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State-to-state dynamics of H + HX collisions. I. The $H + HX \rightarrow H_2 + X$ (X=CI,Br,I) abstraction reactions at 1.6 eV collision energy

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The rotational and vibrational state distributions of the H₂ product from the reactions of translationally excited H atoms with HCl, HBr, and HI at 1.6 eV are probed by coherent anti-Stokes Raman scattering spectroscopy after only one collision of the fast H atom. Despite the high collision energy, only the very excergic ($\Delta H = -1.4 \text{ eV}$) hydrogen atom abstraction involving HI leads to appreciable H_2 product vibrational excitation. For this reaction the H_2 vibrational distribution is strongly inverted and peaks in v' = 1, with 25% of the total available energy partitioned to vibration. For the mildy excergic ($\Delta H = -0.72 \text{ eV}$) reaction with HBr and the nearly thermoneutral ($\Delta H = -0.05 \text{ eV}$) reaction with HCl, very little energy appears in H₂ vibration, 9% and 2%, respectively, and the vibrational state distributions peak at v' = 0. However, in all three reactions a significant fraction, 18% to 21%, of the total energy available appears as H₂ rotation. All three reactions show a strong propensity to conserve the translational energy, that is the translational energy of the $H_2 + X$ products is very nearly the same as that of the H + HX reactants. For the reactions with HCl, HBr, and HI the average translational energy of the products is 1.3, 1.7, and 1.7 eV, respectively, and the width of the translational energy distribution is only about 0.5 eV full width at half maximum. The energy disposal in all three reactions is quite specific, despite the fact that this high collision energy is well above the barrier to reaction in all three systems and a large number of product quantum states are energetically accessible. Only a few of these energetically allowed final states are appreciably populated. Although detailed theoretical calculations will be required to account completely for the state specifity, quite simple models of the reaction dynamics can explain much of the dynamical bias that we observe.

I. INTRODUCTION

The dynamics of all chemical reactions are governed by the nature of the potential energy surface, that is energy effects, and by kinematics, that is mass-related effects. Complete separation of the kinematic and potential energy surface constraints on the collision dynamics is not possible, even in principle. However, some resolution of the different influence of these two factors is desirable, for it should help us understand better the collision dynamics. The homologous series of hydrogen atom abstraction reactions

$$\mathbf{H}' + \mathbf{H}\mathbf{X}(v, J) \to \mathbf{H}'\mathbf{H}(v', J') + \mathbf{X}$$
(1)

(where X = F,Cl,Br, and I) provides an opportunity for such a resolution. Because the H and H₂ masses are much smaller than the mass of any of the halogen atoms, X, the kinematics of these abstraction reactions are essentially independent of the identity of X. The reduced masses of the reactants (products) are 0.95 (1.81), 0.97 (1.89), 0.99 (1.95), and 0.99 (1.97), for the H + HF, H + HCl, H + HBr, and H + HI systems, respectively. Although effectively constant over this homologous series, kinematic effects should still be important in the dynamics of these hydrogen atom abstraction reactions, because of the extreme light–light–heavy mass combination.

While the kinematics in this series of reactions do not depend on the identity of the halogen, quite the opposite is true for the potential energy surface. The large change in bond energy over this series of hydrogen halides dictates that the thermochemistry and the potential energy surfaces vary significantly with the identity of the halogen atom. Table I summarizes the variation in the thermochemistry over this series of reactions, and the influence of that thermochemistry on the reaction barrier heights. The latter are taken from the DIM-3C potential energy surfaces of Baer and Last.¹ These hydrogen atom abstraction reactions vary from highly endoergic with high barrier in the case of H + HF to highly excergic with negligible barrier in the case of H + HI. The large change in barrier height is accompanied by the expected large variation in the geometry at the saddle point. Table II gives the HHX bond lengths at the collinear saddle point, and the differences between these bond lengths and the equilibrium bond lengths in HX and H₂. While the minimum energy path for the abstraction channel is predicted to occur for collinear geometries for all HX, the bend potentials are quite different. The bend potential for HHF is quite steep

TABLE I. Energetics of the $H' + HX \rightarrow H'H + X$ reactions. All energies are given in eV.

