

state which is also formed as a result of geminate recombination. The frequency of this band is very close to the gas phase value^{13,14} of 90/105 cm^{-1} for the A/A' electronic state. In addition, this band has the same time dependence found in earlier transient absorption experiments⁴⁻⁷ for the species assigned to these same excited electronic states. A detailed account of the dynamics of the A/A' electronic state will be discussed in a separate publication.

The broad band from 130 to 210 cm^{-1} in the 0 ps spectrum is assigned to hot vibrational states in the ground electronic state. Based on gas phase spectroscopic constants⁸ these states correspond to vibrational energies of 740–9300 cm^{-1} . This band appears featureless as a result of Raman scattering from a large distribution of vibrational states with slightly different frequencies. In fact, the difference in the Raman frequencies expected for the hot vibrational states can be calculated from the known gas phase spectroscopic constants.⁸ For the vibrational states observed in Figure 1 the frequencies for Raman scattering from any two adjacent vibrational levels $v \rightarrow v+1$ and $v+1 \rightarrow v+2$ differ by a maximum of 2.3 cm^{-1} . Since the spacing between Raman bands from adjacent vibrational levels is so much smaller than the observed linewidth of an individual Raman band (23 cm^{-1}), only a distribution of states is observed.

The arrows in Fig. 1 illustrate the dynamics of the vibrational decay. From 0 ps to 100 ps the peak of the distribution shifts towards the higher frequency vibrational levels located in the lower energy regions of the X state potential. In addition, the distribution appears to become more narrow at later times. This is a result of populating vibrational states with slower relaxation times which allows the population to collect in the lower vibrational levels. It might seem curious that Fig. 1 does not show the eventual repopulation of the lowest energy level with a 212 cm^{-1} energy gap. However, it must be remembered that Fig. 1 is a subtracted pure transient spectrum showing only features which are different from the normal relaxed Raman spectrum. As soon as the distribution cools into the lowest energy levels, the spectrum becomes identical to the relaxed Raman spectrum and is removed by the subtraction procedure.

These results prove that the analysis of the transient absorption spectrum by Harris and co-workers⁵⁻⁷ is remarkably accurate considering the difficulty of interpreting the transient absorption data. That is, the chemical dynamics on the 100 ps time scale is dominated by vibrational cooling on the X state potential. The transient Raman results discussed in this paper show how the distribution of vibrational population evolves in time—with one caveat. The shape of this distribution is presently obscured due to the uncertainties in the wavelength dependence of the resonance Raman enhancement which will affect the relative intensities of the scattering from each individual level. However, it is expected that the Raman enhancement for any particular level remains constant with time. As a consequence, the data in Fig. 1 illustrate the dynamics of the relative populations. A detailed analysis of the population decay will be presented in a separate publication.

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¹A. L. Harris, J. K. Brown, and C. B. Harris, *Ann. Rev. Phys. Chem.* **39**, 341 (1988).

²T. J. Chuang, G. W. Hoffman, and K. B. Eisenthal, *Chem. Phys. Lett.* **25**, 201 (1974).

³P. Bado and K. R. Wilson, *J. Phys. Chem.* **88**, 655 (1984).

⁴D. F. Kelly, N. A. Abul-Haj, and D. J. Jang, *J. Chem. Phys.* **80**, 4105 (1984).

⁵A. L. Harris, M. Berg, and C. B. Harris, *J. Chem. Phys.* **84**, 788 (1986).

⁶M. E. Paige, D. J. Russell, and C. B. Harris, *J. Chem. Phys.* **85**, 3699 (1986).

⁷P. E. Smith and C. B. Harris, *J. Chem. Phys.* **87**, 2709 (1987).

⁸J. A. Coxon, *J. Quant. Radiat. Transfer* **11**, 443 (1971).

⁹L. K. Orman, Y. J. Chang, D. R. Anderson, T. Yabe, Xiaobing Xu, Soo-Chang Yu, and J. B. Hopkins, *J. Chem. Phys.* **90**, 1469 (1989).

¹⁰Y. J. Chang, Xiaobing Xu, T. Yabe, Soo-Chang Yu, D. R. Anderson, L. K. Orman, and J. B. Hopkins, *J. Phys. Chem.* (in press).

¹¹Y. J. Chang, C. Veas, and J. B. Hopkins, *Appl. Phys. Lett.* **49**, 1758 (1986).

