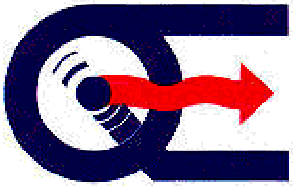
IQEC '84



XIII INTERNATIONAL QUANTUM ELECTRONICS CONFERENCE

TECHNICAL DIGEST

June 18-21, 1984 • Anaheim, California

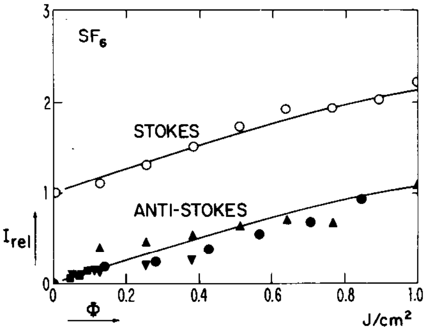


Fig. ThDD1-2. Relative Stokes (open symbols) and anti-Stokes (closed symbols) signals versus infrared laser fluence Φ for various pressures. ○●, 1.05 Torr; ■, 0.50 Torr; ▼, 0.52 Torr; ▲, 0.11 Torr.

occur at relatively high levels of excitation, this indicates that even at these very low fluences some molecules undergo multiphoton excitation, while others remain unexcited. Hence the intermolecular vibrational distribution differs significantly from an equilibrium distribution.

From the ratio between Stokes and anti-Stokes signals one can furthermore determine the total energy stored in the Raman-active mode, which in turn can be compared with the energy in other modes, obtained in a similar way, and to the total amount of absorbed laser energy, known from photoacoustic measurements. Such a comparison has been carried out, and experimental results for several molecular systems are discussed. (12 min.)

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ThDD2. Determination of the H + D_2 Product State Distribution Using a Novel Laser Ionization Mass Spectrometer, E. E. Marinero and C. T. Rettner, *IBM Research Laboratory, Department K46/282, 5600 Cottle Road, San Jose, California 95193,* and R. N. Zare, *Department of Chemistry, Stanford University, Stanford, California 94305.*

The hydrogen atom exchange reaction H + $H_2 \rightarrow H_2$ + H and its isotopic analogs are of fundamental importance to the field of chemical-reaction dynamics. However, this thermoneutral system has a large activation barrier and only a small reaction cross section. In addition, the reaction products are difficult to detect using standard laser techniques. These facts have until recently hindered efforts to determine the nascent quantum-state distributions for these reactions.

We report on a novel laser-based approach for studying these reactions and have obtained the state distribution for the HD product as well as detected nascent D atoms in the H + D_2 reaction at a collision energy of ~1.3 eV.

Our method comprises three important elements: (a) Fast H atoms are produced by laser photolysis of HI at 266 nm. (b) A new highly sensitive multiphoton ionization scheme is utilized for quantum-state specific detection of molecular hydrogen. (c) A differentially pumped time-of-flight mass spectrometer, which incorporates an effusive jet at its source, has been constructed. This provides the high densities required for reaction under conditions compatible with ion detection.

The fast H atoms are generated in the presence of D_2, and reaction products are interrogated by a second laser, which is fired after a delay that is long enough for some reaction to occur but prior to any substantial product-state relaxation.

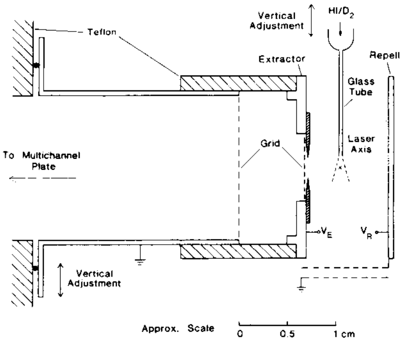

Fig. ThDD2-1. Detailed drawing of the reaction zone and of the differentially pumped region of the time-of-flight mass spectrometer for the study of the H + D_2 reaction dynamics.

