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## DYNAMICS OF H<sub>2</sub> ELIMINATION FROM 1,4-CYCLOHEXADIENE

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### ABSTRACT

The dynamics of H<sub>2</sub> elimination from 1,4-cyclohexadiene (CHDN), dissociated with 212nm light, have been studied by state specific probing of the H<sub>2</sub> product via 1+1 REMPI using a transform limited vuv laser system. The quantum state distributions, the translational energy distribution and the Doppler profiles were measured giving a "rotational temperature" of  $\approx 1600\text{K}$ , a "vibrational temperature" of  $\approx 4000\text{K}$  and a translational energy of  $\approx 30\text{kcal/mole}$  for H<sub>2</sub>. Anisotropy in the Doppler profiles indicates that the H<sub>2</sub>'s velocity vector is aligned parallel to its rotational angular momentum vector.

**DYNAMICS OF H<sub>2</sub> ELIMINATION FROM 1,4-CYCLOHEXADIENE**

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The dissociation dynamics of 1,4-cyclohexadiene (CHDN) to form H<sub>2</sub> and benzene have been of great interest due to their importance in understanding the nature of the transition states of H<sub>2</sub> elimination from large cyclic hydrocarbons. This process is symmetry allowed for 1,4-CHDN in its ground electronic state<sup>1</sup> with a potential energy barrier of 43.8 kcal/mole.<sup>2</sup>

For a concerted decomposition with a substantial exit barrier the nature of the transition state plays an important role in determining how the released energy is distributed among the different degrees of freedom of the products. For example, in the transition state of 1,4-CHDN if both the C-H and H-H bond distances are relatively short the H<sub>2</sub> product will be formed with low vibrational excitation, but will have large translational energy due to the repulsion between the closely placed product molecules. On the other hand, if the transition state is characterized by longer C-H and H-H distances then one would expect higher vibrational excitation in H<sub>2</sub> with lower translational energy. If one measures the final quantum state and translational energy distributions for H<sub>2</sub> product then certain information can be deduced about the potential energy

surface in the transition state region. Complete product characterization is a powerful tool for indirect investigation of transition states.

In this communication we report our experimental investigation of the rotational, vibrational and translational energy distribution in  $H_2$  formed from the dissociation of 1,4-CHDN. The vibrational excitation of 1,4-CHDN was induced through an electronic transition followed by a rapid internal conversion process. The method we employed for the state specific detection of  $H_2$  used an ultra-high resolution vacuum ultraviolet-extreme ultraviolet (VUV-XUV) laser system to ionize  $H_2$  via (1+1) REMPI through either the  $B^1\Sigma_u$  or  $C^1\Pi_u$  states.<sup>3</sup> Taking advantage of the broad tunability and high brightness of the laser system we have been able to probe the  $H_2$  state distribution from  $v''=0$  to 5 and  $J''=0$  to 9 with a detection sensitivity of  $\approx 10^5$  molecules/state/ $cm^3$  within the laser bandwidth of 210MHz. In addition, we studied the Doppler profiles of the individual transitions which not only provided the  $H_2$  translational energy distribution but also gave insight into the correlation between the rotational angular momentum ( $J$ ) and velocity ( $v$ ) of the  $H_2$  fragment.

The details of the VUV-XUV laser system have been described previously.<sup>4</sup> A supersonic beam of CHDN is crossed with a photolysis and a probe laser beam which lie in a common plane. The CHDN was dissociated with 212nm photons, which deposited 135 kcal/mole into the molecules, and the  $H_2$  product

was probed with the aforementioned VUV-XUV laser system. Care was taken so that the  $H_2$  would not undergo collisions before being ionized and that all  $H_2^+$  would be collected. The  $H_2^+$  was mass-selected by time of flight and detected by a Daly type detector. The signal was normalized and averaged before being processed by a computer.

