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ABSTRACT

A comprehensive study of the dynamics of H₂ elimination from 1,4- and 1,3-cyclohexadiene is reported. Rotational and vibrational quantum state distributions as well as translation energy distributions for the H₂ product are measured. State specific detection of H₂ is accomplished with a transform limited vuv-xuv laser system via (1+1) REMPI. Rate constants for the H₂ elimination and 1,4 to 1,3 isomerization reactions are derived. A ($\mathbf{v}, \mathbf{J}$) correlation for H₂ with $\mathbf{v} \parallel \mathbf{J}$ primarily is observed from anisotropy in the Doppler profiles. A clear picture of the transition state configuration of 1,4-cyclohexadiene is provided from the information obtained.

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I. INTRODUCTION

Knowledge of the potential energy surface in the transition state region is paramount in understanding reaction dynamics. In a concerted decomposition eliminating a molecular product the configuration of the molecule at 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 H_2 elimination from 1,4-cyclohexadiene (CHDN), the structure near the transition state will have cyclohexadiene in a boat form with the two hydrogen atoms attached to the 3 and 6 positions pushed toward each other. There are two coordinates which are important in determining the final internal state and the translational energy of the H_2 products. The distance between two H atoms in the transition state region determines the final vibrational excitation of the H_2 product and the separation between the " H_2 " and the departing carbon atoms determines the repulsive energy released in the product formation. By measuring the translational, vibrational and rotational energy of the H_2 products one can deduce the structure of the transition state region especially related to the two orthogonal coordinates mentioned above. Complete characterization of product state distributions and translational energy distributions is a powerful tool for indirect investigation of transition state regions.

Initial experiments of H_2 elimination from cyclic hydrocarbons in our laboratory were carried out in the

photodissociation of cyclohexene, 1,4-cyclohexadiene and benzene.^{1,2} In those studies angularly resolved, mass selected, time of flight product distribution measurements revealed the translational energy distributions of H_2 products which had an average translational energy around 25 Kcal/mole and clearly indicated a strong repulsion between H_2 and the other products. However, it was not possible to estimate the extent of the vibrational and rotational excitation of H_2 , nor can one understand whether the kinetic energy in H_2 is strongly coupled to the internal excitation.

Using an ultra-high resolution vacuum ultraviolet-extreme ultraviolet (vuv-xuv) laser system the relative populations of the different ro-vibrational states of H_2 molecules were investigated by applying state selective detection of H_2 via (1+1) resonance enhanced multi-photon ionization (REMPI).³ In addition to the internal energy, the translational energy distributions of the H_2 products as a function of their quantum states have been obtained from the Doppler profile of the transitions and a correlation between translational and internal energy has been derived.

CHDN was chosen for this study because it has a "clean" H_2 elimination channel as shown in many previous investigations.^{4,5,6,7,8,9,10,11} In considering the photodissociation of CHDN three things stand out: H_2 is only eliminated in the electronic ground state through a concerted reaction, the ring opening channel does not subsequently yield

any measurable amount of H_2 , unless it reverses back to CHDN, and secondary H_2 elimination from benzene is not appreciable.^{1,2} The H_2 $B^1\Sigma_g$ and $C^1\Pi_u$ electronic states are well characterized with the transition frequencies from the ground ($X^1\Sigma_g$) state known to $<0.1\text{cm}^{-1}$.¹² Furthermore, the oscillator strengths for transitions between nearly all the different ro-vibrational states are calculated to a high degree of precision¹³ which allows us to estimate the quantum state distribution from the data obtained via the (1+1) REMPI.

Through-out the course of this experiment we hoped to be able to gain some insight into the nature of the transition state for the elimination of H_2 from 1,4-CHDN. From our preliminary results, reported in an earlier communication,¹⁴ and a more intensive study described in detail below it became clear that this reaction proceeds through a very tight and near symmetric transition state with both the H-H and $H_2-C_6H_6$ distances appearing to be short. Furthermore, a correlation between the recoil velocity vector ($\mathbf{v}$) and the rotational angular momentum vector ($\mathbf{J}$) of the H_2 product was also observed with $\mathbf{v} \parallel \mathbf{J}$ predominately. Two calculations on the transition state configuration and its normal modes have recently been communicated to us.^{15,16} These results agree very well with our observations.

II. EXPERIMENTAL

The laser system and molecular beam source used in this experiment have both been described previously.^{17,18} Other details of the experimental set-up will be given below. A schematic of the experimental set-up is shown in Figure 1. The CHDN is expanded through a 0.5mm diameter nozzle of a pulsed valve, designed by Proch and Trickl¹⁹, into the source chamber the pressure of which is kept below 10^{-4} torr. The main chamber, which contains the interaction region, is differentially pumped and separated from the source chamber by a skimmer with a 2mm diameter aperture. The main chamber pressure was $\approx 5 \times 10^{-7}$ torr while running the beam source. The nozzle-skimmer distance was 2cm and the distance from the skimmer to the interaction region was 3cm. The CHDN beam was crossed with the laser beams at an angle of 98° . The Doppler shift due to the $>90^\circ$ angle and the Doppler broadening due to the molecular beam divergence was negligible compared to that caused by the velocity spread of the H_2 products. The ion optics used for the detection of the products were the same as described previously.²⁰ There was a 1500V drop across the interaction region and ions were eventually accelerated to 2500 eV into the drift region. The ions of different mass were separated with a 1m long time of flight mass spectrometer. The H^+ and H_2^+ peaks were separated by $\approx 1\mu s$ while their widths (FWHM) were only 50ns. The ions were detected with a Daly type scintillation ion detector²¹ using an acceleration voltage of 30kV and an RCA C31000M photomultiplier tube.

With a high H_2 product velocity ($\approx 1 \times 10^6$ cm/s) in the dissociation of CHDN there was a concern that some H_2 might escape detection. It was imperative that all the H_2^+ be collected in order to have accurate quantum state distributions and Doppler profiles. The collection efficiency of the apparatus was tested by measuring H_2 product from the dissociation of formaldehyde. The velocity of H_2 formed in the $v''=1$ state from H_2CO resonantly dissociated on the $2^1A' \rightarrow P_1(1)0$ at 29484.6 cm^{-1} has a narrow velocity distribution with an average velocity of $\approx 1.5 \times 10^6$ cm/s. Doppler profiles corresponding to that velocity with an isotropic angular distribution were obtained in accord with those measured by Butenhoff et. al.²² using LIF detection. This assured that when dissociating CHDN the H_2 product, which has a velocity $< 1.3 \times 10^6$ cm/s, could be collected uniformly without bias towards the slower molecules.

Beams of both the 1,3 CHDN and the 1,4 CHDN were produced neat from a reservoir kept at 0°C giving vapor pressures of approximately 30 torr and 20 torr respectively. 1,3 CHDN was obtained from Aldrich and 1,4 CHDN was obtained from Fluka and were degassed before use. No further purification was performed. CHDN dimers were not observed in the beam, as was expected due to the soft expansion conditions, and no attempt was made to investigate their impact on the experiment.

The probe laser system began with pulse amplification of the output from a Coherent 699-29 ring dye laser. The amplification was done with 450mJ of 532nm light from a Quantel 581C Nd:YAG

laser. The amplifier chain, built in our laboratory, utilized 3 prism dye cells. The output power of the visible light was $>100\text{mJ}$ with a bandwidth of $\approx 95\text{MHz}$ at the peak of the amplifier dyes used (R6G and Kiton Red). The visible light was frequency doubled using a INRAD Autotracker II doubling crystal unit with a 3cm long KD*P crystal which typically gave around 30% conversion. The uv light was then converted to xuv-vuv radiation via straight tripling²⁰ or sum frequency mixing ($2\text{uv}+1\text{vis}$)²³ in a pulsed molecular beam. The use of the pulsed molecular beam allowed for the elimination of windows between the mixing chamber and the interaction region while maintaining a good vuv-xuv conversion efficiency. The vuv-xuv radiation was reflected off a grating in a 1m VUV monochromator into the main chamber. The grating served to recollimate the beam and to allow separation of the uv radiation from the vuv when desired. The size of the probe laser beam at the interaction region was adjustable from a tight focus ($<100\mu\text{m}$) to 3mm by translating the grating inside the monochromator. During scans the grating was set at zeroth order so that the intense residual uv light could be used as the ionization beam in the 1+1 REMPI scheme.

The 699-29 was operated with Rhodamine 6G (R6G) while the amplifier chain was operated with primarily either R6G or Kiton Red covering the regions 565nm to 573nm and 589nm to 595nm respectively. With these dyes we were able to utilize the Xenon 2+2+1 (5ω) mixing resonances from $85,000\text{cm}^{-1}$ to $87,000\text{cm}^{-1}$ and $88,000\text{cm}^{-1}$ to $90,000\text{cm}^{-1}$.²³ In this configuration a 3mm LiF window

was inserted into the beam path in order to filter out any 6ω light generated by tripling of the uv radiation. The intensity of the 6ω radiation was measured to be <1% of that of the 5ω light after the LiF window. Straight tripling (6ω) was done in Argon giving coverage of the regions from $101,000\text{cm}^{-1}$ to $103,000\text{cm}^{-1}$ and $104,000\text{cm}^{-1}$ to $106,000\text{cm}^{-1}$ for Kiton Red and R6G respectively.¹⁷

For the majority of the experiment the CHDN molecules were photodissociated with photons generated around 212nm. The dissociation light source was comprised of a second single-mode pulsed dye laser system operated at $\approx 636\text{nm}$ (using DCM in both the 699-29 and amplifier chain) from which the 3rd harmonic was generated by frequency doubling in a KDP crystal and then mixing the generated uv radiation with the residual visible light in a BBO crystal. The pulse energy from this system was $\approx 6\text{mJ}$. For 1,4-CHDN this excited a symmetry forbidden $\pi \rightarrow \pi^*$ transition^{24,25} while for 1,3-CHDN a symmetry allowed $\pi \rightarrow \pi^*$ transition was excited.^{26,27} The dissociation laser had a beam diameter of 6mm and was sent, unfocused, through a secondary port into the main chamber where it crossed with the molecular beam and the probe beam. Although having a focused photolysis laser beam yielded more signal, the configuration used in the experiment, with a unfocused laser, kept the dissociation area large compared to the probe area which was important in eliminating any artifacts due to beam overlap. A side view of the interaction region is shown in Figure 2.

Additional experiments to measure the kinetic rate constants and to repeat the $(\mathbf{v}, \mathbf{J})$ correlation measurements utilized a Lambda-Physik EMG-103-MSC excimer laser operated with an ArF gas mixture with an output of $\approx 100\text{mJ}$ at 193nm . An unstable resonator was used in the laser cavity to produce a well collimated beam with a uniform intensity cross section. An 8mm diameter section of the beam, containing $\approx 10\text{mJ}$ of energy, was injected into the interaction region. For the kinetic rate constants study this beam was unfocused while for the $(\mathbf{v}, \mathbf{J})$ correlation measurements the beam was softly focused to $\approx 2\text{mm}$ diameter. The pulse-to-pulse timing jitter was $< \pm 1.5\text{ns}$ for the 20ns FWHM beam. A full description of the set-up utilizing this photolysis laser will be given in a future publication.²⁸

The use of a narrow bandwidth tunable photolysis laser allowed us to study the effect on the H_2 elimination process of the frequency of the photon absorbed by the CHDN molecule. Resonances in the 1,4-CHDN excited electronic state (π^*) were looked for briefly by tuning the dissociation laser over a narrow region of 10cm^{-1} and monitoring the H_2 signal intensity from a given ro-vibrational level. The pump laser bandwidth was sufficiently narrow ($< 0.01\text{cm}^{-1}$) to resolve any rotational structure that might be present. No excited state resonances were observed. This is not surprising in view of the expected short lifetime of the 1,4-CHDN excited electronic state.^{1,9}

Time delay scans between the pump and probe lasers were performed for beam diagnostics and kinetic rate constant

measurements. The timing of the whole system was controlled with two SRS 535 Delay/Pulse generators. When utilizing the two single-mode systems the jitter between the two laser pulses was $<\pm 1\text{ns}$. For experiments using the excimer laser as the photolysis source the jitter was somewhat greater ($<\pm 2\text{ns}$). Delay scans were generated and data was taken by a PC interfaced to the pulse/delay generators. The photolysis/probe delay for the population scans was set at the maximum H_2^+ signal as determined by the delay scans. Time delay scans were done for both the 1,4-CHDN and 1,3-CHDN with significant differences between the two isomers observed. The data presented here was taken using the excimer laser as the photolysis source. With laser pulses of 8ns and 20ns for the probe and photolysis lasers respectively the maximum resolution was $\approx 2\text{ns}$ for these scans.