Hydrogen halide	ΔH	$E_b(\theta = 180^\circ)^a$	$\langle E_b(\theta)\sin\theta\rangle^b$	
HF	1.39	1.42	1.96	
HCI	- 0.05	0.22	0.86	
HBr	- 0.72	0.08	0.53	
HI	- 1.42	0.03	0.30	

* Collinear barrier heights from Ref. 1.

^b Weighted average of the barrier height over the range $\theta = 180^{\circ}$ to $\theta = 90^{\circ}$, data from Ref. 1.

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Hydrogen halide	<i>r</i> (H–H) ^a	r(H–X) ^a	$\Delta r(H-H)^{b}$	$\Delta r(H-X)^{b}$
HF	0.78	1.64	0.04	0.72
HCl	1.02	1.39	0.28	0.12
HBr	1.39	1.43	0.65	0.02
HI	1.70	1.61	0.96	0.00

TABLE II. Saddle point geometries for the $H' + HX \rightarrow H'H + X$ reactions. All distances are given in Å.

*Saddle point bond lengths from Ref. 1.

^b Saddle point bond lengths minus the equilibrium bond length of the diatom, using the equilibrium bond lengths from Ref. 2.

(i.e., reaction is strongly favored for collinear geometry) while the bend for HHI is quite shallow (i.e., the barrier height increases slowly as the HHI angle is reduced from 180°).

A complex interplay of the energetic and kinematic constraints controls the dynamics of these reactions and determines the resultant v', J' product state distributions, so even very detailed state-to-state measurements on a single H + HX system might not suffice to resolve the individual roles of these factors. An integrated study of the state-tostate dynamics of the homologous series H + HF, HCl, HBr, HI would greatly facilitate the elaboration and resolution of these interconnected constraints, and such an integrated study is the subject of this report. We describe here an dynamics study the of the experimental of $H + HX \rightarrow H_2 + X$ reactions at 1.6 eV collision energy, for X = Cl, Br, and I. The H + HF reaction is omitted from our investigation because the barrier for this reaction is very high, 1.42 eV in collinear geometry and higher for noncollinear approach (Table I), and the location of the barrier far in the exit channel makes reactant translation ineffective in surmounting this barrier.

Fast H atoms are generated by pulsed-laser photolysis of HI. Vibrational and rotational state distributions are determined for the H_2 reaction product by time-resolved coherent anti-Stokes Raman scattering (CARS) spectroscopy. The conditions of the experiments are such that the product distributions are probed by CARS spectroscopy after only one collision of the fast H atom, and before any relaxation of the H_2 product state distribution can occur. The "universal" detection capabilities of CARS spectroscopy also make it possible to determine absolute partial and total cross sections for the reactions, since using CARS we can measure directly the concentrations of both the reactant and the product diatoms, and indirectly the concentration of the H atom reactant from the difference of CARS spectra of the H atom precursor, HI, with and without photolysis.

These product state distributions and reaction cross sections reveal $H + HX \rightarrow H_2 + X$ reaction dynamics that vary systematically in response to the changes in the potential energy surface that accompany a change in the identity of the halogen X. However, our measurements also show features that are invariant to the identity of the halogen. These reflect the kinematic factors that are invariant in this homologous series. The product vibrational state distributions change the most with various of X, in response to the changing exoergicity of the reaction. The most exoergic reaction, with HI, produces the largest energy, as well as the largest fraction of the available energy, in product vibration. Reactant translation is inefficiently transferred to product vibration in all cases. The product translational distributions are nearly independent of the identity of X, and there is a strong propensity for converting reactant translation to product translation. While the average fraction of the available energy that appears as product rotation is nearly the same for all three reactions, the detailed rotational state distributions of the H₂ product are quite distinctive.

While the level of detail provided by these experiments calls for correspondingly detailed theoretical descriptions and computational simulations, we find that a relatively simple model of the $H + HX \rightarrow H_2 + X$ reaction can account for many of the features we observe in the state-to-state dynamics. Both kinematic and potential energy surface factors are important constraints on the reaction dynamics, and both play a role in determining the product quantum state distributions.

II. EXPERIMENT

Coherent anti-Stokes Raman scattering spectroscopy is used to probe the initial H_2 product quantum state distributions created by H + HX (X = Cl, Br, I) $\rightarrow H_2 + X$ reaction, upon generation of monoenergetic H atoms by UV laser photolysis of HI. A schematic of the apparatus is shown in Fig. 1. The application of CARS to the study of fast H atom reactions has been discussed extensively in Refs. 3–6, and only a brief description of the experiment is given here. The reader is referred to these publications for more details.

