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COMMUNICATIONS

Direct observation of preferential bond fission by excitation of a vibrational fundamental: Photodissociation of HOD (0,0,1)

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The possibility of directing the course of chemical reactions by photoexcitation of specific modes of nuclear motion, so called mode-selective chemistry, continues to intrigue chemists. Both experimental and theoretical activity in this field remain high, as witnessed by a special issue of *Chemical Physics* devoted to mode selectivity in unimolecular reactions.¹ We report here an example of mode selective chemistry, in which excitation of just *one* quantum of the O–H stretching vibration leads to a strong preference for O–H bond fission in the 193 nm photolysis of HOD. Our results show that even the very lowest possible level of vibrational excitation can be “leveraged” to effect selective bond breaking.

The experiments use stimulated Raman excitation (SRE) to prepare the (0,0,1) state of HOD, in one or at most a few rotational levels, and coherent anti-Stokes Raman scattering (CARS) to monitor the HOD (0,0,1).² The excitation is effected with two pulsed, visible-frequency laser beams, one the second harmonic output of a Nd:YAG laser at 532 nm, the other produced by a tunable dye laser operating around 662 nm. The frequency of the dye laser is tuned to sweep the frequency difference between the two lasers over the $\nu = 0 \rightarrow \nu = 1$ Q -branch transition of the ν_3 OH stretch of HOD around 3700 cm^{-1} . Excitation of the HOD is monitored and optimized by measuring the CARS signal generated by the Raman excitation beams. Following the SRE pulse, after a delay of 50 ns, the vibrationally excited HOD (0,0,1) molecules are photodissociated by a 193 nm beam from an ArF excimer laser. After a delay of an additional 50 ns the OH and OD photofragments are probed by saturated laser-induced fluorescence (LIF),³ with 30 μJ pulse of 308 nm focused light from the frequency-doubled output of a second Nd:YAG-pumped dye laser.

The experiments are carried out in a gas cell through which the sample flows at a pressure of 0.35 Torr. The sam-

ple is drawn from a liquid reservoir containing a statistical mixture of HOD, H_2O , and D_2O with H:D ratio of 1. Because of the differences in the vibrational frequencies of HOD and H_2O ,⁴ the SRE produces no vibrationally excited H_2O . At the pressures and delays used in the experiments the OH and OD photofragments are detected under collision-free conditions.

The results of one such experiment are shown in Fig. 1. The top panel (a) shows the CARS intensity monitor of the stimulated Raman excitation of the HOD as the dye laser frequency sweeps the Raman excitation frequency through the HOD ν_3 Q -branch transitions, which are assigned in Table I. Panels (b) and (c) of Fig. 1 show the variation of the OH and OD photofragment yields with this HOD (0,0,1) Raman excitation scan, measured by the fluorescence intensity observed with the LIF probe laser tuned to excite the $R_2(4)$ line of OD ($\nu'' = 0$) or OH ($\nu'' = 0$).

Note that the OD and OH yields track the CARS signal, which measures the extent of vibrational excitation of the HOD. Thus, it appears that production of both the OH and OD fragments are enhanced by vibrational excitation of HOD (0,0,1). However, the measured enhancement is at least 3 times greater for OD than for OH. Only a lower limit on this preferential enhancement can be established at present, because every accessible OH LIF transition is overlapped by an OD line in the LIF spectrum. This overlap might be due to power broadening and to high translational energy of the photofragments. Thus, the OH yield curve shown in Fig. 1(c) actually contains some contribution from OD and the true OH yield cannot yet be established with confidence. Since some OD LIF transitions are not overlapped by OH lines the OD can be measured unambiguously, and the enhancement of the OD fragment yield with HOD (0,0,1) excitation is very clear.

