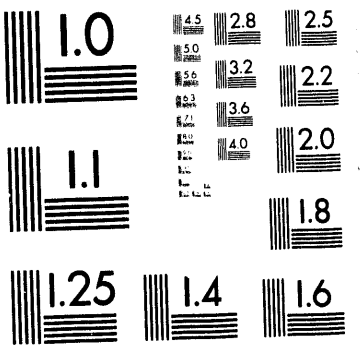
1.0
4.5
2.8
2.5
5.0
3.2
2.2
5.6
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

1 of 1

Conf-9306125--5

UCRL-JC-113549
PREPRINT

COHERENT PHASE CONTROL OF THE PHOTODISSOCIATION OF HOD

RECEIVED
OCT 14 1993
OSTI

S. W. Allendorf and W.E. Conaway
Lawrence Livermore National Laboratory
Livermore, CA

J.L. Krause
University of California, San Diego
La Jolla, CA

This paper was prepared for submittal to

"ICOMP VI: International Conference on Multiphoton Processes"

Quebec City, Quebec, Ontario
June 26-30, 1993

July 19, 1993

Lawrence Livermore National Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Coherent Phase Control of the Photodissociation of HOD

Sarah W. Allendorf, Jeffrey L. Krause, and William E. Conaway*
*Physical Sciences Department, Lawrence Livermore National Laboratory, Livermore, California 94550 and *Chemistry Department, University of California San Diego, La Jolla, California 92093*

1. Introduction

A natural goal of the field of chemical reaction dynamics is to control the course of reactions, that is, to drive the process to the desired end-product.[1] Limited success has been achieved through "mode-specific" and "bond-selective" techniques. The strategy of these methods is a two-step process.[2] First, the target mode or bond is selectively excited with a laser. Second, the excited molecule either reacts or is dissociated while the excitation energy is still localized in the excited bond or mode. Unfortunately, any selectivity is strongly dependent on the potential energy surfaces involved, the dissociation energy provided, and the time scale in which this energy is redistributed in the molecule.

Recently, several theoretical groups have suggested alternative methods of control which rely more strongly on externally controllable parameters. One method involves exciting a molecule with a very short (<100 fsec) laser pulse.[3] After a selected delay a second pulse dissociates the system. A second method uses optimal control theory to design a laser pulse shape that drives the molecule to desired products.[4] In this paper we concentrate on a third method to control chemical reactions, "Coherent Phase Control." This involves the use of such laser parameters as the intensity and phase to actively control reaction dynamics. Brumer and Shapiro have shown that when multiple products are accessible to a reaction system, by definition the system possesses multiple degenerate continuum eigenstates, each of which correlates with a particular product arrangement.[5] To control the relative branching of the various channels, we must control the composition of the coherent linear superposition of these eigenstates. This is accomplished as follows: Given two pathways *a* and *b* to final products, the probability amplitudes to proceed along each pathway are A_a and A_b. If these pathways are excited incoherently, the overall probability will be $P = |A_a|^2 + |A_b|^2$. Alternatively, if the two pathways are excited coherently, the overall probability will be $P = |A_a + A_b|^2 = |A_a|^2 + (A_a A_b^* + A_a^* A_b) + |A_b|^2$. The opportunity for active control arises from the cross term, which is governed by the relative phase and amplitudes of the two excitation processes. Because there are two distinct pathways to the same degenerate final state, the pathways interfere quantum mechanically. In the two-laser experiment described here, the laser fields populate a coherent superposition state which correlates asymptotically to a linear combination of possible reaction products. Thus, by varying the relative phase and amplitude of the two excitation fields we vary the composition of the linear combination of the excited states, and therefore the distribution of final reaction products.

2. Approach

We are examining the photodissociation of monodeuterated water, HOD. This photodissociation reaction provides two isotopically distinct exit channels, e.g. H+OD and D+OH. This system is attractive for our coherent control studies due to the relative simplicity of its energetics, the experimental accessibility, and the availability of molecular structure calculations which make possible detailed dynamics calculations. A simple diagram of the energetics of our experiment is shown in Fig. 1.

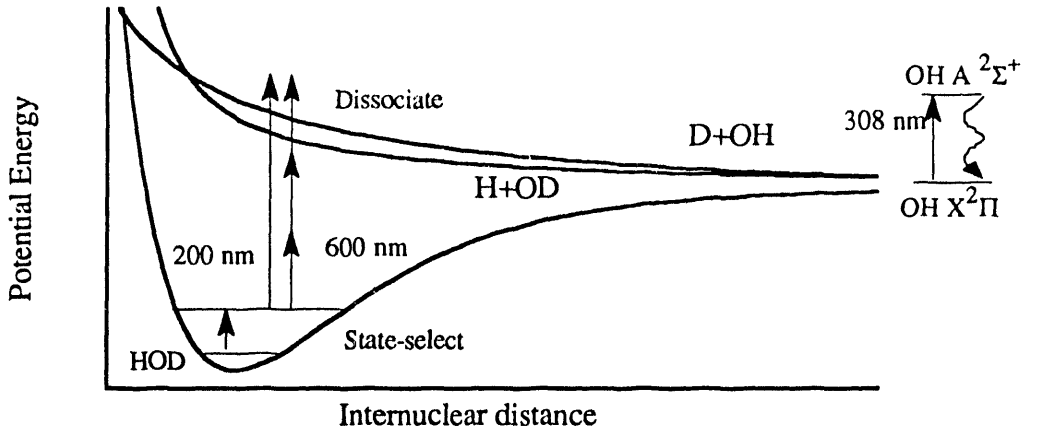

Fig. 1. Schematic of coherent phase control experiment, indicating state-selection, two-color photodissociation, and laser-induced fluorescence detection of OH/OD fragments.