All optical wavelengths used in the experiment are derived from a single Nd:YAG laser (Spectra-Physics DCR-2A). The 1064 nm fundamental of the laser is frequency doubled to produce 532 nm light, giving ~350 mJ, 6-ns, FWHM pulses at 10 pulses-per-second, with a linewidth of about 0.20 cm⁻¹. Two spatially and temporally overlapped laser beams are required to excite a Raman transition via CARS⁷—these are commonly known as the pump (ω_p) and Stokes (ω_s) beams. In the present experiment ω_p is derived by splitting off a portion of the 532 nm beam and using this light directly. The Stokes beam is obtained by using some of the 532 nm laser output to pump a tunable dye laser (Spectra-Physics PDL-2). The ω_p and ω_s beams are expanded by



FIG. 1. Schematic diagram of the experimental apparatus used in these experiments.

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telescopes and collinearly combined at a dichroic mirror. The resultant spatially overlapped beams are focused into the reaction cell. The ω_p and ω_s pulse energies are typically 25 and 15 mJ, respectively. The photolysis beam (ω_{diss}) is derived by passing a portion of the 532 nm beam through a frequency doubler (Spectra-Physics WEX-1). The resultant 266 nm beam is collinearly combined with the CARS beams at a second dichroic mirror and focused directly into the reaction cell. The photolysis pulse energy is 5–15 mJ. A 3.5 ± 0.4 ns delay between the photolysis pulse (ω_{diss}) and the probe pulses (ω_p and ω_s) is set by adjusting an optical delay line.

The beams exiting the reaction cell consist of the photolysis and the CARS probe input beams, as well as the anti-Stokes (ω_{as}) signal beam; $\omega_{as} = 2\omega_p - \omega_s$. Appropriate bandpass filters are used to reject the ω_{diss} , ω_p , and ω_s frequencies so that only the anti-Stokes beam enters the monochromator. A photomultiplier tube (RCA 1P28) is located at the exit slit of the monochromator to detect the anti-Stokes signal. The signal from the PMT is processed by a boxcar integrator (SRS SR250) operated with a 10-ns gate and a 3-s time constant, and then digitized and stored in a microcomputer.

CARS spectra are recorded by tuning ω_s such that the difference frequency, $\omega_p - \omega_s$, scans through the vibrational Q-branch Raman transitions of the H₂ reaction product. Several quickly scanned spectra are averaged to yield those that ultimately are analyzed to obtain quantum state populations. The spectra are corrected for temporal drift in the instrument response by periodically rescanning a particular product CARS transition that serves as a reference signal. Spectra are taken at various ω_s and ω_p pulse energies to ensure that saturation effects are not present.

The reaction cell is an open-ended glass tube (0.3 cm i.d. by 4.0 cm long) fitted with gas sample inlet and outlet ports. This reaction cell is suspended inside a larger tube (7.5 cm i.d. by 125 cm long). The ends of the larger tube are closed by quartz windows, and are fitted with feedthroughs for delivering a buffer gas. The buffer serves to restrict the sample gas to the small volume of the reaction cell. For study of the H + HI reaction the experiments are performed at a total pressure of 10 Torr, consisting of 5 Torr of HI (Ashland Scientific Gas Co., 99.8% Technical Grade), which serves both as a source of fast H atoms and as a reactant, and 5 Torr of Ar buffer gas. For the H + HBr and H + HCl experiments we use 1.5 to 2.5 Torr of the reactant diatom, while 1 Torr of HI serves as the photolytic source of the hot H atoms. In the H + HI experiments only a relatively small fraction of the HI is photolyzed to generate the H atoms, but in the H + HBr(HCl) \rightarrow H₂ + Br(Cl) experiments we effect near total (80%) photolysis of the HI in the CARS probe volume, in order to eliminate the $H + HI \rightarrow H_2 + I$ reaction as an interference. Gas flows are set at 0.2 Torr $L s^{-1}$ to ensure that the reaction cell is swept clean between laser pulses.