To determine the rotational and vibrational state distributions of the H_2 product the H_2 was ionized by (1+1) REMPI using either the $\text{B } ^1\Sigma_u$ or $\text{C } ^1\Pi_u$ states of H_2 . The vibrational coverage was from $v''=0$ to $v''=6$ although for the $v''=6$ scans the signal was barely detectable. The rotational coverage varied for each vibrational level depending on the relative populations and transition strengths but typically was from $J''=0$ to $J''=9$. For higher J'' levels only the odd states were observable due to the hydrogen nuclear spin statistics.

Normalization of the vuv laser intensity dependent H_2^+ signal was accomplished in two different manners. For wavelengths above the LiF cutoff a solarblind PMT (EMR 542G) was

placed in the monochromator to monitor the intensity of the first order vuv diffraction. The tube has a 10^4 discrimination against uv light and a reasonably flat vuv response in the region where it was being used. Operating voltages were typically between 1.6 and 1.8kV. For wavelengths below the LiF cutoff acetylene was seeded into the CHDN beam to produce an additional ion signal that was dependent on the xuv signal. The $C_2H_2^+$ signal was then used to normalize the H_2^+ signal. C_2H_2 has a flat photoionization response in this region and has been successfully used before for xuv normalization.²⁹ The accompanying uv laser has sufficient intensity to ionize all H_2 molecules excited by the vuv laser. The dissociation laser power was stable enough that shot-to-shot normalization to that signal was not necessary although the pulse energy was monitored prior to each scan.

While dissociating 1,3-CHDN and scanning the H_2 $v''=0$ product (when straight tripling was required) there was a large background ion signal at $m/e=26$ ($C_2H_2^+$). This made shot-to-shot normalization with acetylene impossible. In this case the relative xuv intensity was measured by adjusting the monochromator to pass 1st order light through the interaction region and onto an electron multiplier tube (EMT) which measured the beam intensity. The grating was then turned to 0th order for scanning the H_2 transition. The xuv signal was measured before and after each scan and that signal was used to normalize between different scans.

III. RESULTS AND ANALYSIS

A. POPULATION DISTRIBUTION

The different transitions used to generate the quantum state distribution of the H₂ molecule eliminated from CHDN are listed in Table I. The vibrational distribution obtained from this data is shown in Figure 3 while the rotational distributions are shown in Figure 4. Included with each of the distributions are non-linear least-square fits of the data with an appropriate statistical distribution function. These will be discussed in more detail below.

The relative population, $P(v,J)$, for a given ro-vibrational state was calculated according to:

$$P(v,J) \propto \frac{I(v,J) * C * g}{\mu_{if} * E_p}$$

where $I(v,J)$ =normalized integrated line intensity, C =instrument function (boxcar sensitivity, analog processor gain, etc.), g =H₂ nuclear spin statistic degeneracy factor, μ_{if} =line transition strength (including the Franck-Condon and the Höln-London factors), and E_p =photolysis laser (212nm) intensity. The 1,4-CHDN and 1,3-CHDN data were not normalized to each other due to the differences in the beam densities and the absorption cross sections at 212nm of the isomers. The intensity of each scan $I(v,J)$ was measured by numerically integrating the area under each curve after appropriate axis scaling and baseline subtraction. The scans were normalized to the vuv intensity as described in the previous section.

Table I: H ₂ TRANSITIONS USED FOR POPULATION DISTRIBUTION			
Initial Vib. State	Electronic Transition	Initial Rot. States	Trans. Freq. Range
v"=0	C-X (1,0)	J"=0 TO 5	100,500 to 102,600 cm ⁻¹
	C-X (2,0)	J"=5 TO 9	
	C-X (3,0)	J"=9	
v"=1	B-X (1,1)	J"=0 TO 2	87,200 to 88,500 cm ⁻¹
	B-X (2,1)	J"=3 TO 5	
	B-X (3,1)	J"=5 TO 7	
	B-X (4,1)	J"=9	
v"=2	B-X (2,2)	J"=0 TO 4	83,750 to 85,500 cm ⁻¹
	B-X (3,2)	J"=5 TO 7	
	B-X (4,2)	J"=9	
v"=3	B-X (5,3)	J"=0 TO 5	83,750 to 85,500 cm ⁻¹
	B-X (6,3)	J"=4 TO 7	
	C-X (0,3)	J"=1 TO 3	87,200 to 88,500 cm ⁻¹
	C-X (1,3)	J"=7 TO 9	
v"=4	B-X (8,4)	J"=0 TO 3	83,750 to 85,500 cm ⁻¹

In some cases there was overlap between transition profiles due to the large Doppler widths of those transitions. When this happened it was often possible to deconvolute the profiles by fitting one or the other to a lineshape from a transition of similar quantum numbers and rotational branch. While this technique was useful in estimating line intensities it was not used to infer lineshapes. Another difficulty arose when trying to probe high lying vibrational states in the $B^1\Sigma_g$ manifold. The $B^1\Sigma_g$ state correlates to the ion pair H^+ and H^- and as a result of this (1+1) REMPI often causes dissociative ionization, producing both H^+ and H_2^+ . For REMPI through the $B^1\Sigma_g$, $v'=5$ or 6 , state typically from 10% to 30% of the signal is in the H^+ channel. REMPI through higher vibrational states can produce >80% H^+ . While under our experimental conditions there is essentially zero background at $m/e=2$, there is a considerable $m/e=1$ signal due to the tight focusing of the uv required to saturate the ionizing step in the REMPI process. The $m/e=1$ signal can be reduced to tolerable levels by relaxing the probe focus but then one has to account for the non-saturated second REMPI step. A consequence of this was that in order to take the $v''=0$ data it was necessary to ionize through the $C^1\Pi_u$ state (which is non-dissociative). For $v''=3$ the H^+ component was estimated from measured H^+/H_2^+ ratios. For $v''=4$ the rotational populations were taken under non-saturating conditions although the H_2^+ signal for the $J''=1$ transition was measured under saturating conditions. The $v''=5$ and 6 signals (which were ionized

through $v' > 8$ of the B state and were nearly all H^+) were observed with a loosely focused probe beam.

The normalization worked very well for reducing the uncertainty caused by fluctuations in the vuv-xuv power. These fluctuations, which could be greater than 50% of the average vuv intensity, were by far the largest source of uncertainty in the experiment. With proper shot-to-shot normalization very good signal to noise ratios ($>10:1$) were obtained on scans which were not limited by ion counting statistics. However, the ability to reproduce relative integrated intensities of different transitions was somewhat disappointing. Some individual transitions were scanned a number of times in order to get meaningful statistics. From these measurements the accuracy of the quantum state populations is estimated to be $\pm 20\%$. While the uncertainty in the measurements is relatively large the trends in the populations can be clearly seen.

The vibrational distribution, while peaked at $v''=0$, shows a fair amount of vibrational excitation the distribution of which can be statistically fitted with a vibrational temperature of $\approx 3000K$. The functional form used to fit the distribution is:

$$P(v) = P_0 * e^{-\left(v+1/2\right) \frac{\omega_e}{kT} + \left(v+1/2\right)^2 \frac{\omega_e x_e}{kT} - \left(v+1/2\right)^3 \frac{\omega_e y_e}{kT}}$$

The anharmonicity constants were taken from Herzberg.³⁰ The rotational populations peak around $J=2$ or $J=3$ with the rotational temperatures varying from $\approx 1270\text{K}$ to $\approx 730\text{K}$. For the rotational distributions the following statistical function was used in the fitting:

$$P(v, J) = P_0 * (2J+1) * e^{-J(J+1) \frac{B(v)}{kT} + J^2(J+1)^2 \frac{D(v)}{kT} - J^3(J+1)^3 \frac{H(v)}{kT}}$$

Here the vibrationally dependent anharmonicity constants were taken from Dabrowski.¹² The vibrational level populations were calculated from the fits to the rotational levels. The measured temperatures along with their standard deviations are given below in Table II. The rotational excitation of the H_2 fragment is less favorable than vibrational excitation and the amount of rotational energy imparted into the H_2 fragment is relatively decoupled from its final vibrational state.

TABLE II: H ₂ INTERNAL ENERGY DISTRIBUTION TEMPERATURES		
Vibrational Temperature		
T(vib)	3000 +/- 430 K	
Rotational Temperatures		
v"	T(rot)	Std. Dev.
0	1270K	170
1	1030K	160
2	910K	80
3	730K	120

There are a number of important observations that can be made from the rotational and vibrational quantum state distributions of the H_2 product from the unimolecular dissociation of 1,4-CHDN. In the ground state of 1,4 CHDN the 3 and 6 hydrogen atoms are calculated to be $3.0\text{\AA}$ apart.¹¹ In molecular hydrogen the H-H distance is well known to be $0.75\text{\AA}$ in its ground state. The H-H distance is expected to be longer than this value in the critical structure near the transition state. The H atoms must be very close to each other before there is sufficient electronic orbital overlap for a H-H bond to form and two C-H bonds to break simultaneously as is required by the concerted nature of the process. There are two ways to account for this. Either the CHDN ring must be in a severely distorted boat formation at the transition state or the 3 and 6 C-H bond lengths must increase, due to a weakening of the bond by partial relocation of electron density from between the C and H atoms to the π -orbital system of the carbon ring, in order to get the H's close enough for the reaction to take place. Calculations of the ring strain energy needed for the first process show that it is significantly higher than the measured activation energy of 43Kcal/mole for the reaction. Thus it seems obvious that, in addition to the strained boat form, elongation of the C-H bonds is necessary to reach the critical structure. That is not surprising, especially when one considers the stabilizing effect from formation of the benzene ring. This is supported by recent calculations of the transition state configuration of 1,4-CHDN

which show elongated C-H bond lengths and a H-H distance of $\approx 1\text{\AA}$.^{15,16}

In a sense, the experimental probing of the vibrational and translational energies of H₂ products should reveal the average H-H and C-H distances in the critical structure near the transition state. Vibrational relaxation of H₂ during the repulsive separation of products is expected to be inefficient and the H₂ vibrational energy will depend on the average H-H distance at the transition state. In a concerted decomposition, when bonding electrons between C-H bonds rearrange into the benzene ring and H₂ molecules, C-H interaction between H₂ and nascent benzene will be repulsive and the repulsive energy will depend on the C-H distances in the transition state region.

Since the beam of cyclohexadiene in this experiment is produced by supersonic expansion, the rotational temperature is expected to be very cold. The rotational energy of H₂ which is associated to the original rotational motion of CHDN should be negligible and if the transition state structure for H₂ elimination is symmetric, the synchronous concerted decomposition will not exert any torque on the departing H₂ molecules. It is not surprising that the various rotational distributions observed are peaked at relatively low J given the high total amount of energy available in the system.

The angular momentum of H₂ is undoubtedly created during the repulsive release of the potential energy. To understand this one must first consider how rotational energy would be imparted

into the H_2 fragment. Vibrational energy would come from different H-H separations at the transition state but rotational energy would have to come from either a twisting of the two C-H bonds away from the symmetry plane which contains the 3 and 6 carbon atoms in the ring or a non-symmetric boat formation (i.e. one side flipped up more than the other). The first would send the H_2 off like a helicopter with its imparted velocity and rotational angular momentum vectors parallel while the later would induce a Frisbee like motion where the two vectors are perpendicular. Given the low amount of rotational energy in the fragment the distortion from the symmetric transition state, especially the twisting of the H_2 with respect to the two C atoms along the C-H-H-C coordinate, should not be extensive. The second observed trend, that the amount of rotation is decoupled from the amount of vibration, also supports this view since even in the vibrational ground state where there is much more available energy for rotation little such excitation occurs. Thus, while the bending of the ring occurs quite readily it appears that even though the energy of excitation is far above that required to reach the transition state, the molecules dissociate from a very symmetric transition state structure with little distortion involved.