Figure 1 shows two typical signal traces obtained by scanning over two different  $H_2$  electronic transitions with a linearly polarized laser. From the properly integrated intensities of each transition one can calculate the ro-vibrational state population from the oscillator strength<sup>5</sup> and other experimental parameters. The rotational distribution in each vibrational level peaks at  $J''=2$  or 3 with the rotational energy decreasing slightly for the higher vibrations. The vibrational distribution peaks at  $v''=0$  with a moderate amount of population in the higher vibrational levels. These distributions can be characterized by a "rotational temperature" of  $\approx 1600K$  and a "vibrational temperature" of  $\approx 4000K$ . From the vibrational distribution one can infer that the transition state is fairly "tight", as shown qualitatively in the upper right corner of Fig. 1, with the two H-atoms moving from  $3\text{\AA}$  apart in  $1,4\text{-CHDN}^6$  to near  $0.7\text{\AA}$  apart in  $H_2$ . Small rotational excitation implies a very symmetric transition state in which the 1 and 4 H's are confined by their respective C-H bonds in the carbon ring frame until the last moment of release.

The  $H_2$  translational energy, measured by the Doppler

profiles, is in accord with previous measurements by Zhao et. al.<sup>7</sup> with an average kinetic energy of  $\approx 30$  kcal/mole and a FWHM of  $\approx 15$  kcal/mole. Moreover, we observed that the  $H_2$  velocity only decreased slightly with increasing internal energy. This extended the conclusion of the previous experiment showing that the translational energy gained by  $H_2$  in a given ro-vibrational state is mainly dominated by the release of potential energy along the reaction coordinate to that level.

By far the most exciting finding of this project is the observation of the vector correlation between the rotational angular momentum  $J$  and the recoil velocity  $v$  of the  $H_2$  fragment. As shown in Fig. 1, the R branch transition for  $H_2$  formed in the  $v''=0, J''=3$  state is dipped in the center while the Q branch transition is more rounded. According to recent theoretical work,<sup>8,9</sup> this anisotropy corresponds to a preferential alignment of  $v$  parallel to  $J$ . Physically, this would mean that  $H_2$  recoils from benzene with a "helicopter" type motion. A critical configuration near the transition state which would lead to this type of excitation is shown in Fig. 1. When the excess internal excitation distorts the molecule and pushes the 1 and 4 H atoms close together the H atoms are more likely to move in a plane parallel to the two double bonds rather than perpendicular to it. The details of the lineshape analysis and experimental results will be fully described in a forthcoming publication.



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**REFERENCES**

1. R. Hoffman, Trans. N.Y. Acad. Sci. 475 (1966).
2. S.W. Benson and R. Shaw, Trans. Faraday Soc. **63**, 985 (1967).
3. A.H. Kung, T. Trickl, N.A. Gershenfeld and Y.T. Lee, Chem. Phys. Lett. **144**, 427 (1988).
4. E.F. Cromwell, T. Trickl, Y.T. Lee and A.H. Kung, Rev. Sci. Inst. **60**, 2888 (1989).
5. E. Roueff, private communication.
6. G. Dallinga and L.H. Toneman, J. Mol. Structure **1**, 117 (1967).
7. X. Zhao, R.E. Continetti, A. Yokoyama, E.J. Hintsa and Y.T. Lee, (to be published).
8. G.E. Hall, N. Sivakumar, D. Chawla, P.L. Houston and I. Burak, J. Chem. Phys. **88**, 3682 (1988).
9. R.N. Dixon, J. Chem. Phys. **85**, 1866 (1986).

**FIGURE CAPTION**

Figure 1. (Top trace)  $H_2$  Doppler profile for the  $C^1\Pi_u + X^1\Sigma_g(1,0)$  R(3) transition ( $\nu_0 = 101271.0 \text{ cm}^{-1}$ ) with its corresponding fit ( $\beta_{\text{eff}} = -0.39$ ,  $v(H_2) = 1.3 \times 10^6 \text{ cm/s}$ ). (Bottom trace)  $H_2$  Doppler profile for the  $C^1\Pi_u + X^1\Sigma_g(1,0)$  Q(3) transition ( $\nu_0 = 101037.6 \text{ cm}^{-1}$ ) with its corresponding fit ( $\beta_{\text{eff}} = 0.29$ ,  $v(H_2) = 1.2 \times 10^6 \text{ cm/s}$ ). Profiles were fit using a non-linear least squares method with the function  $1/\nu_d^*(1 + \beta_{\text{eff}} P_2(\cos\theta) P_2(X))$  from Ref. 9 convoluted with a Gaussian  $H_2$  velocity distribution. (Upper right) Qualitative view of a critical configuration near the transition state for dissociation of CHDN.