Photolysis of HI at 266 nm creates H atoms with laboratory velocities of 1.75×10^6 and 1.13×10^6 cm s⁻¹ for production of I(${}^2P_{3/2}$) and I(${}^2P_{1/2}$), respectively, with quantum yields of 0.66 and 0.34, respectively.⁸ For collision with the heavy HX target the center-of-mass collision velocities are nearly identical to the H atom laboratory velocities, giving collision energies of 1.6 and 0.68 eV. The very high H + HXcollision velocities imply correspondingly high collision frequencies. For example, if the hard-sphere collision diameter for H + HI is assumed to be equivalent to that for H + Xe, 0.23 nm, $[d_{H-Xe} = d_{Xe}/2 + d_{H_2}/4, d_{Xe} = 0.34$ nm,⁹ d_{H_2} = 0.23 nm (Ref. 9)] then under the experimental conditions described above the mean time between H + HI elastic collisions is 3.0 ns for the 1.6 eV H atoms and 4.7 ns for those at 0.68 eV. Consequently, we set the delay between the photolysis and probe beams to be very short, 3.5 ± 0.4 ns, to ensure that the measured H₂ product quantum state distributions are those resulting from a single collision of the H atom with HX. Therefore, the reaction products we observe are those produced only by H atom collisions with HX at the relative energies of 1.6 and 0.68 eV. Reaction of less energetic H atoms, produced by collisional cooling, is not significant on our experimental time scale. Even though the experiments are carried out under single-collision conditions, the presence of H atoms giving two different collision energies introduces some ambiguity into the interpretation of the results. As discussed in Sec. IV, this ambiguity is largely removed by the small quantum yield for the slower H atoms and their small contribution to product formation, relative to that of the faster H atoms.

Collisional deactivation of the quantum state distributions of the H₂ products is expected to be highly unlikely on the experimental time scale used here, since the mean time between energy redistributing collisions of the products with any other molecules is much longer than the time scale of our experiments. For the H₂ product the probability of a hardsphere elastic collision with the Ar buffer gas or the unreacted HX is not negligible, but the probability of an energy redistributing collision is insignificant. For example, if all the available energy in the H + HI reaction were channeled into product translation, the mean times for collision of the H₂ product with room temperature Ar and HI would 1.7 and 2.0 ns, respectively, using hard-sphere collision diameters of 0.26 nm for $H_2 + Ar$ $[d_{H_2-Ar} = (d_{H_2} + d_{Ar})/2, d_{Ar} = 0.29 \text{ nm}, {}^9d_{H_2} = 0.23 \text{ nm} (\text{Ref. 9})]$ and 0.29 nm for shorter than the delay time between photolysis and probe pulses used in our experiment. It is unlikely, however, that the measured H₂ vibrational or rotational distributions have suffered collisional deactivation, as the cross sections for relaxation by Ar and HX are expected to be much, much smaller than gas kinetic.

We know of no measurements of state-to-state vibrational or rotational relaxation of H₂ by either Ar or HCl, HBr, and HI. However, the available experimental results for H₂-H₂ relaxation rates, which should be much greater than the relaxation rates for H₂-Ar or H₂-HX, indicate that in our experiments relaxation is highly improbable. For example, the cross section for $V \rightarrow V$ energy transfer in HD + HD collisions is only about 10^{-2} Å² for the v = 2level and falls with increasing v, while the cross section for HD + HD $V \rightarrow T$ energy transfer is less than 10^{-4} Å² for

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 $v \leq 4$.¹⁰ These cross sections imply that under the conditions of our experiments the mean time between $V \rightarrow V$ relaxing collisions should be greater than 4 000 ns and between $V \rightarrow T$ relaxing collisions greater than 400 000 ns, that is infinitely long on the 3.5 ns time scale for our measurements. The cross sections for rotational relaxation are certainly larger than the cross section for $V \rightarrow V$ energy transfer, but even these rotation-relaxing collisions are unimportant on our time scale. For example, the recent HD-HD state-to-state rotational energy transfer measurements of Chandler and Farrow¹¹ indicate that for HD J = 6 the cross section for $\Delta J = -2$ is 0.5 Å² and for $\Delta J = -4$ it is 0.03 Å². (For H₂, $\Delta J = \pm 2$ are the smallest J changes that nuclear exchange symmetry allow.) Using these cross sections as an upper limit on the cross sections for H2-Ar and H2-HX rotational relaxation we find that for our experiments the mean time between collisions giving $\Delta J = -2$ is greater than 80 ns and for $\Delta J = -4$ greater than 1 300 ns.