Part of the impetus for looking at both isomers of CHDN was to see if there was a rapid isomerization of the two isomers in the excited state before molecular dissociation. If elimination of H_2 took place from both isomers then one might expect to see a

bimodal H₂ vibrational distribution. On the other hand, if 1,3-CHDN isomerized to 1,4-CHDN before eliminating H₂, then one would expect a single vibrational distribution with the 1,3-CHDN mimicking that of the 1,4-CHDN. Within the experimental error the quantum state distributions from the two isomers are identical. This, combined with the fact that the translational energies are identical and the rate of dissociation of 1,3-CHDN, as measured from the time dependence of the accumulation of H₂ products, is slower supports the later process where 1,3-CHDN isomerizes to 1,4-CHDN before eliminating H₂.

B. TRANSLATIONAL ENERGY

As discussed previously, the translational energy of the product H₂ molecule was determined through the Doppler profiles of the transitions measured. The individual lineshapes were fit using a non-linear least squares method with the function:

$$I \propto \frac{1}{v_D} * [1 + \beta * P_2(\cos\theta) * P_2(\chi)] \quad (4)$$

where v_D =maximum doppler shift, β =effective anisotropy parameter, P_2 =second order Legendre polynomial, θ =angle between the electric field vector of the linearly polarized photolysis laser and the direction of the probe laser and χ =Doppler shift/ v_D . This function was convoluted with a normalized Gaussian H₂ velocity distribution of a variable width. The H₂ translational energy

was then calculated from the Doppler shift observed and the transition frequency. A listing of the H_2 translational energies and velocities measured is given in Table III. We were not able to measure velocities for a number of quantum states due to interference in the Doppler profiles from other close lying transitions.

TABLE III: H_2 TRANSLATIONAL ENERGY FROM 1,4-CHDN			
VIB. STATE	ROT. STATE	VELOCITY (CM/S)	E_{Tr} (Kcal/MOLE)
$v''=0$	$J''=3$	1.25×10^6	37
	$J''=7$	1.2×10^6	34
$v''=1$	$J''=1$	1.0×10^6	24
	$J''=3$	9.95×10^5	24
	$J''=5$	1.0×10^6	24
$v''=2$	$J''=0$	9.3×10^5	21
	$J''=1$	9.7×10^5	22.5
	$J''=5$	9.9×10^5	23.4
	$J''=7$	1.0×10^6	24
$v''=3$	$J''=1$	9.5×10^5	22
	$J''=3$	9.4×10^5	21
	$J''=9$	1.0×10^6	24

A measurement of the translational energy distribution of H_2 product was done previously via photofragmentation translational spectroscopy¹ and it was found that the H_2 translational energy peaked at 25 Kcal/mol. In this study the CHDN molecule was dissociated in two manners: with 193nm photons and through an infra-red multi-photon process. The H_2 translational energy distribution from these two methods peaked at the same energy. The only difference was in the widths of the distributions. This indicated that the kinetic energy imparted into the H_2 fragment was dependent mainly on potential energy barrier in the exit channel and not on the total amount of energy available.

If the repulsive energy release dominates the separation of products unless there is an extremely strong dependence of the repulsive potential energy on the H-H vibrational coordinate one would expect that the H_2 translational energy should not depend strongly on the final rotational or vibrational state of the molecule provided that the transition state has a symmetric structure and the decomposition is synchronous and concerted. Our results show that the H_2 kinetic energy only decreases slightly as its internal energy increases. The lineshapes for the $J''=1$ states from $v''=1$ to $v''=3$ are shown in Figure 5 with their respective fits and measured widths. As one can see, the translational energy decreases from ~34Kcal/mole for $v''=0$ to ~22Kcal/mole for $v''=3$ while at the same time the H_2 internal energy has increased by >30Kcal/mole. Similar behavior was observed for the $v''=4$, $v''=5$, and $v''=6$ transitions although the

uncertainty is much greater in these measurements. The widths of the H_2 velocity distributions also increase as one goes to higher internal energy. This would explain the difference between the $P(E)$ curves seen by Zhao et. al in their experiments using IRMPD and 193nm excitation. The 193nm dissociation, with a much higher average excitation energy per molecule, is expected to produce more vibrationally excited H_2 with wider velocity distributions than the IRMPD experiment. Thus the former process produced a wider $P(E)$ curve but the maximum translational energy remained fairly constant for both experiments.

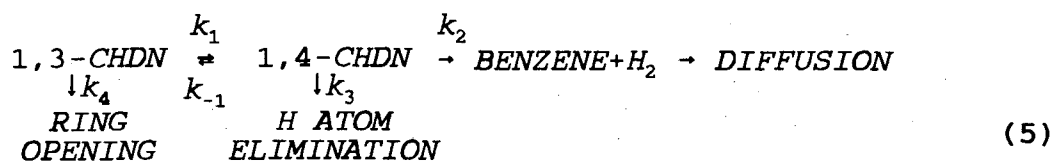
There are two important things to consider in explaining the translational energy distribution in the H_2 fragment. The first is the concerted nature of the reaction. As explained previously,¹ in a concerted process there is a large repulsion between the product molecules immediately after the reaction has occurred when they are closely placed in the region of the transition state. This potential energy is mainly channeled into translational energy of the H_2 product. A second reason is the presence of a large number of degrees of freedom in the parent molecule. Depending on how many active modes there are in the CHDN and in despite of the deposition of 134Kcal/mole of energy there will only be 3-5 Kcal/mole of energy in any given ro-vibrational degree of freedom. Thus translational energy imparted to the H_2 from energy coupled to the reaction coordinate by an excited parent molecule will be a relatively small fraction of the total translational energy of the fragment. Of course,

the repulsion between H_2 and benzene formed near the transition state is expected to depend slightly on the H-H distance, or the vibrational excitation of H_2 .

C. REACTION KINETICS

Photolysis/probe laser delay scans for both the 1,3-CHDN and 1,4-CHDN are shown in Figure 7. The H_2^+ signal from the 1,4-CHDN photofragmentation peaks at 20ns while the corresponding signal for the 1,3-CHDN case peaks at 80ns. This difference is independent of the vibrational or rotational state being probed within the experimental resolution. Diffusion effects were minimized by having the photolysis beam diameter much greater than that of the probe beam. To get the best possible representation of the H_2 evolution the delay scans were taken under identical alignment conditions.

The relative heats of formations of 1,3-CHDN, 1,4-CHDN, and Benzene+ H_2 are shown in Figure 6. The two CHDN isomers are nearly equal in energy with the heat of formation of 1,3-CHDN being ≈ 3 Kcal/mol lower. According to the Woodward-Hoffman selection rules the direct H_2 elimination from 1,3-CHDN is forbidden in its ground electronic state while from 1,4-CHDN it is allowed.^{31,32} With this in mind we used the following kinetic model to explain the differences between the decomposition of the two isomers.



If one neglects the diffusion process initially the appearance of H_2 as a function of time obeys the following set of rate equations:

$$\frac{dX}{dt} = k_1 \cdot Y - k_{-1} \cdot X - k_2 \cdot X - k_3 \cdot X \quad (6)$$

$$\frac{dY}{dt} = k_{-1} \cdot X - k_1 \cdot Y - k_4 \cdot Y \quad (7)$$

$$\frac{dZ}{dt} = k_2 \cdot X \quad (8)$$

where $X = [1,4\text{-CHDN}]$, $Y = [1,3\text{-CHDN}]$ and $Z = [\text{H}_2]$. From (6) and (7) the following differential equation for X can be derived:

$$\frac{d^2X}{dt^2} + (k_1 + k_{-1} + k_2 + k_3 + k_4) \cdot \frac{dX}{dt} + [k_1 \cdot k_{-1} - (k_1 + k_4) \cdot (k_{-1} + k_2 + k_3)] \cdot X = 0 \quad (9)$$

This can be simplified further by letting $k_1 \approx k_{-1}$ since the energy difference between 1,4-CHDN and 1,3-CHDN is only 3Kcal/mole in their ground electronic states and the barrier height to isomerization is >60Kcal/mole, much smaller than the excitation energy which is as high as 148Kcal/mole.

If one lets $X = e^{\lambda t}$ and then substitutes into (9) and solves for λ one finds that:

$$\lambda_{1,2} = 1/2 \cdot \{ -(2 \cdot k_1 + k_2 + k_3 + k_4) \pm [4 \cdot k_1^2 + k_2^2 + 2 \cdot k_2 (k_3 - k_4) + (k_3 - k_4)^2]^{1/2} \} \quad (10)$$

Thus:

$$X = C_1 * e^{\lambda_1 * t} + C_2 * e^{\lambda_2 * t} \quad (11)$$

where C_1 and C_2 are determined by initial conditions. Solving (8) one obtains the following equation for the appearance of H_2 as a function of time:

$$K_{H_2}(t) = \alpha * e^{\lambda_1 * t} + \beta * e^{\lambda_2 * t} - (\alpha + \beta) \quad (12)$$

with,

$$\begin{aligned} \alpha &= k_2 * \frac{C_1}{\lambda_1} \\ \beta &= k_2 * \frac{C_2}{\lambda_2} \end{aligned} \quad (13)$$

From the initial conditions of the experiment solutions for C_1 and C_2 can be calculated from equations (6)-(8) for the 1,4-CHDN and 1,3-CHDN cases. For the dissociation of 1,4-CHDN the following values of α and β are obtained:

$$\alpha = D_0 * k_2 * \frac{[-\lambda_2 - (k_1 + k_2 + k_3)]}{\lambda_1 * (\lambda_1 - \lambda_2)} \quad (14)$$

$$\beta = D_0 * k_2 * \frac{[\lambda_1 + (k_1 + k_2 + k_3)]}{\lambda_2 * (\lambda_1 - \lambda_2)}$$

For the dissociation of 1,3-CHDN the values of α and β are:

$$\alpha = D_0 * k_2 * \frac{k_1}{\lambda_1 * (\lambda_1 - \lambda_2)} \quad (15)$$

$$\beta = -D_0 * k_2 * \frac{k_1}{\lambda_2 (\lambda_1 - \lambda_2)}$$

The delay curves shown in Figure 7 were taken using the ArF excimer laser (193nm) described previously as the dissociation source. The theoretical fits were calculated according to equation 11 with the appropriate α and β 's as given by equations 14 and 15. Full delay curves (which included the rising edge due to H_2 evolution and the decaying part due to H_2 moving away from the probe region) were measured for various pump beam diameters. The falling edge was successfully modeled using the geometrical factors of the experiment but since there is no dynamical information in this part of the delay curve these results will not be presented. A pump beam diameter of 8mm was used for the curves shown in Figure 7 under which conditions the H_2 signal did not start falling off until after 200ns, well after both the 1,3-CHDN and 1,4-CHDN signals had leveled off.

In order to successfully fit the time dependent yield curves it was necessary to include a correlation function between the two lasers. This was accomplished as follows. The probe laser was set resonant with the H_2 C-X (1,0) Q(1) transition, the monochromator was set to 1st order and a small amount of H_2 (1×10^{-5} torr) was introduced into the main chamber through a

needle valve. The excimer laser was then used as the ionizing laser for the (1+1) REMPI of the H_2 . The laser correlation function was then measured by varying the pump/probe laser delay and monitoring the H_2^+ signal. This curve was fit fairly well with a Gaussian distribution with a FWHM=12ns. This Gaussian was then convoluted with the H_2 evolution functions given above to fit the delay curves in Figure 7.

An RRKM calculation was performed with 26 modes counted to obtain theoretical values for k_1 , k_2 , k_3 , and k_4 . The results of this calculation are given in Table IV along with the experimentally obtained results from the best fits of the delay curves. As one can see there is fairly good agreement among all the rates except for k_4 , which is the ring opening process. The initial ring opening process from the electronically excited state should be even faster than the rate calculated using RRKM theory. One explanation for the much smaller rate for k_4 might lie in the fact that after the initial ring opening this process is reversible. If the ring opening and closing processes are fast on the time scale of the experiment, which is indicated by the RRKM calculation and other reported results,⁹ an equilibrium would be quickly reached between the linear and ring compounds and the effect on the long term reduction of H_2^+ signal would be small. Thus, the experimentally measured k_4 would represent the decay of 1,3-CHDN by some other process, such as H atom elimination, rather than by isomerization.