¹²Y. J. Chang, D. R. Anderson, and J. B. Hopkins, *International Conference on Lasers 1986* (McMillan, New York, 1987), p. 169.

¹³J. Tellinghuisen, *J. Mol. Spectrosc.* **94**, 231 (1982).

¹⁴K. S. Viswanathan, A. Sur, and J. Tellinghuisen, *J. Mol. Spectrosc.* **86**, 393 (1981).

D + H₂($v=1, J=1$): Rovibronic state to rovibronic state reaction dynamics

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An ultimate goal in the experimental study of the dynamics of elementary chemical reactions is the specification of the relative translational and internal energies of the reagents and the measurement of the resulting translational and internal energies of the products.^{1,2} To date, rovibronic state to rovibronic state experiments have been limited to only a few systems.^{3,4} We report here the first such experiment for the simplest neutral bimolecular chemical reaction, the hy-

drogen atom-hydrogen molecule exchange reaction. The isotopic variant chosen for study is $D + H_2(v, J) \rightarrow HD(v', J') + H$, where H_2 is prepared in the rovibronic level ($v=1, J=1$) by stimulated Raman pumping (SRP)⁵ and the populations of the $HD(v', J')$ product levels are measured by (2 + 1) resonance-enhanced multiphoton ionization (REMPI).⁶⁻⁹

Several recent experiments on the $H + H_2$ reaction fam-

ily have employed quantum-state-specific detection of the products,¹⁰⁻¹⁹ but all have had a distribution of reactant internal states. Some degree of reagent rotational state selection has been achieved by the use of para- H_2 ,¹⁴ which contained nearly equal amounts of $\text{H}_2(v=0, J=0)$ and $(v=0, J=2)$ and some $(v=0, J=4)$. Previous studies have succeeded in preparing the molecular hydrogen reagent in an excited vibrational level using either a discharge²⁰⁻²² or thermal source,^{23,24} but without rotational state selectivity.

SRP allows the preparation of a single rovibrational level in the ground electronic state of a molecule on a time scale short compared to that of subsequent collisions. SRP requires two laser beams whose frequency difference matches a Raman-allowed transition. With currently available lasers, the $\text{H}_2 \Delta v=1$ transition can be saturated,²⁵ and the $\Delta v=2$ overtone transition has been observed.²⁶ This technique also allows M -state preparation.²⁷ Previously, SRP has been used to study energy transfer processes in H_2 ,^{5,22,25,26,28-32} HD,^{33,34} D_2 ,^{31,35,36} HCl ,³⁷ N_2 ,²⁷ NO ,³⁸ CO_2 ,³⁹ and glyoxal.⁴⁰ The experiment reported here is the first to use SRP for reagent preparation in a chemical reaction.

The present apparatus is similar to that used for our studies of the $\text{H} + \text{D}_2$ reaction.^{17-19,41} DBr and H_2 , premixed in a 1.0:3.5 concentration ratio, flow effusively into a high vacuum chamber. This vertical reagent beam is crossed by the focused, copropagating SRP beams about 1 mm below the nozzle. The wavelengths of the SRP beams are 532 nm (Nd:YAG, second harmonic) and 683 nm (first Stokes from the 532 nm beam passing through an H_2 Raman cell, 35 psig). The SRP beams pump $\sim 19\%$ of the $\text{H}_2(v=0, J=1)$ population ($\sim 13\%$ of the total population) into $(v=1, J=1)$, as measured by the depletion of the $\text{H}_2(v=0, J=1)$ level with $(2+1)$ REMPI. After a delay of ~ 20 ns, a second laser (~ 210 nm) is fired to photodissociate the DBr, yielding fast D atoms, and to detect the HD reaction product via REMPI. The ~ 210 nm radiation is generated by frequency-doubling and then sum-frequency mixing the output of a Nd:YAG-pumped dye laser in β -barium borate crystals, yielding ~ 2 mJ/pulse. Note that the same laser pulse effects both photolysis and detection, so that the reaction occurs during the pulse duration (~ 5 ns).¹⁸ The HD^+ ions are detected in a shuttered time-of-flight mass spectrometer.⁴¹ Ions at $m/e=2$ (D^+) distort the arrival time of the $m/e=3$ (HD^+) signal for $J' > 8$. The data collection electronics are gated around the $m/e=3$ peak at each J' .