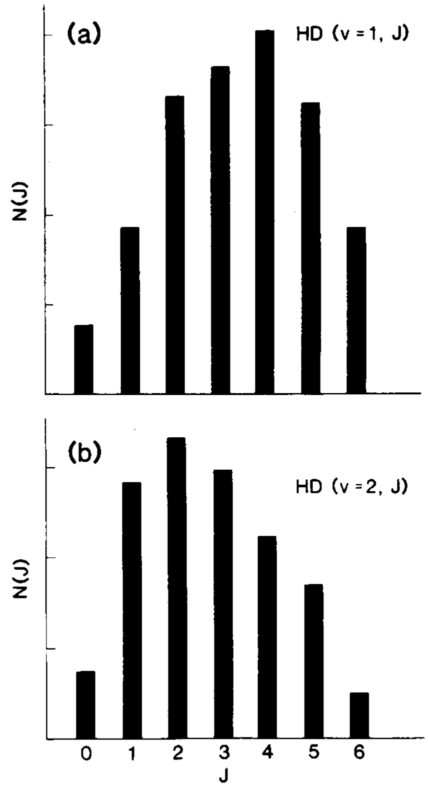

Fig. ThDD2-2. Relative rotational distributions of the reaction product (a) HD (V = 1) and (b) HD (V = 2) obtained for a delay time of ~60 nsec.

As shown in Fig. ThDD2-1, the reaction occurs in a well-defined effusive flow that emerges from a glass tube placed between the acceleration plates of a differentially pumped time-of-flight mass spectrometer. Thus we are able to produce high reagent densities (up to 60 mTorr) in a highly localized volume that interferes little with ion extraction through the slit assembly (V_E) into the high-vacuum field-free region of the mass spectrometer.

Using our technique, we have measured relative formation rates for HD (V = 1, 2; J = 0–6). Relative rotational populations are presented in Fig. ThDD2-2 for HD (V = 1, J) and HD (V = 2, J) for a delay time of 60 nsec between the photolysis and probe lasers.

These results are discussed in detail, and a comparison of our data is made with recent experimental and theoretical works on the H + D_2 dynamics.

The system reported here promises to be of extreme value in reaction dynamics experiments in which a high flux of reagents as well as sensitive quantum-state specific detection are needed. (12 min.)

We thank the Shell Foundation, Inc., the U.S. Office of Naval Research under N0014-C-78-0403, the U.S. Air Force Office of Scientific Research under AFOSR F49620-83-C-0033, and the National Science Foundation under NSF CHE 80-06524 and 81-08823. We are also grateful for the loan of equipment from the San Francisco Laser Center operated under NSF CHE 79-16250.

ThDD3. Discretization in the Quasi-Continuum, Ronald S. Burkey and C. D. Cantrell, *Center for Quantum Electronics, University of Texas at Dallas, Richardson, Texas 75083-0688.*

Beginning with Rice in 1929, many authors have considered a model of the so-called "quasi-continuum" in which a distinguished ground state is coupled to a band of N upper states, which are not coupled to one another (see Fig. ThDD3-1). These efforts are summarized nicely by Shore.[1] The (1,N) system allows many analytic results to be derived because it has a simple eigenvalue equation[2] and because it is susceptible to analysis using the Laplace transform.[3,4] In the special case (the Rice model) of evenly spaced sublevels of the upper band, Schrödinger's equation can be transformed into a delay-differential equation[5,6] and hence exhibits recurrences in which the ground-state probability experiences quasi-periodic growth and decay (see Fig. ThDD3-2).

The results we report here concern the simplification in two steps of a quasi-continuum of closely spaced discrete levels: first, replacement of the quasi-continuum by a true continuum; second, approximation of the continuum by a very much smaller number of effective discrete levels. While this language suggests that only a crude approximation could be made in this way, we have found that in fact for certain rather broad classes of band shapes of quasi-continua we are able to obtain extremely accurate results for the dynamics of the associated continuum using the methods summarized below. These results are significant because