TABLE IV: KINETIC RATES FOR PHOTODISSOCIATION OF CHDN		
RATE	EXP. VALUE	RRKM VALUE
k_1	0.07ns^{-1}	0.23ns^{-1}
k_2	0.3ns^{-1}	0.94ns^{-1}
k_3	0.18ns^{-1}	0.93ns^{-1}
k_4	0.005ns^{-1}	11.0ns^{-1}

D. V-J CORRELATION

In the previous angularly resolved, but non-state-selective, experiments involving photofragmentation translational energy spectroscopy the H_2 was observed to have an isotropic distribution. This confirmed the expectation of a long dissociation lifetime (greater than one rotational period). As a result of this one would not expect to see any correlation between the electric field vector of the dissociation laser and the velocity ($\mathbf{v}$) or rotational angular momentum ($\mathbf{J}$) vectors of the H_2 product. However, this does not rule out the possibility of a correlation between $\mathbf{v}$ and $\mathbf{J}$. Evidence of a ($\mathbf{v}, \mathbf{J}$) correlation for H_2 would show up in differences in lineshapes between parallel (Q-branch) and perpendicular (P or R branch) transitions. The theory behind this has been well documented elsewhere and so will not be discussed in any detail here.^{33,34,35,36,37,38}

Classically, one can calculate the expected lineshapes for pure $\mathbf{v} \parallel \mathbf{J}$ and $\mathbf{v} \perp \mathbf{J}$ using rotation matrices to project the transition dipole of the absorbing molecule onto the electric

field vector of the probe light. The classical Doppler profiles for both a Q branch and a P or R branch transition where $\mathbf{v} \parallel \mathbf{J}$ and $\beta=0$ are shown in Figure 8. These were calculated for a single product velocity according to Hall et. al.³³ However, this analysis is only good in the high J limit ($J > 7$) where the H_2 can be thought of as a rigid rotor. For H_2 formed in a low J state quantum effects become quite important and one must take into account the projection of the rotational angular momentum vector along the electric field vector axis, m_J . A series of lineshapes for $J=1$ to 9 for both a Q-branch and a R-branch transition resulting from pure $\mathbf{v} \parallel \mathbf{J}$ correlation are also shown in Figure 8. These were calculated using a quantum mechanical formulation given by Hall et. al.³³

A series of Doppler profiles for H_2 product formed in the $v''=0$ state from the photodissociation of 1,4-CHDN is shown in Figure 9. Figure 9A shows a R(3), a P(7) and a P(9) transition while in 9B is shown a Q(3), a Q(5) and a Q(9) transition. The fitting was done in the same manner as described in section III(B). The data presented in Figure 9 was taken under slightly different conditions than the previous data. The dissociation laser was the excimer laser (discussed above) and it was aligned counter propagating to the probe beam with a spot size of 3mm diameter. The dissociation laser was unpolarized and the pump/probe timing was 20ns. A direct comparison of the P and Q-branch transitions for $J''=9$ is shown in Figure 10.

This data fits well with the interpretation of having $\mathbf{v} \parallel \mathbf{J}$

for H_2 in the $v''=0$ state. The Q-branch transition lineshapes are rounded, with the roundness becoming much more pronounced as J increases, while the P and R-branch lineshapes are much more square. However, the anisotropy is not as pronounced as is predicted by the quantum mechanical calculations. Two reasons for this are that the spread in the H_2 velocities tends to "wash out" any features in the Doppler profile and, perhaps most importantly, the $(\mathbf{v}, \mathbf{J})$ correlation is not perfect.

In the previous communication regarding this experiment¹⁴ the R(3) transition had a more pronounced dip. We feel that this might have been caused by too long of a delay between the photolysis and probe laser ($>100\text{ns}$). This effect, reported previously as velocity aligned Doppler spectroscopy (VADS),³⁹ is a result of product with zero Doppler shift (where the velocity vector is aligned perpendicular to the probe beam) flying out of the probe region and thus being discriminated against. Since the Q(3) transition did not exhibit the same effect this means that the interpretation of having a $(\mathbf{v}, \mathbf{J})$ correlation with $\mathbf{v} \parallel \mathbf{J}$ is still valid but that the correlation is just not as strong.

From this data we conclude that the H_2 comes away from the transition state with a "helicopter" type motion, albeit a wobbly helicopter. A cartoon of a critical configuration that would lead to this type of motion is shown in Figure 11. This is the first known observation of this type of correlation for H_2 .

There was no conclusive evidence of any $(\mathbf{v}, \mathbf{J})$ correlation for H_2 generated in higher vibrational states. Unfortunately it

was not possible to measure any Q-branch transitions for states with $v'' > 0$ although many attempts were made. One possible explanation is that the transition states leading to vibrationally excited H_2 are significantly enough distorted to destroy any correlation or, at least, to wash it out to the point where we were not able to detect it.

IV. SUMMARY

The analysis of product quantum state and translational energy distributions can be a powerful tool for investigation of the transition state region of any reactive process. In the case of the photodissociation of 1,4-cyclohexadiene to form H_2 and benzene the characterization of the H_2 product in this way is particularly illuminating. The H_2 vibrational and rotational energy distributions indicate a tight and symmetric transition state which is supported by theoretical calculations. The distribution of H_2 translational energy both over a given rovibrational state and over all the populated quantum states confirms the concerted and synchronous nature of the dissociation process and the dominance of the potential energy barrier to the release of the translational energy of the H_2 product. Further information has also been derived from a correlation between the velocity and rotational angular momentum vectors of the H_2 product indicating that the H_2 moves away from the transition state complex with a helicopter type motion.

In conjunction with the angularly resolved photofragment translational energy measurements of the photodissociation of 1,4-CHDN, which provide a "global" picture of the reaction process, the results described above give a nearly complete picture of the H_2 elimination in this unimolecular decomposition. It is beyond the scope of these experiments to fill in the missing part, the internal energy distribution of the benzene fragment. It should be possible for future experiments to distinguish for a given reaction H_2 product from different reactive pathways as long as there is enough difference in either translational, rotational or vibration energy.

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FIGURE CAPTIONS

Figure 1. Schematic of the experimental set-up for the detection of H_2 product from the dissociation of 1,4-CHDN. SBPMT=Solarblind photomultiplier tube, EMT=Electron multiplier tube.

Figure 2. Side view of the interaction region. The arrows indicate the polarizations of the various laser beams which propagate perpendicular to the page. The photolysis (212nm) and ionizing (uv) beams are polarized vertically while the vuv polarization can be vertical or horizontal depending on the four-wave mixing scheme used.

Figure 3. Vibrational state distribution of H_2 product from the photodissociation of 1,4-CHDN at 212nm. The solid bars are the experimental data points while the hatched bars are the statistical fit.

Figure 4. Rotational state distributions of H_2 product from the photodissociation of 1,4-CHDN at 212nm for the vibrational levels $v''=0$ through $v''=3$. The solid bars are the experimental data points while the hatched bars are the statistical fits.

Figure 5. Variation of the translational energy with vibrational level of H_2 product from the photodissociation of 1,4-CHDN at 212nm. Bottom Trace (■): H_2 B-X (1,1) R(1) transition

($v_D=2.70\text{cm}^{-1}$, $v(0)=87,358.60\text{cm}^{-1}$, $E_{tr}=20.6\text{Kcal/mole}$). Middle Trace (+): H_2 B-X (2,2) R(1) transition ($v_D=2.63\text{cm}^{-1}$, $v(0)=84,714.92\text{cm}^{-1}$, $E_{tr}=20.7\text{Kcal/mole}$). Top Trace ($\diamond$): H_2 B-X (5,3) R(1) transition ($v_D=2.51\text{cm}^{-1}$, $v(0)=84,652.91\text{cm}^{-1}$, $E_{tr}=18.9\text{Kcal/mole}$). The theoretical fits were calculated using a non-linear least squares fit to the function $1/v_D(1+\beta P_2(\cos\theta)P_2(\chi))$ (where v_D =Doppler shift) given in Ref. 33.

Fig. 6: Potential energy diagram for the isomerization and H_2 elimination reactions of 1,4-CHDN.

Fig. 7: Appearance of H_2 product from the photodissociation of 1,4-CHDN and 1,3-CHDN as a function of the delay between the photolysis and probe lasers. The rate constants obtained are: $k_1=0.06\text{ns}^{-1}$, $k_2=0.5\text{ns}^{-1}$, $k_3=0.001\text{ns}^{-1}$, $k_4=0.06\text{ns}^{-1}$.

Figure 8. Calculated lineshapes for $\mathbf{v} \parallel \mathbf{J}$ according to Ref. 33 for H_2 C $\leftarrow$ X transition when $J''=1$, $J''=3$, $J''=5$, $J''=9$, and the classical limit ($J''=\infty$). The $\parallel$ transition (Q-branch) lineshapes are shown in 8A and the $\perp$ transition (R-branch) lineshapes are shown in 8B.

Figure 9. Measured Doppler profiles showing variation of lineshapes with increasing J'' quantum number. 9A Bottom Trace ($\diamond$): H_2 C $\leftarrow$ X (1,0) Q(3) ($\beta=0.19$, $\gamma=3.33\text{cm}^{-1}$, $v(0)=101,037.63\text{cm}^{-1}$); Middle Trace (Δ): H_2 C $\leftarrow$ X (2,0) Q(5) ($\beta=0.35$, $\gamma=3.30\text{cm}^{-1}$,

$\nu(0)=100,509.99\text{cm}^{-1}$); Top Trace (+): $\text{H}_2 \text{C} \leftarrow \text{X}$ (2,0) Q(9) ($\beta=0.65$, $\nu_D=3.50\text{cm}^{-1}$, $\nu(0)=100,898.40\text{cm}^{-1}$) transitions. 9B Bottom Trace (■): $\text{H}_2 \text{C} \leftarrow \text{X}$ (1,0) R(3) ($\beta=-0.06$, $\nu_D=3.30\text{cm}^{-1}$, $\nu(0)=101,270.95\text{cm}^{-1}$); Middle Trace (+): $\text{H}_2 \text{C} \leftarrow \text{X}$ (2,0) P(7) ($\beta=-0.15$, $\nu_D=3.24\text{cm}^{-1}$, $\nu(0) = 101,531.22\text{cm}^{-1}$); Top Trace (□): $\text{H}_2 \text{C} \leftarrow \text{X}$ (3,0) P(9) ($\beta=-0.13$, $\nu_D=3.65\text{cm}^{-1}$, $\nu(0)=102,447.60\text{cm}^{-1}$) transitions.

Figure 10: Comparison of the $\text{H}_2 \text{C} \leftarrow \text{X}$ (3,0) P(9) (top trace: ■) and (2,0) Q(9) (bottom trace: +) transitions shown in Figure 9.

Fig. 11: Cartoon of H_2 elimination from 1,4-CHDN showing a side and a top view of the transition state region and the helicopter motion of H_2 product.