Because the DBr is photolyzed by the tunable probe laser, the photolysis wavelength and therefore the collision energy is varied as different rovibronic levels are detected. This complication is minor within a given product vibrational level, as documented by the ability of Blais and Truhlar to model the probe-laser-induced $\text{H} + \text{D}_2$ reaction by quasi-classical trajectory (QCT) calculations.⁴² For the levels reported here, the center-of-mass collision energy changes from 1.07 eV for $\text{HD}(v'=1, J'=0)$ to 0.99 eV for $\text{HD}(v'=1, J'=12)$. This variation is approximately equal to the thermal spread in the collision energy (about ± 0.06 eV).

Photolysis of DBr at for example 210 nm yields two different center-of-mass collision energies, 1.06 and 0.83 eV,

corresponding to the production of $\text{Br}(^2P_{3/2})$ and $\text{Br}^*(^2P_{1/2})$, respectively. For the photolysis wavelengths employed in the present study, the contribution from the slow D atoms is expected to be minor. Magnotta, Nesbitt, and Leone⁴³ reported that at 193 nm the yield of Br^* is $\sim 15\%$, while at 210 nm Kleinermanns, Linnebach, and Pohl⁴⁴ reported a Br^* yield of $\sim 0\%$. The possible contribution of the Br^* channel is further diminished by (1) the lower collision frequency associated with the lower relative velocity, and (2) the reduced specific rate for the production of vibrationally excited product from the lower translational energy. Therefore, it appears justified to neglect the slow D-atom contribution in what follows.

Figure 1(a) shows the $\text{HD}(v'=1)$ rotational distributions measured without SRP (dashed curve) and with SRP (solid curve). The ~ 1.0 eV collision energy is above the 0.42 eV classical reaction barrier⁴⁵; hence, HD product is observed in the absence of the SRP beams. The contribution of the $\text{D} + \text{H}_2(v=0, J \text{ thermal})$ reaction (dashed curve) must be subtracted from the SRP distribution (solid curve) in order to obtain the product distribution of the $\text{D} + \text{H}_2(v=1, J=1)$ reaction [Fig. 1(b)].

Figure 1(b) shows our preliminary $\text{D} + \text{H}_2(v=1, J=1) \rightarrow \text{HD}(v'=1, J') + \text{H}$ state-to-state distribution. This distribution was obtained by subtracting 87% of the unpumped distribution from the distribution taken with

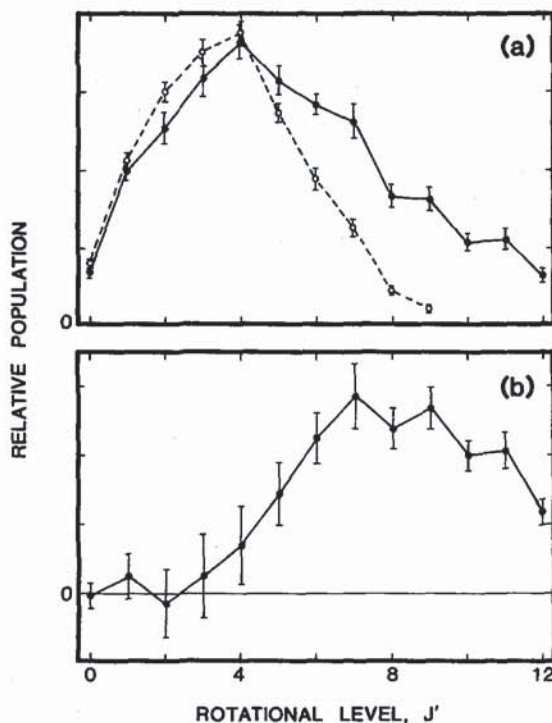


FIG. 1. Rovibronic population distributions of the $\text{HD}(v'=1, J')$ product from the $\text{D} + \text{H}_2$ reaction at about 1.0 eV center-of-mass collision energy. Error bars represent one standard deviation. (a) The dashed curve shows the "unpumped" distribution from $\text{D} + \text{H}_2(v=0, J \text{ thermal})$ and the solid curve shows the "pumped" distribution measured after stimulated Raman pumping of the H_2 reagent. (b) The distribution from $\text{D} + \text{H}_2(v=1, J=1)$ obtained by subtracting 87% of the unpumped distribution from the pumped distribution.

SRP (the 87% takes into account the $\sim 13\%$ depletion of $v = 0$ by SRP).

