energetically expected approximate values of *R*, $R_{\rm exp}$, where excitation to the \tilde{A} state potential surface should occur from.

H ₂ O state	$\langle R \rangle_{\mathrm{H_{2}O}}$ (Å)	$R_{\rm exp}$ (Å)
$\begin{array}{l} (5\nu_{\rm OH}) \ + \ 288 \ {\rm nm} \\ (4\nu_{\rm OH}) \ + \ 288 \ {\rm nm} \\ (4\nu_{\rm OH}) \ + \ 240 \ {\rm nm} \\ (1\nu_{\rm OH}) \ + \ 193 \ {\rm nm} \end{array}$	$\begin{array}{r} 1.26 \pm 0.10^{a} \\ 1.11 \pm 0.09^{a} \\ 1.06 \pm 0.06^{a} \\ 1.05 \pm 0.04^{a} \end{array}$	~ 1.40 ~ 1.49 ~ 1.27 ~ 1.27

^aTaken from Ref. 5.

considerably smaller than those expected on energetic grounds and to fluctuate over a considerable range (~ 0.2 Å).⁵ These parent molecule state-averaged values of R, $\langle R \rangle_{\rm H_2O}$, are shown in Table V along with the energetically expected values of R. The original Franck-Condon model (poorly) reproduces the experimental OD rotational distributions from the VMP of HOD using values of $R \sim 0.97$ Å (see Figure 7), much smaller than those required in the H_2O simulations. The torque produced by the departing H atom in HOD dissociation generates approximately one unit of angular momentum in the rotating OD fragment, whereas in HOH dissociation, the same torque generates only $\sim 0.7-0.8$, which the modified Franck-Condon model cannot accommodate. This would suggest that the OH photofragment rotational distributions arising from the VMP of H₂O VMP are influenced by the impulsive torque exerted during the dissociation, but to a lesser extent than the OD fragment in HOD photolysis. A proper treatment of the exit channel torque within a full 2-D or 3-D calculation would be required to confirm this. Such calculations would of course be valuable in helping to ascertain the origin of the small differences between the modified Franck-Condon calculated and the experimental OD distributions presented here. They may also shed light on why the returned best-fit values of R obtained using the modified Franck-Condon model (see Table III) tend to decrease with increasing J in the parent HOD molecule, since, as suggested in the preceding section, this behaviour might reflect the influence of HOD bound-state rotational-vibrational couplings not incorporated in the Franck-Condon treatment.

In addition to the modification of the oscillatory structure in the photofragment lambda-doublet distributions, the exit-channel torque is also found to be the cause of the slight cooling of the overall rotational excitation in the OD photo fragment (with respect to that of OH produced in the VMP of $H_2O(n\nu_{OH})$), which is reflected in the rotational temperatures shown in Table II. This conclusion is consistent with the much larger cooling of the photofragment distributions observed in the photodissociation of excited bending vibrational states of H_2O ,^{3,5} which sample more anisotropic regions of the \tilde{A} state potential surface; the cooling of these fragment rotational distributions, compared with those predicted by the (unmodified) Franck-Condon model, was ascribed by Crim and Schinke and co-workers to exit channel effects.³

VII. CONCLUSIONS

HOD molecules, rotationally state selected in the third and fourth OH stretching overtones levels have been photodissociated at 288 nm via the A state. A branching ratio between the H + OD and D + OH dissociation channels is estimated to be $\Phi(OD)/\Phi(OH) > 23$ and > 12 for the higher and lower overtone experiments respectively. The small shift in the centre-of-mass arising from deuterium atom substitution is shown to have a marked effect on the rotational distributions of the OD photofragment, which are more sensitive to the exit-torque applied by the departing H atom than are the OH distributions produced in H₂O dissociation. Calculations using a modified Franck-Condon model, which accounts approximately for the effects of an impulsive exitchannel torque, are able to reproduce qualitatively the experimental distributions at values of R that are in agreement with those expected energetically, based on the current knowledge of the X and A potential energy surfaces. These calculations indicate that, in addition to being sensitive to small changes in the inertial properties of the bound state parent molecule, the OD photofragment rotational distributions (and to a lesser extent the OH distributions from the VMP of H_2O are also sensitive to the small final-state interaction on the dissociative potential surface.

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