Successful "coherent phase control" depends on minimizing the effects of uncontrolled channels. The control step of previous experiments in this field has been a bound-bound transition; energy requirements limit the number of pathways. Our HOD photodissociation experiment involves control of a bound-free transition. Unfortunately, this means the energy requirements are not very stringent: many initial states, of differing rotational energies, can be dissociated. Since these different rotational levels will be excited to different energies in the dissociation continuum, these pathways do not interfere quantum mechanically. These extra dissociation channels are uncontrollable. In order to have the fewest number of pathways into the continuum, we must first select a single (v,J) subset of HOD quantum states. To do this, we use Stimulated Raman Excitation (SRE). Two lasers fields, one fixed at 532 nm ("Pump laser"), and the second tunable around 662 nm (OH stretch) or 626 nm (OD stretch) ("Stokes laser"), are used to effect SRE in HOD. The Stokes laser wavelength is chosen so that the difference in energy between the Stokes and Pump laser frequencies is exactly equal to the energy required to excite a rotational level in a vibrationally excited water molecule. Using SRE we can access all variations of vibrational excitation, both the OH and OD stretches in H_2O, D_2O, and HOD.[6]

A fixed frequency laser at 600 nm and its third harmonic at 200 nm is used to simultaneously and coherently photodissociate the rovibrationally-excited parent molecules. Active control is achieved by varying the relative phase and amplitude of the two dissociation wavelengths. The relative phase of these two fields can be controlled by passing the laser beams through a cell containing a low-pressure gas which exhibits a large difference in index of refraction at the two laser wavelengths. The relative phase difference is then easily scanned by adjusting the pressure in the cell. We detect the branching ratio between the two product channels by Laser-Induced Fluorescence (LIF) of the OH and/or OD radicals. LIF can also provide critical information about the internal state distribution of the OH/OD products, for example their rotational and vibrational energy as well as alignment and relative Lambda-doublet populations.

Preliminary experiments have focussed on confirming individual steps of this complex experiment. For example, we have confirmed the bond-selective experiments of Crim and coworkers: excite $v_{OH}=4$, dissociate with 266 nm radiation, then detect the OH/OD fragments using LIF detection.[7] Equally critical to the success of our coherent control experiments is the ability to observe three-photon dissociation. Figure 2 shows the results of three-photon dissociation of $H_2O(v=0,J)$ using 532 nm radiation, with LIF

detection of the OH fragments. Coupled with intensity- and density-dependence measurements, this measurement gives us confidence we will be able to effect three-photon dissociation of state-selected HOD(v=1,J) molecules.

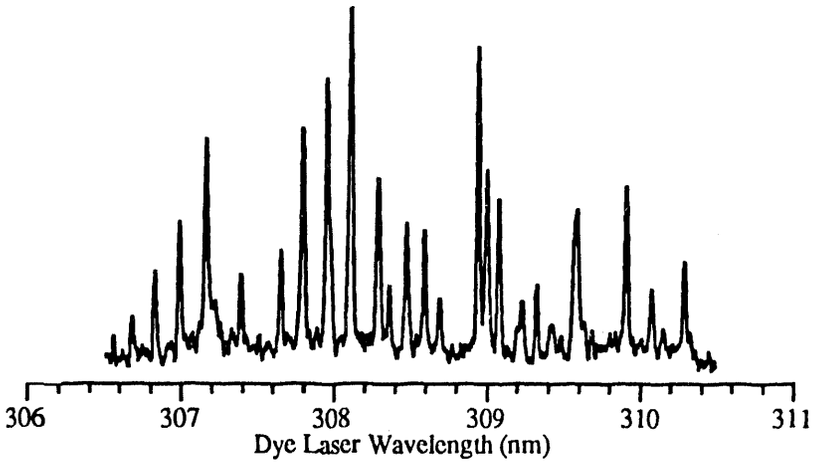

Fig. 2. LIF of OH fragments following three-photon dissociation of H_2O using 532 nm radiation

In tandem with our experiments we are performing 3-dimensional, quantum mechanical wave-packet calculations of this system using a recently developed method.[8] This method is formally exact and can handle the high energies and complicated multi-surface dynamics involved in experiments such as the photodissociation of HOD. These calculations allow the tracking of the energy flow through the system, and the identification of the critical experimental features that control bond selectivity. Calculations of single- and three-photon dissociation indicate the two channels produce different final state distributions. Work is in progress to calculate the product branching ratios as a function of the relative phase between the two dissociation channels.

Acknowledgments Work at LLNL was performed under the auspices of the the U.S. Department of Energy at Lawrence Livermore National Laboratory under contract number W-7405-Eng-48.

4. References

1. R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, (Oxford, New York, 1987).
2. For example, M. J. Bronikowski, W. R. Simpson, and R. N. Zare, *J. Phys. Chem.* **97** (1993) 2194.
3. For example, D. J. Tannor and S. A. Rice, *Adv. Chem. Phys.* **70** (1988) 441
4. For example, W. S. Warren, H. Rabitz, and M. Dahleh, *Science* **259** (1993) 1581.
5. For example, P. Brumer and M. Shapiro, *Accts. Chem. Res.* **22** (1989) 407; J. L. Krause, M. Shapiro, and P. Brumer, *J. Chem. Phys.* **92** (1990) 1126.
6. D. David, A. Strugano, I. Bar, and S. Rosenwaks, *Appl. Spec.***46** (1992) 1149.
7. For example, F. L. Vander Wal, J. L. Scott, F. F. Crim, K. Weide, and R. Schinke, *J. Chem. Phys.* **94** (1991) 3548.
8. J. L. Krause, A. E. Orel, K. C. Kulander, and J. C. Light, *J. Chem. Phys.* **96** (1992) 4283.

DATE
FILMED
11/26/93

END