This procedure neglects any dependence of reactivity on reagent rotation. SRP perturbs the ground-state rotational distribution, but a simple calculation shows that this perturbation is small under our experimental conditions. At 294 K, the ratio of the rotational populations in $H_2(v = 0)$ is 0.20:1.00:0.18:0.13 for $J = 0:1:2:3$. After removal of 19% of $H_2(v = 0, J = 1)$ by SRP, the ratio is 0.25:1.00:0.22:0.16. Furthermore, at the present collision energies, QCT calculations⁴⁶ predict that the reaction cross section is nearly constant for $J = 0-3$.

We have also observed an SRP-enhancement in the production of $HD(v' = 2)$ from the $D + H_2$ reaction.

For the $D + H_2$ reaction, vibrational excitation of the H_2 reagent results in substantial rotational excitation of the $HD(v' = 1)$ product. The first moment of the $HD(v' = 1)$ rotational distribution from $D + H_2(v = 0, J \text{ thermal})$ is $\langle J' \rangle = 3.69 \pm 0.07$ (894 cm^{-1} of rotational energy)⁴⁷ while that from $D + H_2(v = 1, J = 1)$ is $\langle J' \rangle = 8.1 \pm 0.7$ (3180 cm^{-1}),⁴⁷ assuming that the populations of the unmeasured levels are zero. The corresponding fractions of the available energy appearing as product rotation are $g_R = 0.17$ for the unpumped reaction and $g_R = 0.34$ for reaction with $H_2(v = 1, J = 1)$. This behavior can be understood in terms of an opening of the reactive cone of acceptance upon elongation of the H-H bond.⁴⁸

We estimate that the reaction cross section into $HD(v' = 1)$ is at least 4 times larger for $D + H_2(v = 1, J = 1)$ than for $D + H_2(v = 0, J \text{ thermal})$, consistent with the vibrational adiabaticity predicted for this reaction by both QCT⁴⁹ and quantum-mechanical⁵⁰ calculations.

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¹ *State-to-State Chemistry*, edited by P. R. Brooks and E. F. Hayes, ACS Symposium Series 56 (American Chemical Society, Washington, D.C., 1977).

² R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford University, New York, 1987).

³ D. J. Rakestraw, K. G. McKendrick, and R. N. Zare, *J. Chem. Phys.* **87**, 7341 (1987).

⁴ R. Zhang, D. J. Rakestraw, K. G. McKendrick, and R. N. Zare, *J. Chem. Phys.* **89**, 6283 (1988).

⁵ F. DeMartini and J. Ducuing, *Phys. Rev. Lett.* **17**, 117 (1966).

⁶ E. E. Marinero, C. T. Rettner, and R. N. Zare, *Phys. Rev. Lett.* **48**, 1323 (1982).

⁷ E. E. Marinero, R. Vasudev, and R. N. Zare, *J. Chem. Phys.* **78**, 692 (1983).

⁸ K.-D. Rinnen, D. A. V. Kliner, R. N. Zare, and W. M. Huo, *Isr. J. Chem.* **29**, 369 (1989).

⁹ K.-D. Rinnen, D. A. V. Kliner, M. A. Buntine, R. N. Zare, and W. M. Huo (unpublished).

¹⁰ D. P. Gerrity and J. J. Valentini, *J. Chem. Phys.* **81**, 1298 (1984).

¹¹ D. P. Gerrity and J. J. Valentini, *J. Chem. Phys.* **82**, 1323 (1985).

¹² J. J. Valentini and D. P. Gerrity, *Int. J. Chem. Kinet.* **18**, 937 (1986).

¹³ H. B. Levene, D. L. Phillips, J.-C. Nieh, D. P. Gerrity, and J. J. Valentini, *Chem. Phys. Lett.* **143**, 317 (1988).

¹⁴ J.-C. Nieh and J. J. Valentini, *Phys. Rev. Lett.* **60**, 519 (1988).

¹⁵ D. L. Phillips, H. B. Levene, and J. J. Valentini, *J. Chem. Phys.* **90**, 1600 (1989).

¹⁶ E. E. Marinero, C. T. Rettner, and R. N. Zare, *J. Chem. Phys.* **80**, 4141 (1984).

¹⁷ R. S. Blake, K.-D. Rinnen, D. A. V. Kliner, and R. N. Zare, *Chem. Phys. Lett.* **153**, 365 (1988).

¹⁸ K.-D. Rinnen, D. A. V. Kliner, R. S. Blake, and R. N. Zare, *Chem. Phys. Lett.* **153**, 371 (1988).