These results are qualitatively similar to those reported

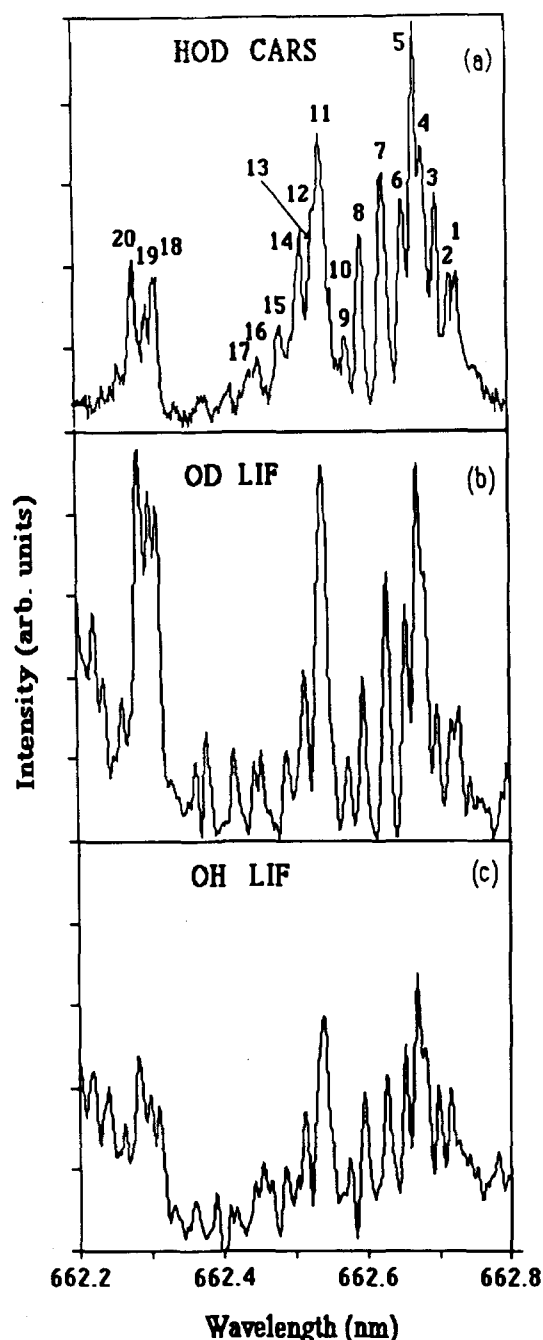


FIG. 1. OH and OD photofragment LIF signal intensity as a function of SRE excitation of HOD (0,0,1) for 193 nm photodissociation. Panel (a) shows the CARS signal monitor of the SRE excitation as the SRE dye laser wavelength is scanned to sweep over the HOD ν_3 $v=0 \rightarrow v=1$ Q -branch transitions. Panels (b) and (c), where the vertical scale is the same, show the fluorescence intensity for LIF excitation of the $R_2(4)$ transition of OD and OH, respectively. The numbers above the peaks in the CARS spectrum label different rotational transitions, which are explained in Table I.

by Vander Wal *et al.*,⁵ who observed preferential O–H bond breaking in HOD induced by excitation of *four* quanta of the O–H stretch vibration. In those experiments the vibrational excitation is quite high, about 1.7 eV or 33% of the 5.1 eV HOD bond dissociation energy. However, in our experiments the vibrational excitation energy is very small, only 9% of the dissociation energy, and only 7% of the 6.4 eV

TABLE I. Assignment of the HOD ν_3 $v=0 \rightarrow v=1$ Q -branch rotational transitions⁴ monitored via CARS.

No. in Fig. 1	$J_K \rightarrow J'_K$
1	$0_{00} \rightarrow 1_{01}$
2	2_{02}
3	3_{03}
4	$1_{10}, 1_{11}, 2_{11}$
5	$3_{12}, 2_{12}, 4_{04}$
6	$4_{13}, 3_{13}$
7	$5_{14}, 5_{05}, 4_{14}$
8	$6_{15}, 5_{15}$
9	6_{06}
10	6_{16}
11	$2_{21}, 2_{20}, 7_{16}, 3_{21}, 4_{22}$
12	$3_{22}, 5_{23}$
13	$7_{25}, 6_{24}$
14	$5_{24}, 4_{23}, 7_{07}, 7_{17}$
15	$8_{26}, 8_{17}$
16	$6_{25}, 8_{08}$
17	8_{18}
18	$3_{30}, 3_{31}, 4_{32}, 4_{31}$
19	$5_{32}, 5_{33}$
20	$6_{33}, 7_{34}, 6_{34}$

energy of the photons that effect dissociation. Selective bond breaking effected with just one quantum of vibrational excitation as in our experiment is particularly clean. Coupling to other vibrational modes is negligible for such excitation and individual rotational levels can be pumped and selectively dissociated.

Our observations are in qualitative agreement with the predictions of theory. Quantitative agreement cannot be established because we can set only the bound $OD/OH \geq 3$. Theoretical calculations,^{6,7} using an *ab initio* potential energy surface,⁸ predict a very large, > 10 , OD/OH ratio for 193 nm photolysis of HOD (0,0,1). The calculations show that the enhancement of OD fragment for photolysis of HOD (0,0,1) is the result of better Franck–Condon overlap of the (0,0,1) vibrational wave function with the $OD + H$ channel than with the $OH + D$ channel on the dissociative excited state.

These theoretical descriptions predict OD/OH ratios that are in excellent agreement with the results for photodissociation of HOD (0,0,4),⁵ and for 157 nm photolysis of HOD(0,0,0).⁹ Extensive state-resolved photofragment spectroscopy measurements on water,^{10–12} including experiments on $H_2O(0,0,1)$,¹⁰ and resonance Raman spectra of dissociating water^{13,14} are similarly in good agreement with the theory.^{6,7,15}

Note that in our experiments we observe OH and OD fragments from photodissociation of H_2O , HOD, and D_2O at 193 nm even without the SRE. The absorption of 193 nm light by the water isotopomers in their ground vibrational states is small, but apparently not zero at 193 nm. SRE of HOD to produce the (0,0,1) state is accompanied by a significant enhancement in the production of OD even though the Raman excitation volume is much smaller than the volume excited by the photolysis beam and the fraction of the HOD molecules in this volume that are excited is quite

small, a few percent of those having Raman transitions within the bandwidth of the laser. The efficiency of the SRE pumping can be increased, however.¹⁶

The Raman vibrational excitation is effected with rotational state selection, so it affords an opportunity to investigate state-to-state photodissociation dynamics, e.g., the predictions about the influence of rotational excitation on symmetry breaking in photodissociation.¹⁷

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