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LETTERS TO THE EDITOR

COMMUNICATIONS

Dynamics of H_2 elimination from 1,4-cyclohexadiene

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The dissociation dynamics of 1,4-cyclohexadiene (CHDN) to form H_2 and benzene have been of great interest due to their importance in understanding the nature of the transition states of H_2 elimination from large cyclic hydrocarbons. This process is symmetry allowed for 1,4-CHDN in its ground electronic state[1] with a potential energy barrier of 43.8 kcal/mol.[2]

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_2 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_2 with lower translational energy. If one measures the final quantum state and translational energy distributions for H_2 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 ultrahigh 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.[3] 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 210 MHz. 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 ($\mathbf{J}$) and velocity ($\mathbf{v}$) of the H_2 fragment.

The details of the VUV–XUV laser system have been described previously.[4] 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 212 nm photons, which deposited 135 kcal/mol 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 rovibrational state population from the oscillator strength[5] 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 ≈ 1600 K and a "vibrational temperature" of ≈ 4000 K. 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 Å apart in 1,4-CHDN[6] to near 0.7 Å 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.[7] with an average kinetic energy of ≈ 30 kcal/mol and a FWHM of ≈ 15 kcal/mol. 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 rovibrational state is mainly dominated by the release of potential energy along the reaction coordinate to that level.
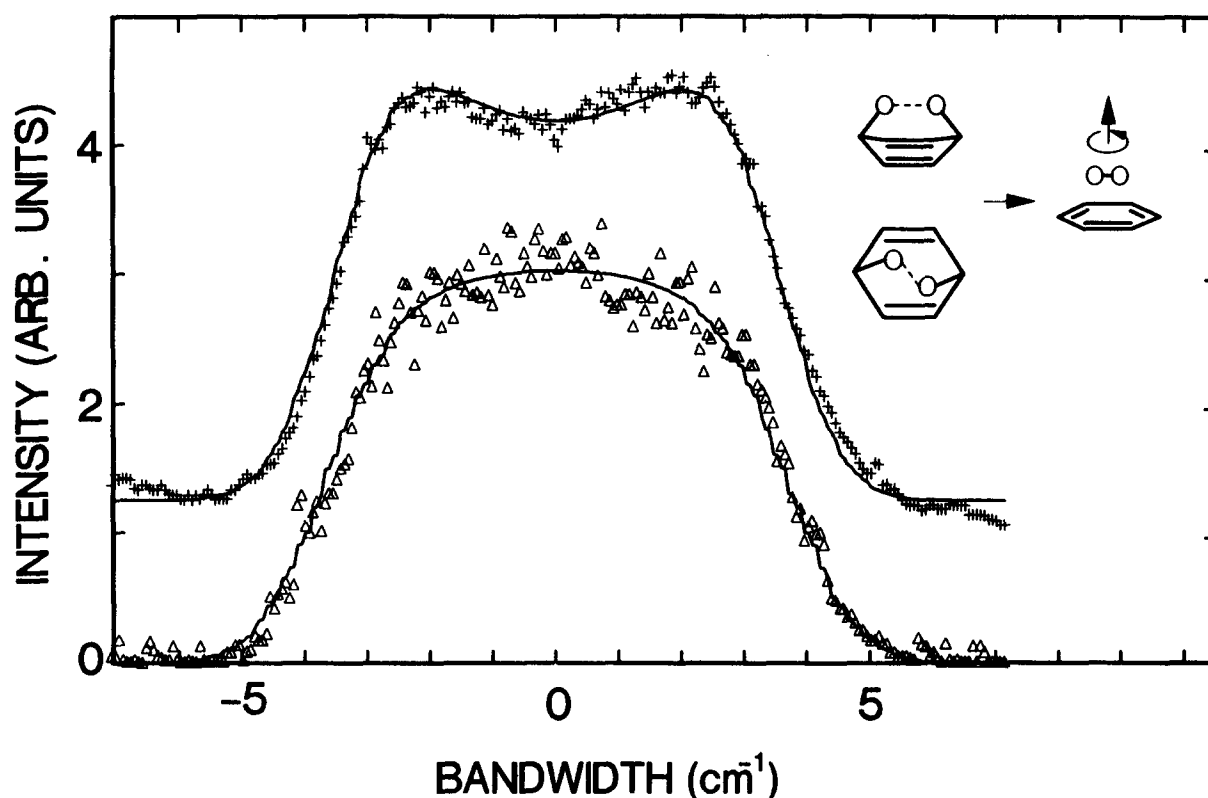
By far the most exciting finding of this project is the

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FIG. 1. Top trace: H_2 Doppler profile for the $C\,^1\Pi_u \leftarrow X\,^1\Sigma_g\,(1,0)$ $R(3)$ transition ($\nu_0 = 101\,271.0$ cm^{-1}) with its corresponding fit ($\beta_{eff} = -0.39$, $v(H_2) = 1.3 \times 10^6$ cm/s). Bottom trace: H_2 Doppler profile for the $C\,^1\Pi_u \leftarrow X\,^1\Sigma_g\,(1,0)$ $Q(3)$ transition ($\nu_0 = 101\,037.6$ cm^{-1}) with its corresponding fit ($\beta_{eff} = 0.29$, $v(H_2) = 1.2 \times 10^6$ cm/s). Profiles were fit using a nonlinear least squares method with the function $1/v_d^*\,[\,1 + \beta_{eff}\,P_2(\cos\theta)P_2(X)\,]$ 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.

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,[8,9] 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 line-shape analysis and experimental results will be fully described in a forthcoming publication.

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