¹⁹ K.-D. Rinnen, D. A. V. Kliner, and R. N. Zare, *J. Chem. Phys.* **91**, 7514 (1989).

²⁰ G. P. Glass and B. K. Chaturvedi, *J. Chem. Phys.* **77**, 3478 (1982).

²¹ T. Dreier and J. Wolfrum, *Int. J. Chem. Kinet.* **18**, 919 (1986).

²² J. Wolfrum, *Farad. Discuss. Chem. Soc.* **84**, 191 (1987).

²³ V. B. Rozenshtein, Yu. M. Gershenzon, A. V. Ivanov, S. D. Il'in, S. I. Kucheryavii, and S. Ya. Umanskii, *Chem. Phys. Lett.* **121**, 89 (1985).

²⁴ R. Gotting, V. Herrero, J. P. Toennies, and M. Vodegel, *Chem. Phys. Lett.* **137**, 524 (1987).

²⁵ J. Arnold, T. Dreier, and D. W. Chandler, *Chem. Phys.* **133**, 123 (1989).

²⁶ T. G. Kreutz, J. Gelfand, R. B. Miles, and H. Rabitz, *Chem. Phys.* **124**, 359 (1988).

²⁷ G. O. Sitz and R. L. Farrow, poster presented at the 1989 Conference on the Dynamics of Molecular Collisions, Asilomar, CA (July 16-21, 1989).

²⁸ M. A. Kovacs and M. E. Mack, *Appl. Phys. Lett.* **20**, 487 (1972).

²⁹ M. M. Audibert, C. Joffrin, and J. Ducuing, *Chem. Phys. Lett.* **25**, 158 (1974).

³⁰ M. M. Audibert, R. Vilaseca, J. Lukasik, and J. Ducuing, *Chem. Phys. Lett.* **31**, 232 (1974).

³¹ W. Meier, G. Ahlers, and H. Zacharias, *J. Chem. Phys.* **85**, 2599 (1986).

³² R. L. Farrow and D. W. Chandler, *J. Chem. Phys.* **89**, 1994 (1988).

³³ C. Barroux and M. M. Audibert, *Chem. Phys. Lett.* **66**, 483 (1979).

³⁴ D. W. Chandler and R. L. Farrow, *J. Chem. Phys.* **85**, 819 (1988).

³⁵ J. Lukasik and J. Ducuing, *Chem. Phys. Lett.* **27**, 203 (1974).

³⁶ J. Lukasik and J. Ducuing, *J. Chem. Phys.* **60**, 331 (1974).

³⁷ E. A. Rohlfing, D. W. Chandler, and D. H. Parker, *J. Chem. Phys.* **87**, 5229 (1987).

³⁸ P. Esherick and A. Owyong, *Chem. Phys. Lett.* **103**, 235 (1983).

³⁹ A. M. Brodnikovskiy, S. M. Gladkov, and N. I. Koroteev, *Opt. Commun.* **40**, 312 (1982).

⁴⁰ A. B. Duval, D. A. King, R. Haines, N. R. Isenor, and B. J. Orr, *J. Opt. Soc. Am. B* **2**, 1570 (1985).

⁴¹ K.-D. Rinnen, D. A. V. Kliner, R. S. Blake, and R. N. Zare, *Rev. Sci. Instr.* **60**, 717 (1989).

⁴² N. C. Blais and D. G. Truhlar, *Chem. Phys. Lett.* **162**, 503 (1989).

⁴³ R. Magnotta, D. J. Nesbitt, and S. R. Leone, *Chem. Phys. Lett.* **83**, 21 (1981).

⁴⁴ K. Kleinermanns, E. Linnebach, and M. Pohl, *J. Chem. Phys.* **91**, 2181 (1989).

⁴⁵ B. Liu, *J. Chem. Phys.* **80**, 581 (1984).

⁴⁶ C. A. Boonenberg and H. R. Mayne, *Chem. Phys. Lett.* **108**, 67 (1984).

⁴⁷ K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

⁴⁸ I. Schechter, R. Kosloff, and R. D. Levine, *Chem. Phys. Lett.* **121**, 297 (1985).

⁴⁹ N. C. Blais and D. G. Truhlar, in *Potential Energy Surfaces and Dynamics Calculations*, edited by D. G. Truhlar (Plenum, New York, 1981).

⁵⁰ J. Z. H. Zhang and W. H. Miller, *J. Chem. Phys.* **91**, 1528 (1989).