The strongest evidence for the absence of reactant H atom thermalization or H_2 product relaxation in the experiments described here comes from our previous measurements of the time-dependence of measured H_2 product population distributions in hot atom experiments. For example, for the HD product of $H + D_2$ collisions,³⁻⁶ we found no measurable change in the product state distributions at time delays less than 10 ns for the experimental conditions used here.



FIG. 2. CARS spectrum of H_2 from the H + HCl reaction at 1.6 eV. The measured *Q*-branch peaks for the H_2 product are shown. The v', J' quantum numbers identifying the transition are given to the right of each peak.

III. RESULTS

A. Spectra and analysis

Portions of the vibrational Q-branch CARS spectra of the H_2 product of the H + HCl, H + HBr, and H + HI reactions are shown in Figs. 2-4. The highest energetically accessible H_2 vibrational state is v' = 3 for H + HCl, v' = 5for H + HBr, and v' = 7 for H + HI. However, the highest observed vibrational states are only v' = 1, v' = 3, and v' = 4, for these three reactions. A careful inspection of Fig. 4 shows that the phase of the dispersive line shape for the peaks associated with lower J' of v' = 0 for the H₂ product from H + HI is opposite the phase of those for v' = 1, 2, and 3 and for higher J' in v' = 0. This behavior, which is explained in detail below, is indicative of a vibrational population inversion between the low J' states of v' = 0 and 1. This phase difference disappears for the rotational states with J' > 11 indicating that the population inversion is rotational state dependent. For the H_2 product of the H + HBr and H + HCl reactions the phase of the dispersive CARS line shape indicates that no population inversions are produced.

The magnitude of the CARS signal is given by⁷

$$S(\omega_{\rm as}) = \int g(\omega; \omega_{\rm as}) F_2 |\chi^{(3)}|^2 \, d\omega \,, \qquad (2)$$

where $g(\omega;\omega_{as})$ is the CARS laser line shape function, F_2 a factor determined by the CARS laser frequencies and focusing conditions $(F_2 = 4\pi^2/[1 + (2\omega_p + \omega_s)/(2\omega_p - \omega_s)]^2)$, and $\chi^{(3)}$ is the third-order susceptibility of the medium being probed. $\chi^{(3)}$ consists of three terms,

$$\chi^{(3)} = \chi^{NR} + \chi' + i\chi'' .$$
 (3)

The first term in this equation is the frequency-independent nonresonant part of $\chi^{(3)}$. The second and third terms are the frequency-dependent Raman resonance functions, which

$$H + HBr -> H_a + Br$$



FIG. 3. CARS spectrum of H_2 from the H + HBr reaction at 1.6 eV. The measured *Q*-branch peaks for the H_2 product are shown. The v', J' quantum numbers identifying the transitions are given to the right of each peak.

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FIG. 4. CARS spectrum of H_2 from the $H + HI \rightarrow H_2 + I$ reaction at 1.6 eV. The measured Q-branch peaks for the H_2 product are shown. The v',J' quantum numbers identifying the transitions are given to the right of each peak.

are related to the population difference, $\Delta N(v, J) - N(v + 1, J)$ between the upper, v + 1, J, and lower, v, J states connected by the Raman Q-branch transition,

$$\chi' = \left[\frac{\Delta N c^4}{\hbar \omega_s^4}\right] \left[\frac{d\sigma}{d\Omega}\right]$$
$$\times \frac{\omega_R \left[\omega_R^2 - (\omega_p - \omega_s)^2\right]}{\left[\omega_R^2 - (\omega_p - \omega_s)^2\right]^2 + \Gamma_R^2 (\omega_p - \omega_s)^2} \quad (4)$$

and

$$\chi'' = \left[\frac{\Delta N c^4}{\hbar \omega_s^4}\right] \left[\frac{d\sigma}{d\Omega}\right] \\ \times \frac{\omega_R \Gamma_R (\omega_p - \omega_s)}{\left[\omega_R^2 - (\omega_p - \omega_s)^2\right]^2 + \Gamma_R^2 (\omega_p - \omega_s)^2}.$$
 (5)

In the above equations, ω_R , Γ_R , and $d\sigma/d\Omega$ are the frequency, linewidth, and cross section of the vibrational *Q*-branch Raman transition.