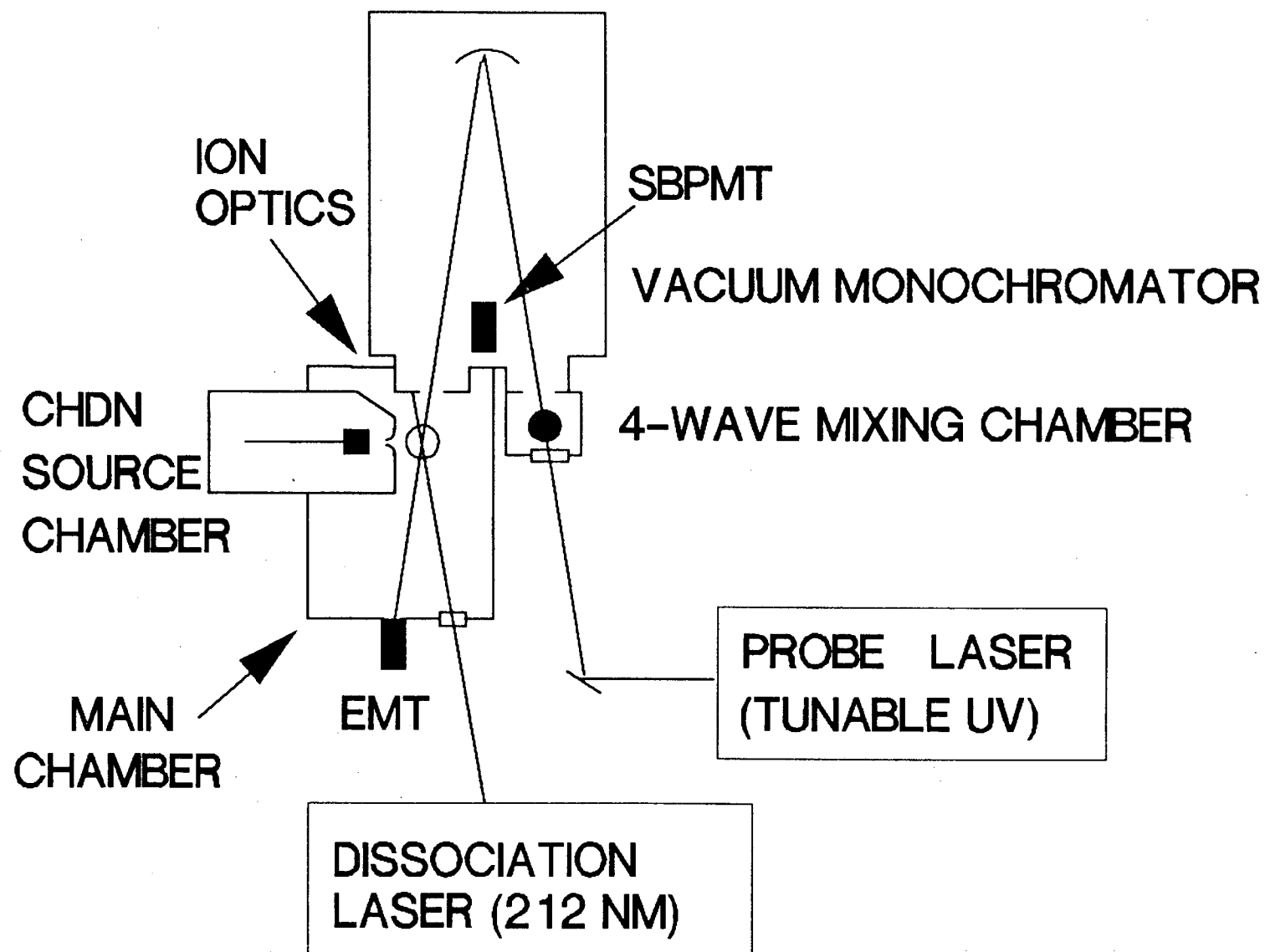


Figure 1

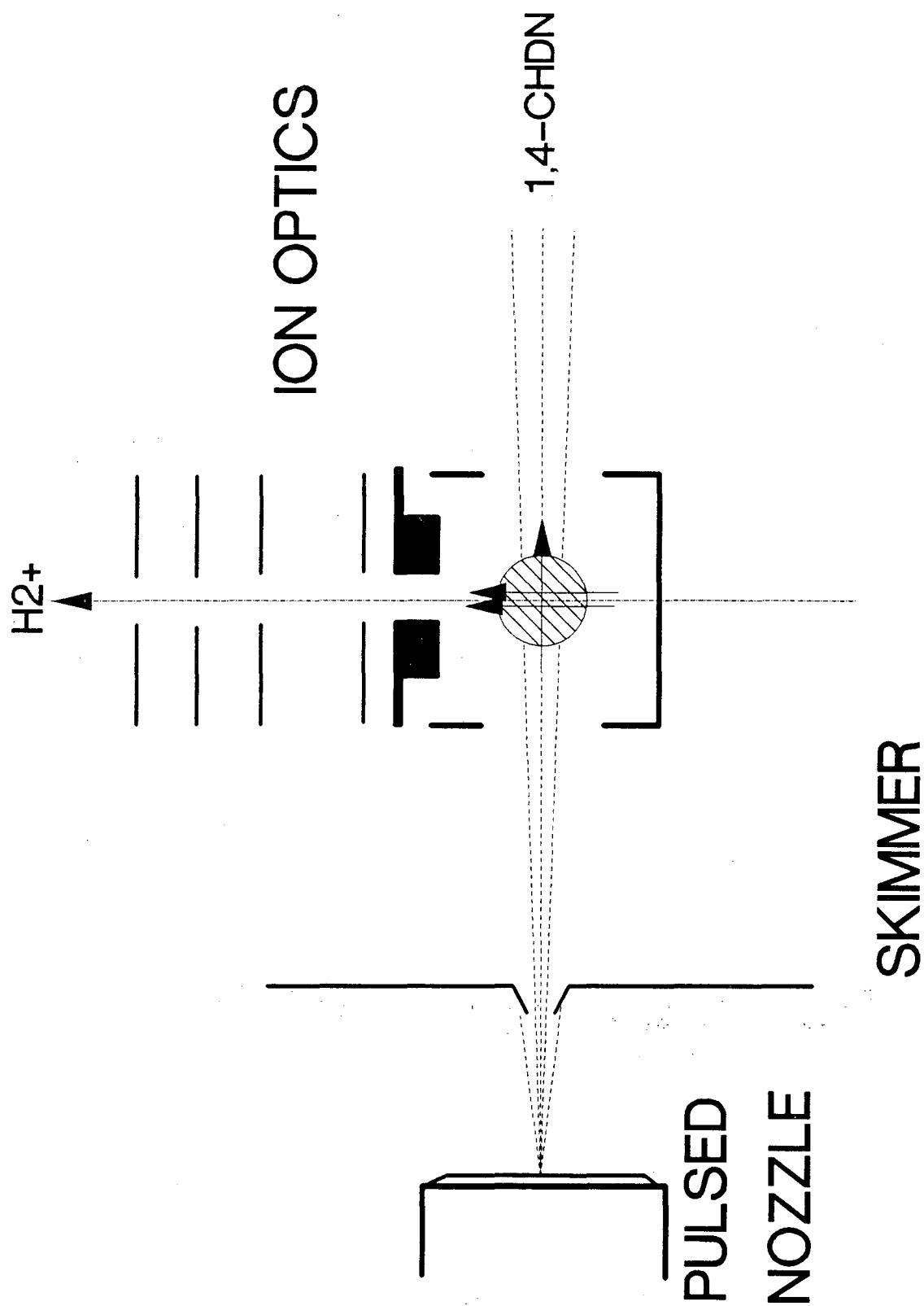


Figure 2

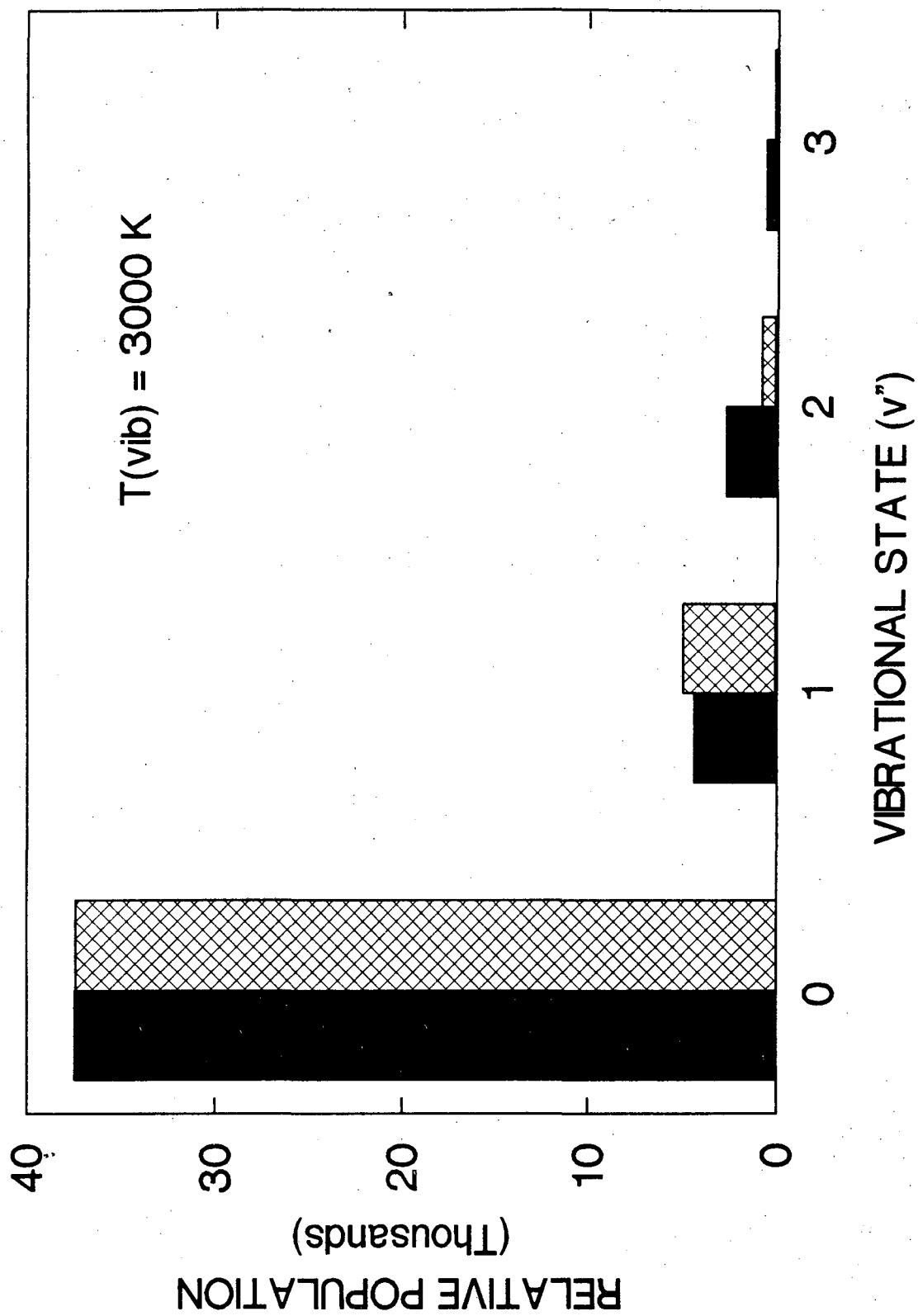


Figure 3