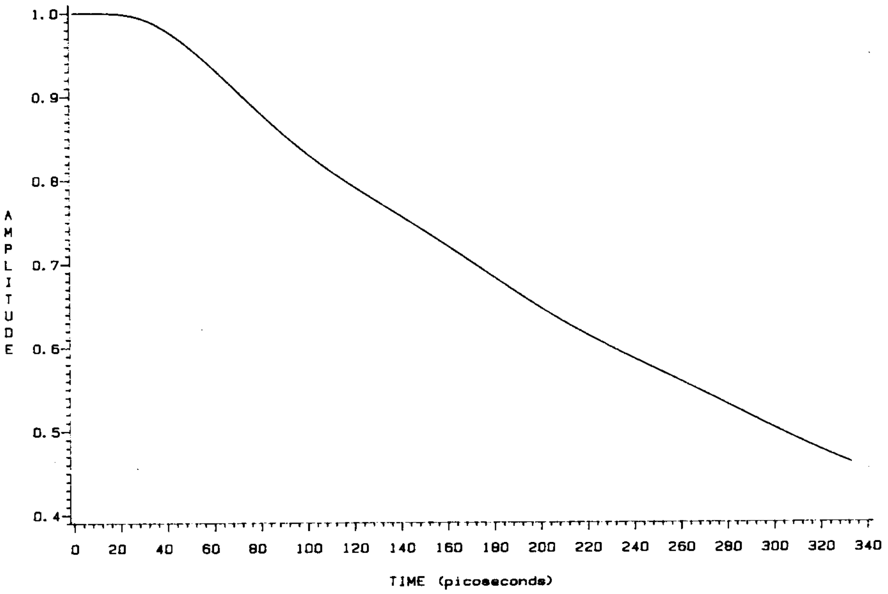

Fig. ThDD3-1. Ground-state probability amplitude for a uniform rectangular band of full width 0.6 cm^{-1}, as calculated by our technique using 16 levels in the discretized band. This result is accurate to about six decimal places.

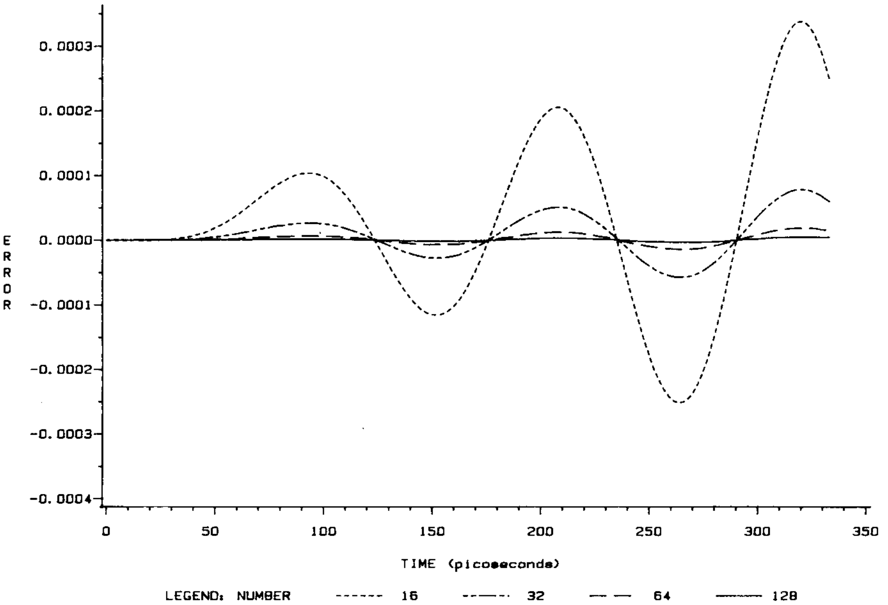

Fig. ThDD3-2. Error resulting from Rice discretizations of 16, 32, 64, and 128 evenly spaced levels in the calculation of the ground-state probability amplitude of a uniform rectangular band of full width 0.6 cm^{-1}. The zero point of error is taken to be the amplitude calculated using our method.

we expect that our methods will make possible numerical or analytical studies of much more complicated (and realistic) multilevel systems than have been feasible to study in the past—and for arbitrarily time-varying fields.

In general, previous investigations dealt with the case of a known (simple, classical) form of the electric field acting on a two-level system or else with a constant electric field. [The case of a sinusoidal field under the rotating-wave approximation (RWA) and the case of a suddenly turned-on field, while physically different from the constant-field case, are mathematically identical to it for times later than the switch-on time.] For an investigation of a laser pulse passing through a medium[6] these assumptions about the electric field may not be justified owing to reshaping of the initial pulse as a result of propagation, so it is necessary to consider the case of a time-varying field. Peterson *et al.*[7] have studied the adiabatic case, in which the field is turned on slowly rather than suddenly, and have shown that on laboratory time scales even quite fast pulses can sometimes be in the adiabatic rather than the sudden regime.

Yeh *et al.*,[4] in contrast to the above, have recently dealt with the quasi-continuum in the case of a (slowly) time-varying field envelope in their "interrupted coarse-graining" theory. For the weak-field case their limitation on the pulse turn-on time is just that given in Ref. 7 as a condition for adiabaticity.

Witriol *et al.*[8] have considered the problem of reducing the number of levels in a model of a laser-stimulated molecular species reacting to form another species that is removed from the population. This model is, in some ways, more general than the $(1,N)$ model, but the level-reduction scheme is strongly dependent on values of the various system parameters.