The magnitude of the Raman Q-branch cross section is a function of the vibrational and rotational quantum numbers³⁻⁷:

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{\hbar}{2m\omega_R} \left(\frac{\omega_s}{c}\right)^4 (\alpha^2 + 4/45b_{J,J}\gamma^2)(v+1).(6)$$

Here v is the vibrational quantum number, m is the reduced mass, α and γ are the mean value and anisotropy of the polarizability derivative, and $b_{J,J}$ is the Placzek-Teller coefficient, given by [J(J+1)]/[2J-1)(2J+3)]. Equation (6) is only approximate, but its use introduces only small errors in the analysis.¹² For example, for H₂ the accurately calculated¹³ Raman cross section dependence on v differs from the v + 1 dependence of Eq. (6) by less than 5% for $v \leq 4$, and the exact J dependence gives cross sections that differ from Eq. (6) by less than 5% for $J \leq 25$.

Equations (2)-(5) can be combined to give

$$S(\omega_{\rm as}) = \left[\frac{\Delta N c^4}{\hbar \omega_{\rm s}^4}\right]^2 \left[\frac{d\sigma}{d\Omega}\right]^2 \int g(\omega;\omega_{\rm as}) F_2[f'^2 + f''^2] d\omega + 2\left[\frac{\Delta N c^4}{\hbar \omega_{\rm s}^4}\right] \left[\frac{d\sigma}{d\Omega}\right] \chi^{\rm NR}$$
(7)

 $\times \int g(\omega;\omega_{\rm as})F_2f'd\omega + (\chi^{\rm NR})^2 \int g(\omega;\omega_{\rm as})F_2\,d\omega\,,$

$$f' = \frac{\omega_R \left[\omega_R^2 - (\omega_p - \omega_s)^2 \right]}{\left[\omega_R^2 - (\omega_p - \omega_s)^2 \right]^2 + \Gamma_R^2 (\omega_p - \omega_s)^2}$$

and

where

$$f'' = \frac{\omega_R \Gamma_R (\omega_p - \omega_s)}{\left[\omega_R^2 - (\omega_p - \omega_s)^2\right]^2 + \Gamma_R^2 (\omega_p - \omega_s)^2}$$

Equation (7) is solved to find ΔN for each observed CARS transition. $S(\omega_{as})$ is computed for a range of ΔN values by numerical integration of Eq. (7), and comparison of the calculated $S(\omega_{as})$ values to the experimentally measured $S(\omega_{as})$ determines the correct value of ΔN . Quantum state populations N(v', J') are extracted from the $\Delta N(v', J')$ using the boundary conditions $N(v'_i, J') = 0$, where v'_i is the lowest vibrational state for which the population is zero. The identity of v'_i is determined either by energy conservation or by direct experimental observation.

The experimentally meausured peaks are dispersive in character because the CARS signal contains a contribution from the nonresonant part of the third order susceptibility. As Eq. (2) shows, the signal is proportional to the square of the modulus of the susceptibility:

$$|\chi^{(3)}|^2 = (\chi')^2 + (\chi'')^2 + (\chi^{NR})^2 + 2\chi'\chi^{NR}.$$
 (8)

When the cross term $2\chi'\chi^{NR}$ is small, $|\chi^{(3)}|^2 \approx (\chi'')^2 + (\chi')^2 + (\chi^{NR})^2$ and the CARS signal is positive for all $\omega_p - \omega_s$ and symmetric about ω_R . However, when $\chi^{NR} \gg \chi'', \chi'$, the cross term becomes dominant and $|\chi^{(3)}|^2 \approx 2\chi'\chi^{NR} + (\chi^{NR})^2$. Since χ' is dispersive about ω_R , with phase determined by the sign of ΔN , the resultant CARS signal is a dispersive one on a large frequency-independent background. Since the reaction product densities are low in these single collision experiments, $\chi^{NR} \gg \chi', \chi''$ and the dispersive character is always present in the CARS signals.