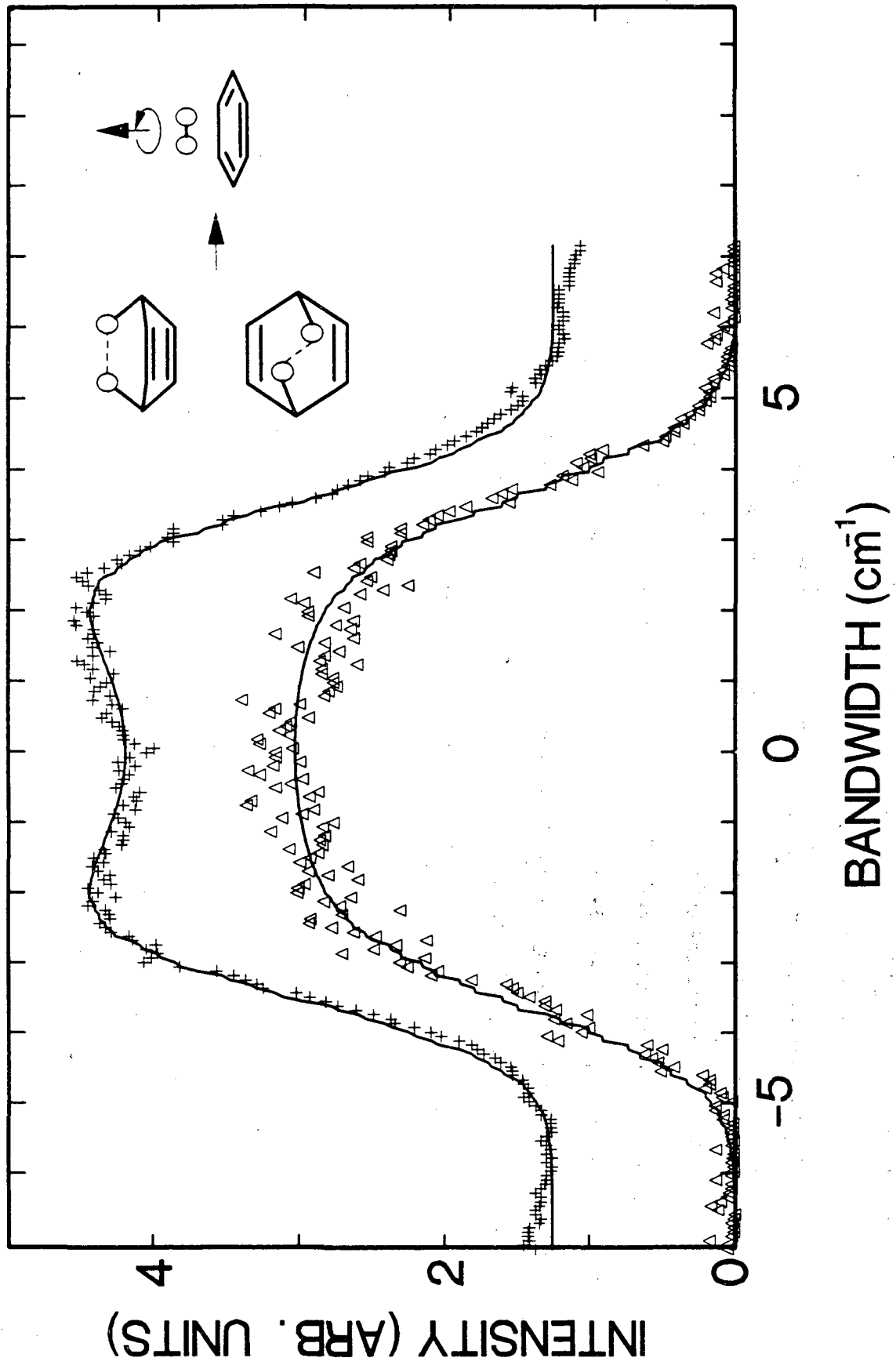


Fig. 1

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