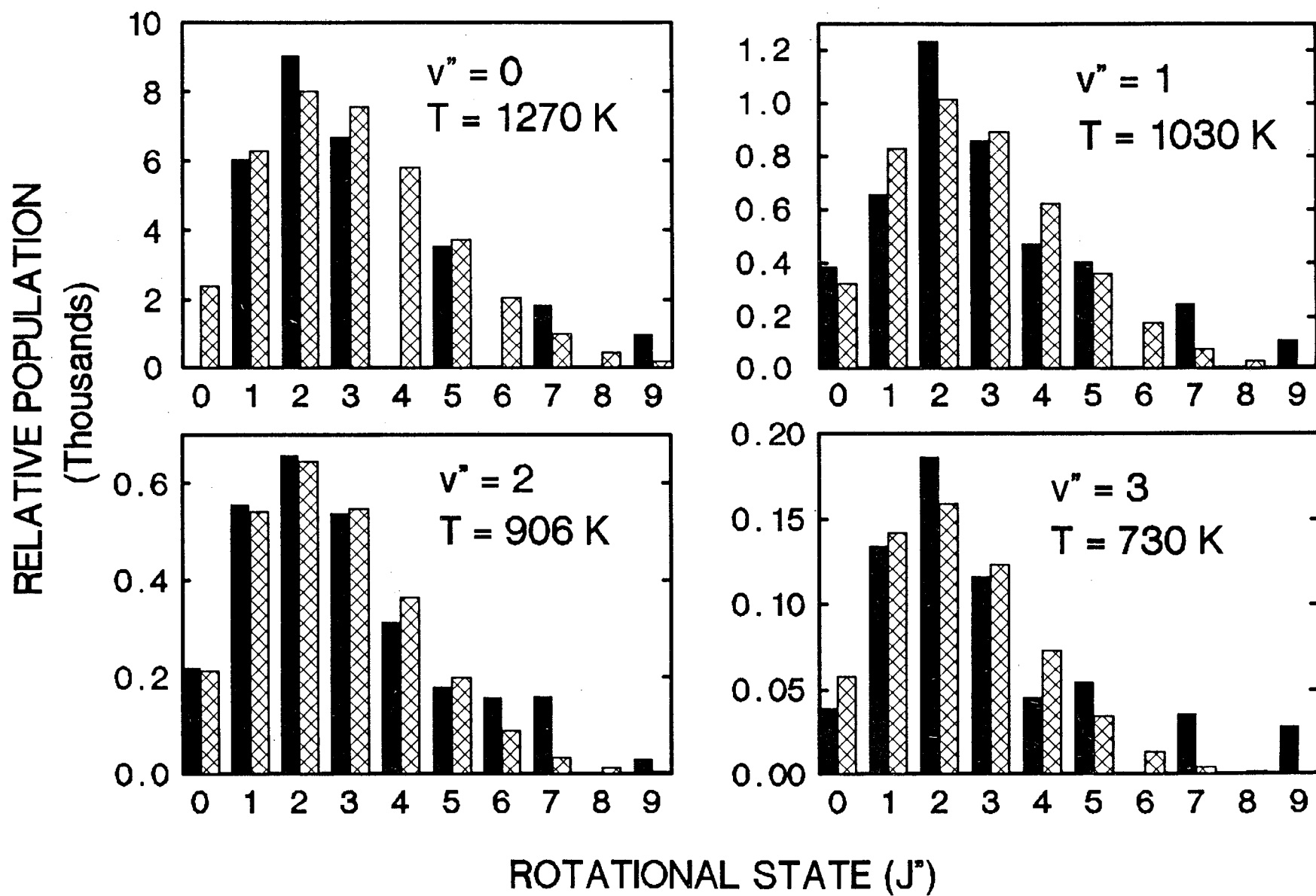


Figure 4

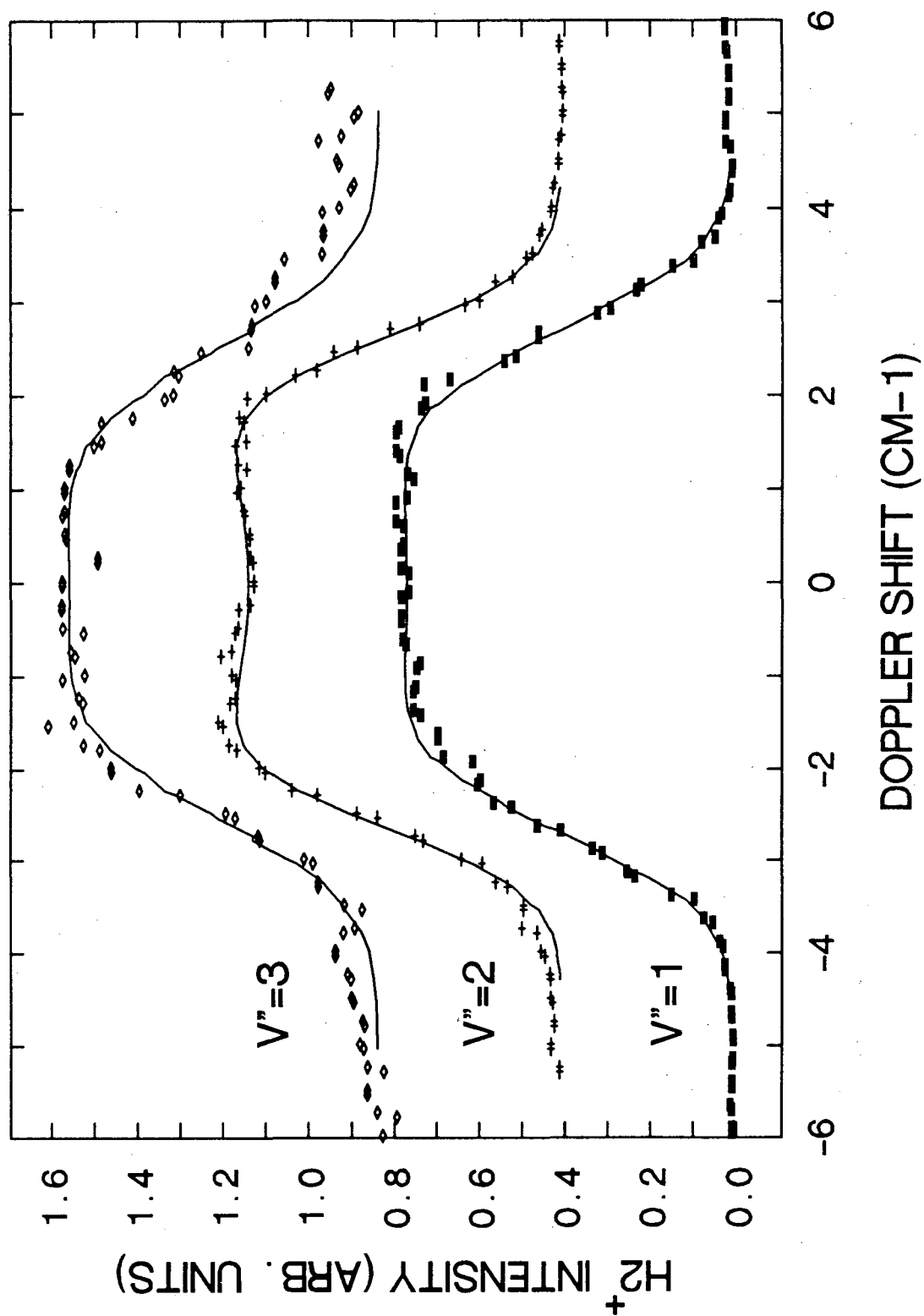


Figure 5

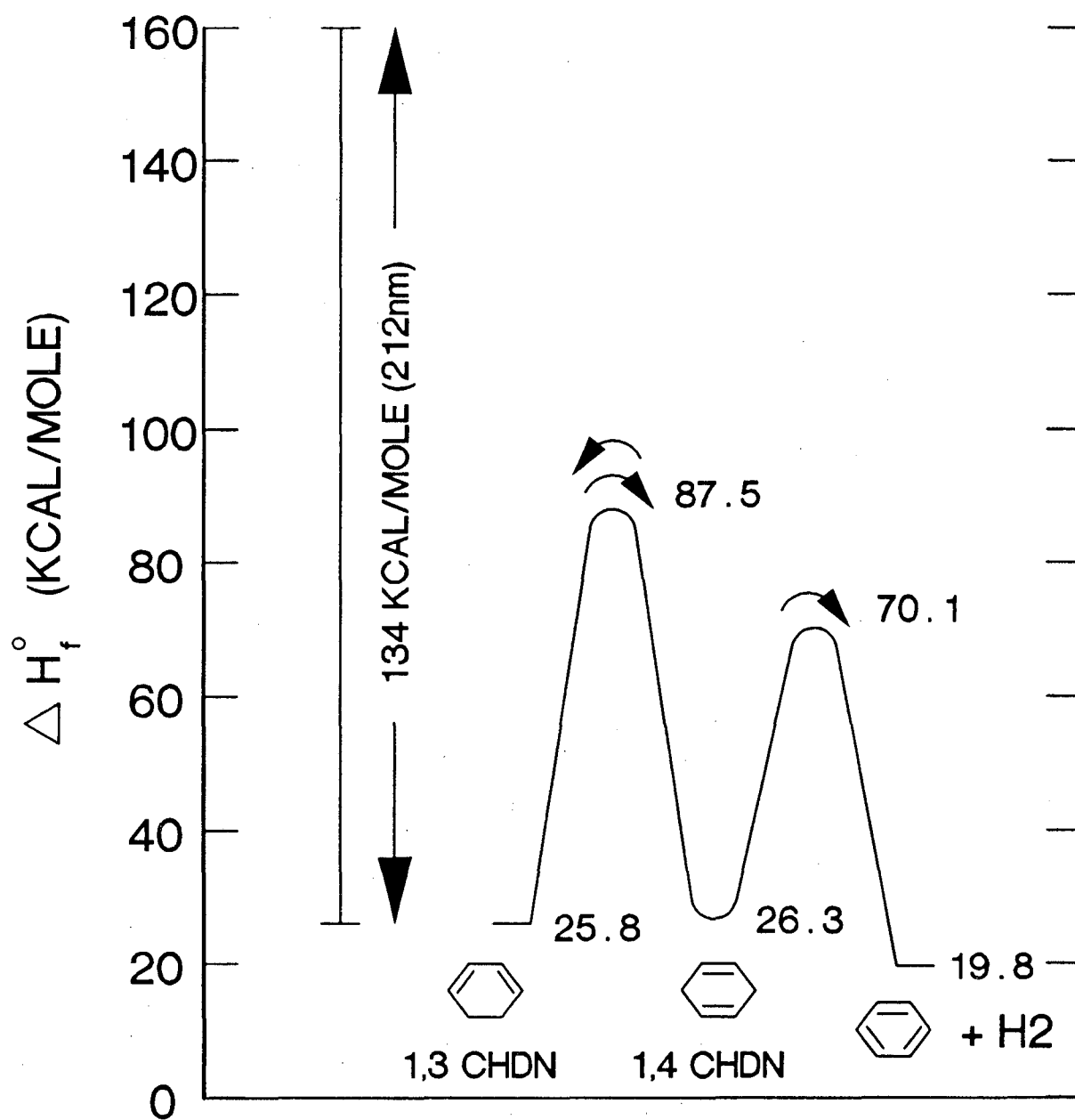


Figure 6

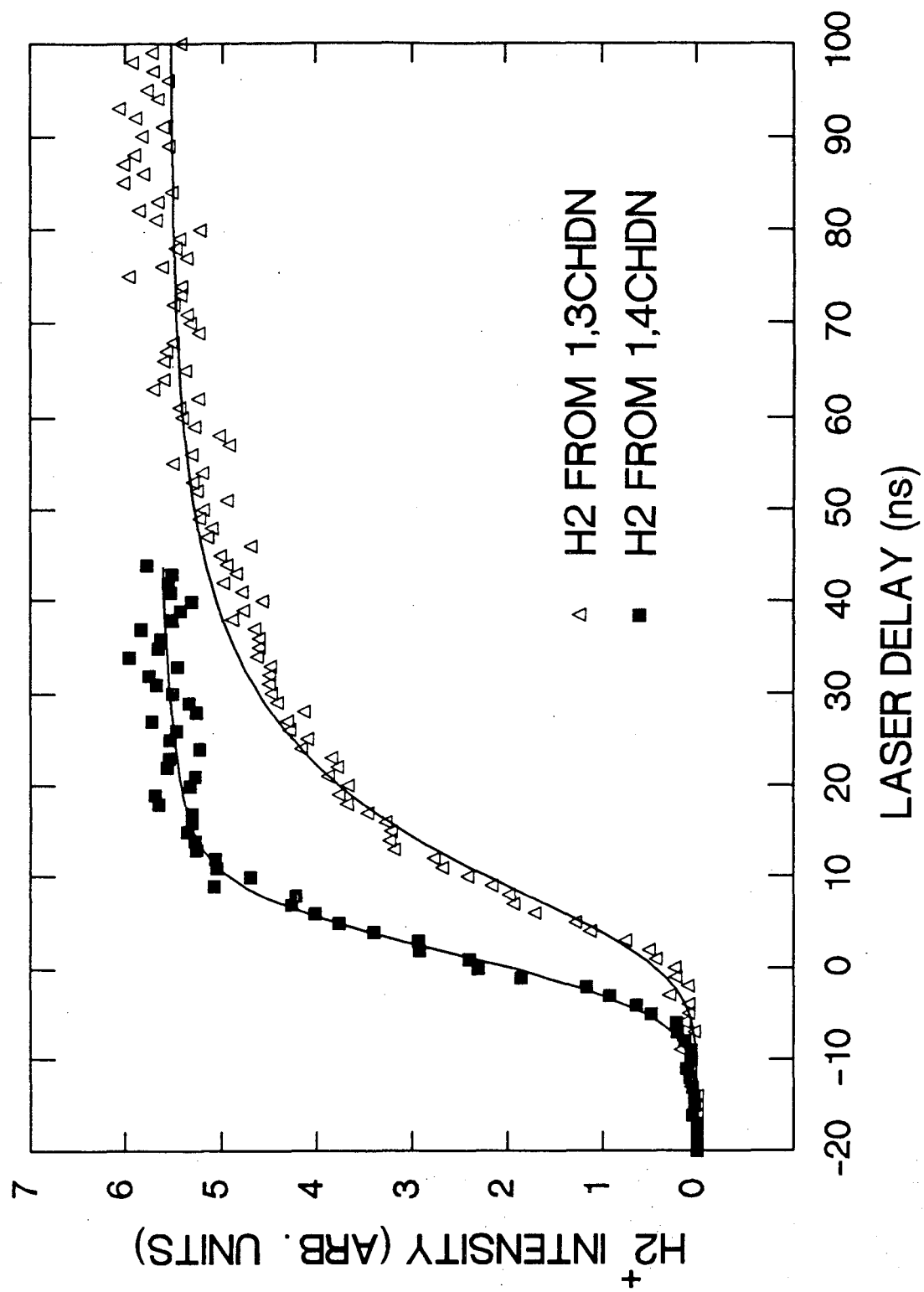