B. ABSOLUTE REACTION CROSS SECTIONS

The absolute partial and total cross sections for the $H + HX \rightarrow H_2 + X$ reactions are calculated using

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$$\sigma(v', J') = [H_2(v', J')] / [HX]_0 [H]_0 v_{\rm rel} \Delta t, \qquad (9)$$

and

$$\sigma_{\text{total}} = \sum_{v', J'} \sigma(v', J') , \qquad (10)$$

where [] denotes the concentration in particles cm^{-3} , v_{rel} is the collision velocity $(1.75 \times 10^6 \text{ cm s}^{-1})$, and Δt is the time delay between the photolysis and probe lasers $(3.5 \pm 0.4 \text{ ns})$. [HX]₀ and [H]₀ are the concentrations of HX and H immediately after the photolysis pulse but before reaction. The HX concentration is directly determined by CARS spectroscopy. The H concentration is also determined by CARS spectroscopy, but indirectly, from spectra of the HI precursor with and without the UV photolysis beam. Calibration of the CARS spectra to allow absolute number densities to be extracted from the CARS signal intensities is carried out by referencing the HX reactant spectra and the H₂ rection product spectra to CARS spectra of these species measured under conditions for which the molecular density is known independently. Using Eqs. (9) and (10) we find that the total reaction cross section for the H + HX H atom abstraction reactions are $2 \pm 1 \text{ Å}^2$, 3 ± 1 $Å^2$, and $2 \pm 1 Å^2$ for X = Cl, Br, and I, respectively.

We use a single relative velocity in Eq. (9) to determine the absolute cross sections, the relative velocity of H + HX collisions for the fast (1.6 eV relative energy) H atoms. In our experiments there are slower H atoms (0.68 eV relative energy), from HI photolysis to give H + $I({}^{2}P_{1/2})$, that also may contribute to the H₂ product yields. Our neglect of this contribution, by our use of the relative velocity appropriate for the faster H atoms, introduces some additional uncertainty into the cross section calculations. However, the quantum-yield-weighted average of the relative velocities of the fast and slow H atoms is only 9% smaller than the relative velocity of the fast H atoms, so this uncertainty is a small one.



FIG. 5. Rotational state distribution for the H_2 product of the H + HCl reaction at 1.6 eV. The symbols with error bars give the measured distribution. The solid lines are the linear rotational surprisal best fits to the data, with the surprisal parameters given.



FIG. 6. Rotational state distribution for the H_2 product of the H + HBr reaction at 1.6 eV. The symbols with error bars give the measured distribution. The solid lines are the linear rotational surprisal best fits to the data, with the surprisal parameters given.

C. ROTATIONAL AND VIBRATIONAL STATE DISTRIBUTIONS FOR $H + HX \rightarrow H_2 + X$

The rotational distributions measured for the H₂ product of the H + HCl reaction are shown in Fig. 5, while for the H_2 product of the H + HBr and H + HI reactions the rotational distributions are given in Figs. 6 and 7, respectively. Since we have made absolute cross section measurements, these relative populations can be converted to absolute cross sections. Rather than present additional plots of the data, we merely note that "10" in the arbitrary units of Fig. 5 corresponds to a cross section of 0.017 \pm 0.002 Å², while for Fig. 6 this scale factor is "10" = $0.066 \pm 0.007 \text{ Å}^2$, and for Fig. 7 "10" = 0.034 \pm 0.004 Å². Most of the product population appears in the odd J' states of H_2 . This is due not to some dynamical restriction on the reaction, but rather to the nuclear spin degeneracy of H_2 , which is 3 for odd J' and 1 for even J'. Since the dependence of the CARS signal on the population difference is between linear and quadratic [see



FIG. 7. Rotational state distribution for the H_2 product of the H + HI reaction at 1.6 eV. The symbols with error bars give the measured distributions. The solid lines are simple smooth lines hand drawn through the data.

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Eq. (7)], the spin degeneracy difference makes the CARS signals for odd J' states a factor of 3 to 9 times greater than the CARS signals arising from even J' states of H₂. Although CARS signals for the even J' states of the H₂ product were observed, the lower signal-to-noise ratio made signal averaging more difficult, and we did not record many of the even J' signals. The rotational distributions are broad enough that the incompleteness of the even J' data is of little consequence.

Since we use HI as the H atom precursor in all three reactions, the H₂ from the H + HI \rightarrow H₂ + I reaction in an interference in our measurements of the H₂ from the H + HBr and H + HCl reactions. We minimize this interference by using high enough photolysis pulse energy to dissociate essentially all the HI in the CARS probe volume, $\approx 10^{-4}$ cm³. What residual contribution the H + HI reaction makes to H₂ product formation can be easily subtracted from the H₂ product of the H + HBr or H + HCl reactions, because the three reactions have such different rotational and vibrational state distributions as a consequence of their significantly different energetics.