We consider the discretization of systems consisting of a single ground state and a band of upper levels [with density $g(\Delta)$, where $\Delta = \omega - E/\hbar$ is the detuning from resonance] that interact with the ground state, but not with each other, as the result of driving by a laser field $E_0(t)$. This band is envisioned as a continuum, and the problem is to introduce in place of the band a discrete set (we hope finite) of quantities that can be used to calculate the ground-state amplitude and the complex polarization. This is not the same problem as computing the eigenvalues and eigenvectors (dressed states) since we want our discretization to be useful in the case of a time-varying electric field $E(t)$. In fact, we have considered only reductions that are good in the case of a totally general $E(t)$ and as general as possible a dipole-transition-moment distribution $\mu(\Delta)$.

We find two essentially separate cases. In the one case, in which $w(\Delta) = \mu(\Delta)^2 g(\Delta) \sim |\Delta|^{-n}$ (for some n) as $|\Delta| \rightarrow \infty$, $w(\Delta)$ can be approximated as a rational function $p(\Delta)/q(\Delta)$. We show how to find N quantities [where the degree of $q(\Delta)$ is $2N$] for which we know the equations of motion and in terms of which we can express the equation of motion of the ground-state amplitude $a(t)$. These equations of motion resemble those for an $(N + 1)$-level Schrödinger equation, except that the Hamiltonian need not be Hermitian. There is no approximation in these equations, and the ground-state amplitude and complex polarization can be computed [for arbitrary fields $E(t)$] after arbitrarily long times in the reduced system.

In the second case, where $w(\Delta)$ dies to zero faster than any power of $|\Delta|$ as $|\Delta| \rightarrow \infty$, we find a similarity transformation that tridiagonalizes the Hamiltonian.[9] The tridiagonal Hamiltonian is discrete but infinite, and the only approximation involved is in the truncation of this matrix to give a finite system. The similarity transformation is completely independent of time so that once again the reduced system can be used in the case of a time-varying field. Furthermore, the only elements of the Hamiltonian matrix that depend on the field connect the ground state with the next higher level. Thus only these two levels have to be known accurately to compute the complex polarization. Since any truncation of the Hamiltonian (or, possibly, replacement of the upper states by a reservoir) will leave the equations of motion of these levels unchanged (though altering the actual values of some of the probability amplitudes entering into them), the effect of such an approximation on the ground-state amplitude or the complex polarization can only be indirect. We also give the matrix obtained from a certain similarity transformation of the truncated tridiagonal Hamiltonian and shown how it can be used to give an expression for the error involved in the truncation. (12 min.)

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ThDD4. Laser Photoacoustic Spectroscopy and Detection of Intramolecular Vibrational Energy Redistribution and Unimolecular Reaction Processes,

T. D. Kunz and M. J. Berry, *Department of Chemistry and Rice Quantum Institute, William Marsh Rice University, P.O. Box 1892, Houston, Texas 77251.*

Formyl fluoride (HFCO) is a model unimolecular chemical reactant that is known to form HF + CO reaction products owing to both photon activation[1] (in the UV and vacuum-UV spectral regions) and thermal activation.[2] In both cases,[3] rovibronic line broadening of the reactant may accompany the reaction process.

We have used intracavity cw dye-laser techniques to measure visible (540–900 nm) absorption spectra of gas-phase formyl fluoride and to photoactivate this unimolecular reactant with bond-selective excitations involving CH stretch overtone transitions. A computer-controlled cw ring dye-laser photoacoustic spectrometer[4] provided nearly Doppler-limited spectra of highly optically forbidden vibrational transitions. We were able to measure line broadening of individual rovibronic transitions in the CH stretch overtone bands centered at ~11 190 cm^{-1} ($4\nu_{CH}$) and 13 690 cm^{-1} ($5\nu_{CH}$). We believe that the homogeneously broadened linewidths that we observe provide information on the time scale and mechanism of intramolecular vibrational energy redistribution processes[5] that precede molecular predissociation as well as information on direct lifetimes for unimolecular reaction.