Figure 7

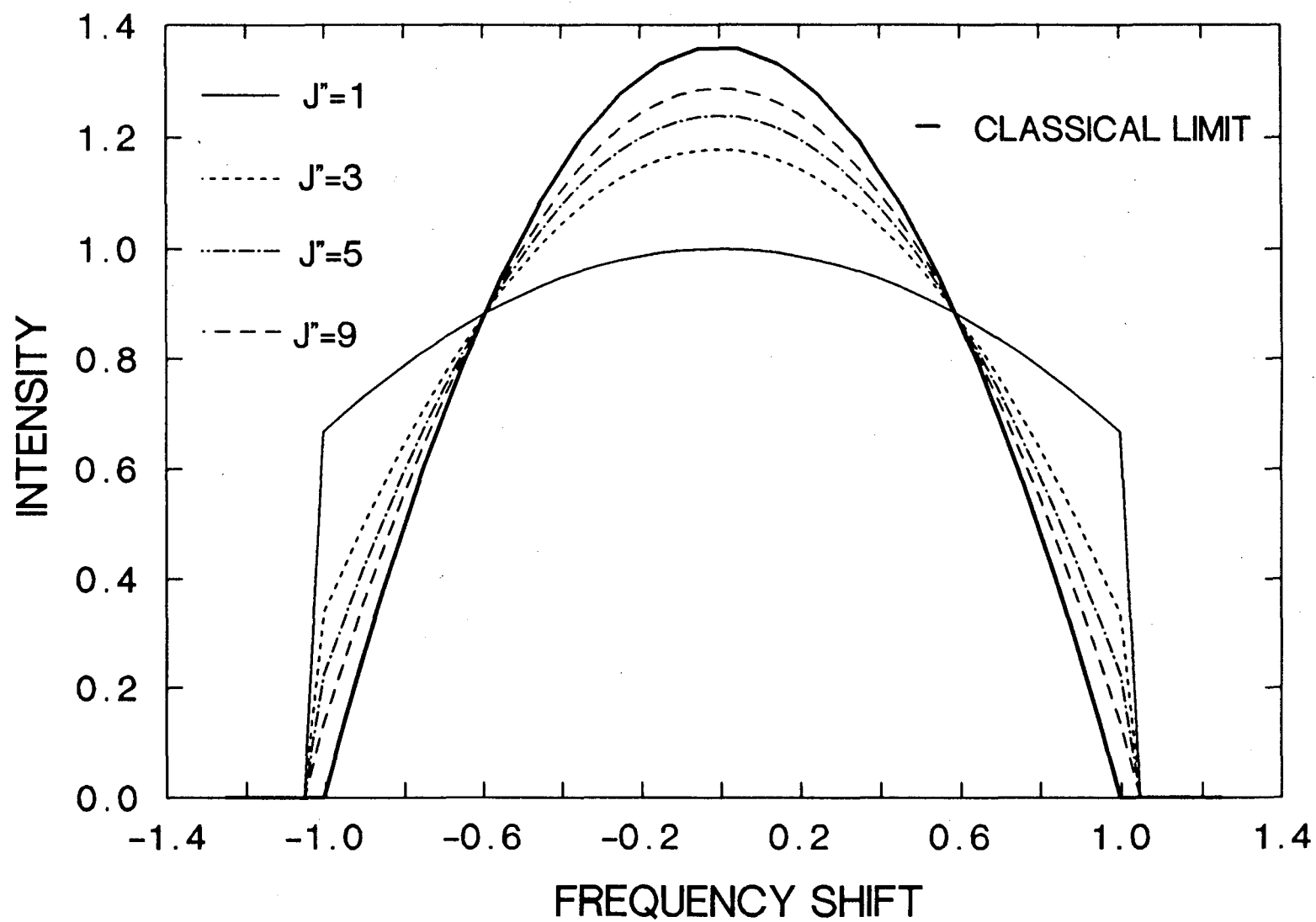


Figure 8(a)

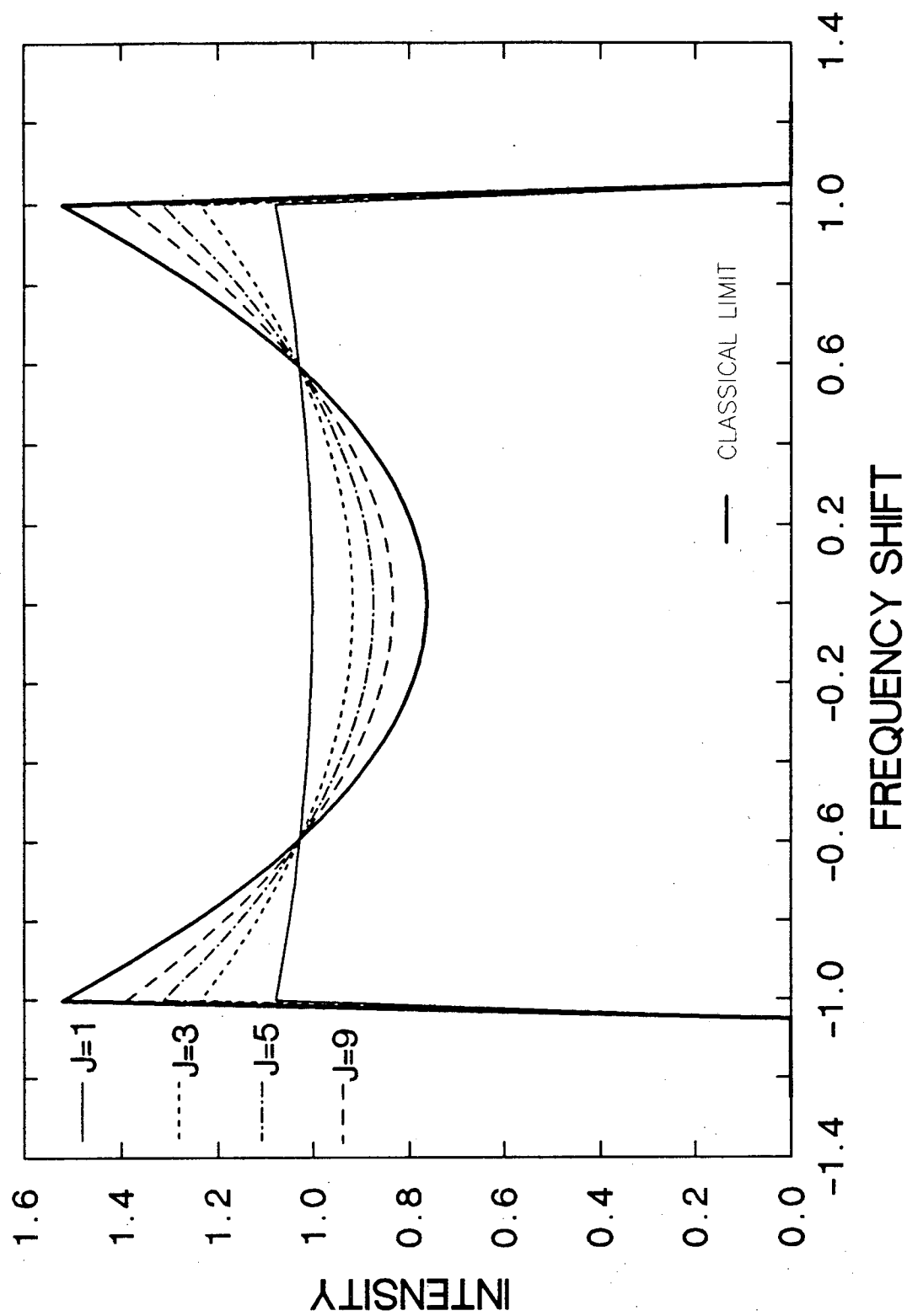


Figure 8 (b)

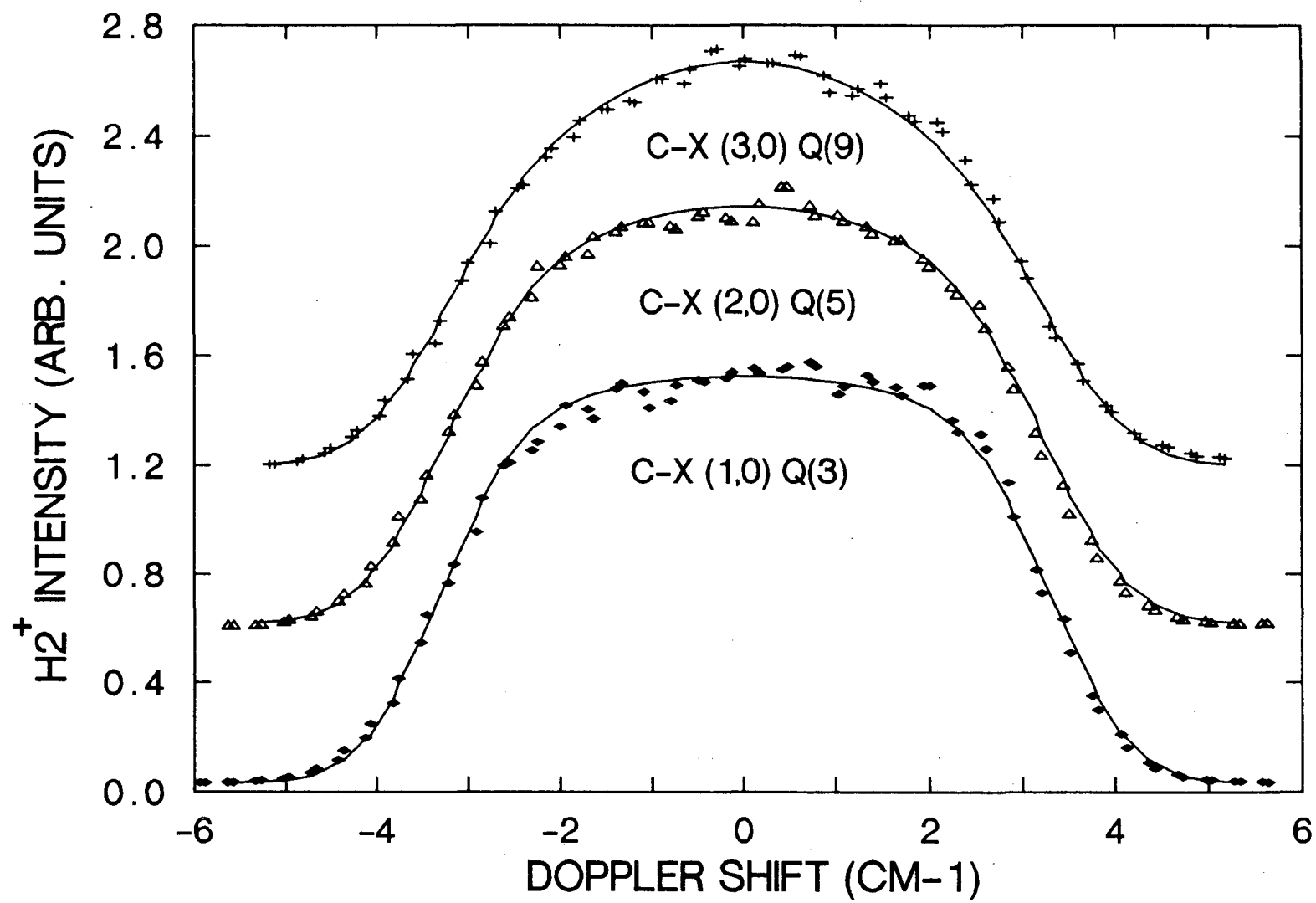


Figure 9(a)