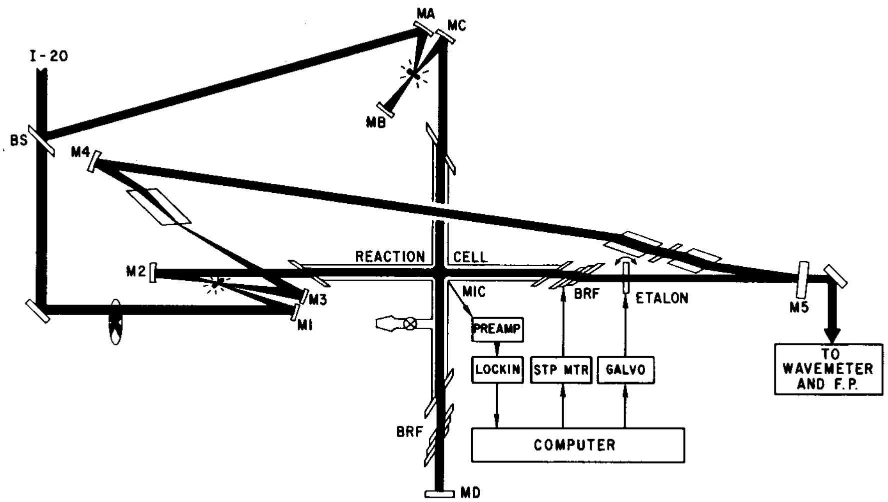

Fig. ThDD4-1. Two-laser pump and probe photochemical reactor. Two cw dye lasers (a linear laser with its optical cavity defined by mirrors MB through MD and a ring laser with its cavity mirrors M2 through M5) are pumped by one ion laser that is beam split (BS) into two portions for dye pumping (using mirrors MA and M1). Both dye lasers are tuned by birefringent filters (BRF). In addition, the photoacoustic cw dye-laser spectrometer is fine tuned with an étalon to match HF absorption lines.

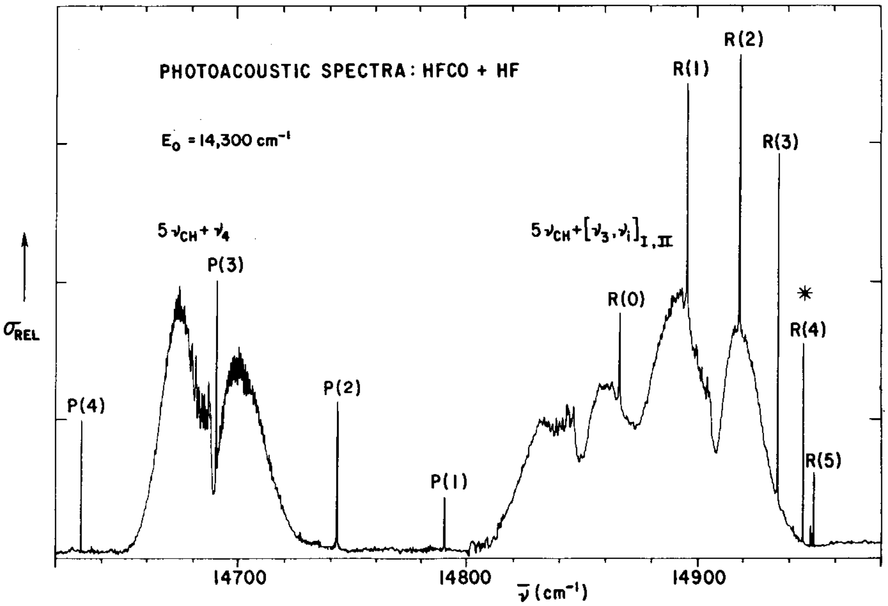

Fig. ThDD4-2. Photoacoustic spectra of formyl fluoride reactant and hydrogen fluoride product. Sharp lines labeled P(1) through P(4) and R(0) through R(5) are part of the $v' = 4 \leftarrow v'' = 0$ band of HF; R(4) was ordinarily used for product monitoring. Broad bands with partially resolved rotational structure are combination bands of the formyl fluoride reactant.

We have also studied vibrational photochemistry in formyl fluoride that is due to direct single-photon energization. *In situ* photoacoustic detection of the HF photochemical reaction product was carried out using a two-laser configuration (Fig. ThDD4-1) for photochemical reactant pumping and photochemical product probing. Briefly, a cw linear dye laser was used to excite formyl fluoride (typically, within the fifth-overtone CH stretch absorption near 623 nm) while our computer-controlled cw ring dye laser continuously monitored the formation of hydrogen fluoride product using its sharp rovibronic spectral lines near 682 nm (see Fig. ThDD4-2). (12 min.)

This work was supported, in part, by the National Science Foundation and by the Robert A. Welch Foundation.

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