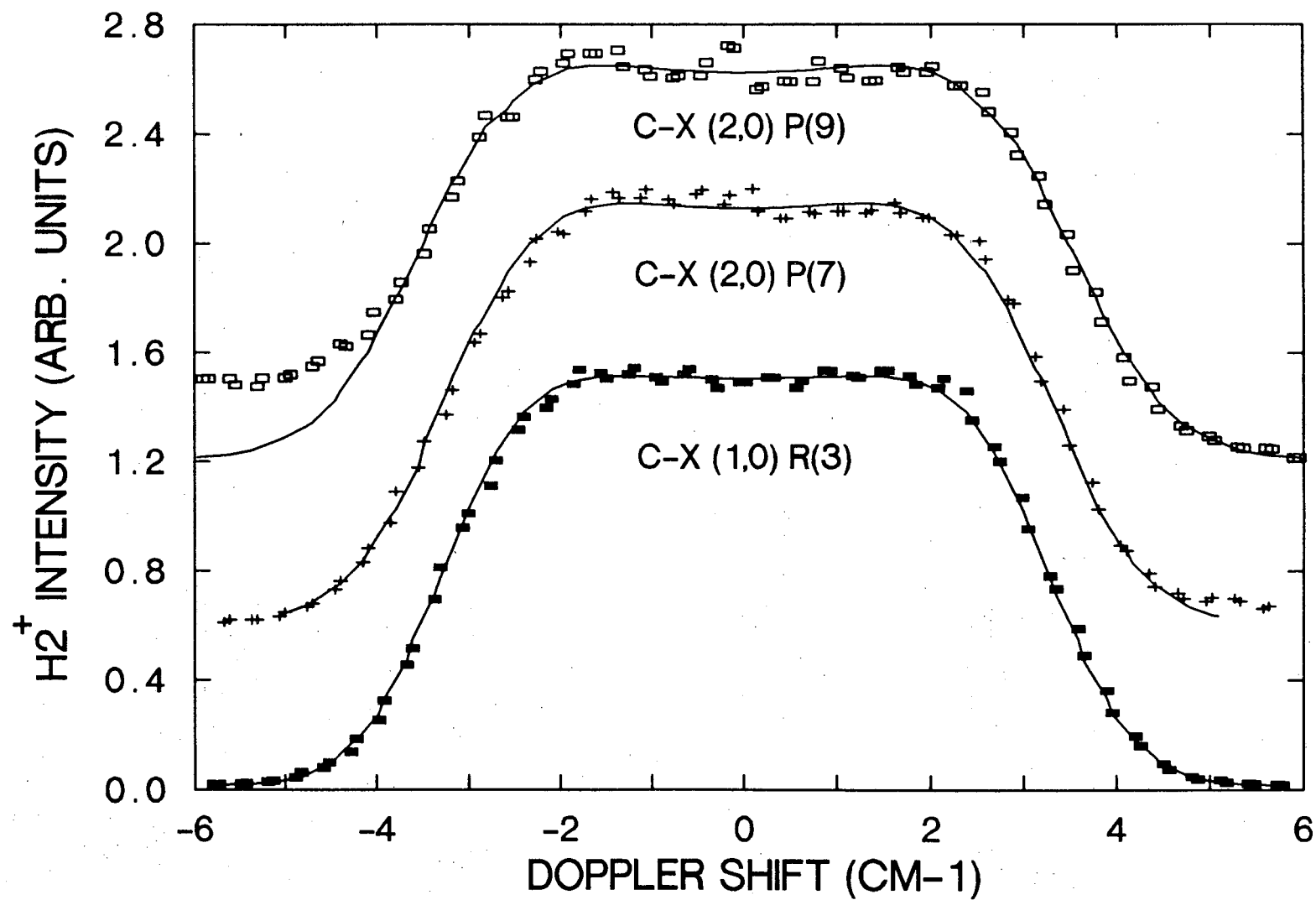


Figure 9(b)

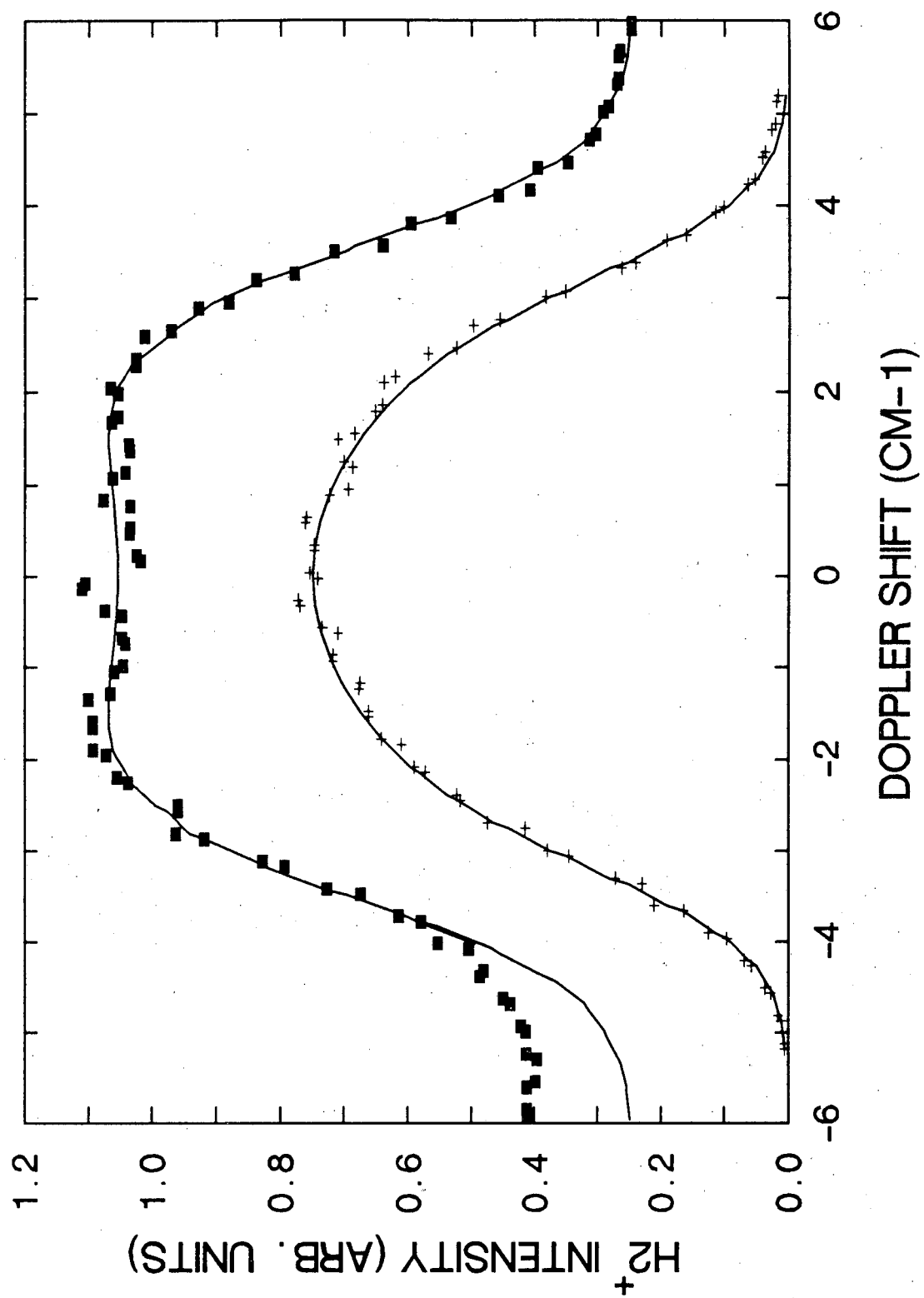


Figure 10

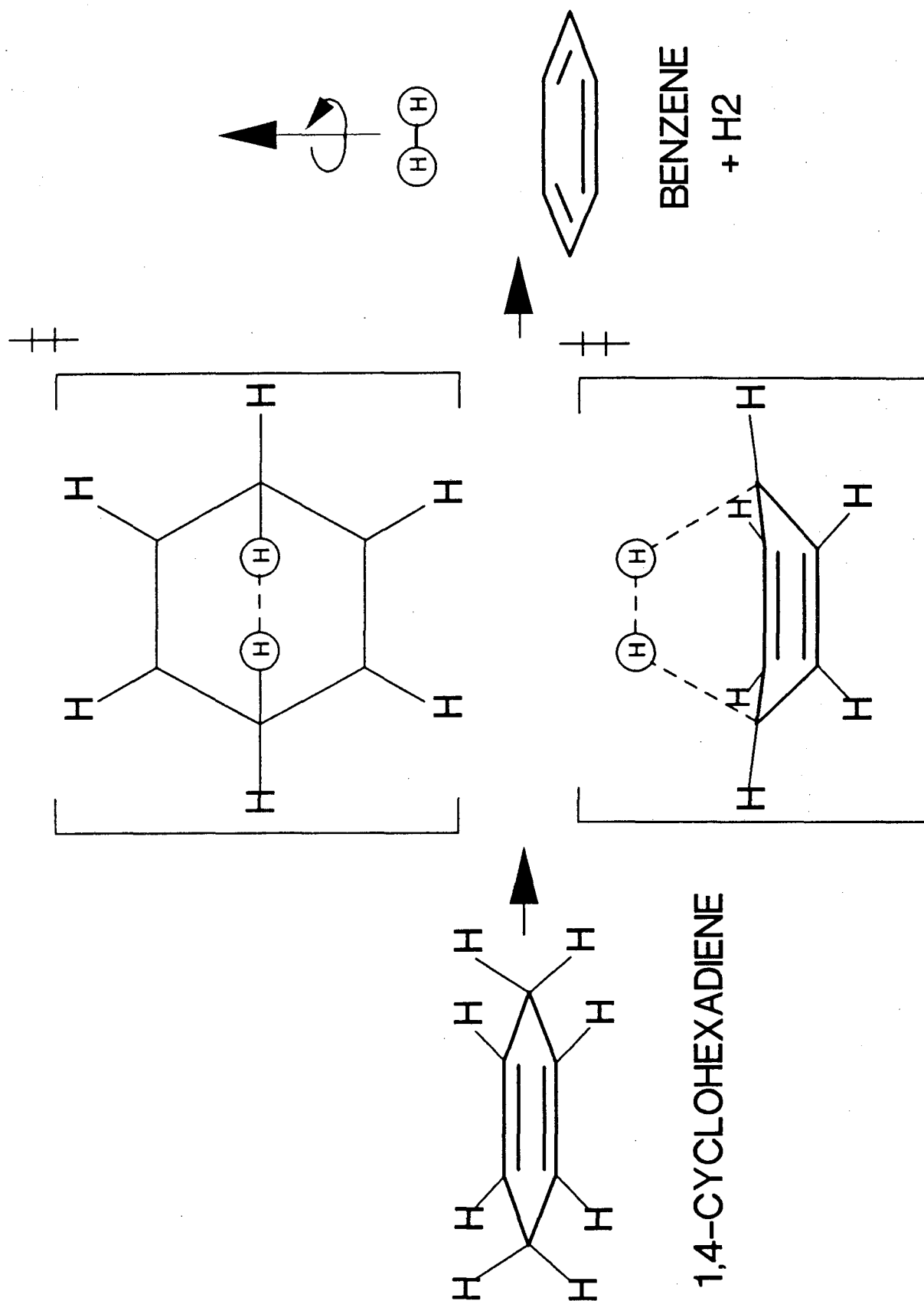


Figure 11

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