The H₂ product rotational distributions in the three reactions are indeed quite different. It is not at all surprising that the H_2 state distributions shift to higher J' along the series H + HCl, H + HBr, H + HI, since the energy available to the products almost doubles along this series, 1.6 eV for reaction with HCl, 2.3 eV for reaction with HBr, and 3.0 eV for reaction with HI. For $H + HCl \rightarrow H_2 + Cl$ the rotational distribution peaks at very low J', 5 and 3 in v' = 0 and 1, respectively. Even though these are states of quite small angular momentum, they are not of small rotational energy, since the rotational constants of H₂ is so large, ≈ 60 cm⁻¹. To illustrate this point, we note that a 300 K Boltzmann rotational distribution for H₂ has appreciable population only for $J \leq 3$, and the most probable J is 1. In fact for the $H + HCl \rightarrow H_2 + Cl$ reaction the fraction of the available energy appearing in product rotation, f'_r , is significant, 0.21 ± 0.01 . The H₂ product of the substantially exoergic H + HBr and H + HI reactions peak at higher J', for example J' = 7 and 13, respectively for v' = 0, but the fraction of the available energy in product rotation is essentially the same for these reactions as for the nearly thermoneutral H + HCl reaction. For H + HBr and H + HI the f'_r is 0.19 ± 0.02 and 0.18 ± 0.03 , respectively.

While the average fractional energy disposal in rotation is essentially invariant in this homologous series of $H + HX \rightarrow H_2 + X$ reactions, the detailed form of the rotational state distributions is quite characteristic of the identity of the halogen. In the next section we discuss how these rotational state distributions reflect the details of the differences in the potential energy surfaces for the reactions, specifically differences in the HHX bending potential. Here, we simply point out one measure of the these differences, by reference to a linear surprisal analysis. Using a nonlinear least-squares analysis we attempt to fit the distributions within each vibrational level to a linear rotational surprisal:¹⁴

$$P(J') = P^{0}(J') \exp\left[-\theta_{0} - \theta_{R}g_{R}(J')\right], \qquad (11)$$

where $P^{0}(J')$ is the prior distribution, $g_{R}(J')$ is the fraction

of the available energy in rotation for state J', and θ_R is the rotational surprisal parameter. For the H₂ product of the reaction with HCl this works well. The best-fit linear surprisal distributions are plotted as solid lines in Fig. 5, and these clearly provide adequate representations of the actual measurements, with θ_R values of 3.7 \pm 2.1 and 7.4 \pm 4.0 for the v' = 0 and 1 levels, respectively. The large uncertainty in the populations in v' = 1 leads to large uncertainty in the linear rotational surprisal for that state, and in fact a single θ_R value around 4.0 adequately describes the H₂ rotational distribution in both vibrational levels. For the H₂ product of the H + HBr reaction we find $\theta_R = 1.6 \pm 1.6$, 5.1 ± 2.5 , and 9.4 \pm 3.4, for v' = 0 through 2, and the distributions given by these parameters are plotted as solid lines in Fig. 6. While the surprisal function reproduces the distributions actually measured for most J', it gives significant population above J' = 13 in v' = 0 and above J' = 5 in v' = 3, where we find the population so small as to be immeasurable. Moreover, a single surprisal parameter is clearly not adequate to represent the H_2 rotational state distribution in all v'. For the H_2 product of the H + HI reaction no linear surprisal function can adequately represent the observed rotational distribution. For this reaction the measured distributions in the v' = 3 and 4 levels somewhat match those given by surprisals with $\theta_R = 4.2 \pm 1.5$ and 3.5 ± 3.5 , respectively, within the signal-to-noise of the experiment, but this is not the case for the v' = 0, 1 and 2 levels. For these three levels the best-fit linear surprisal distributions, characterized $\theta_R = -3.6 \pm 3.4, 2.3 \pm 1.3, \text{ and } 4.1 \pm 1.4, \text{ respectively},$ are considerably broader than the measured distributions, and the peaks of the calculated distributions do not match the peaks of the measured distributions. In all cases the "best fits" of the linear surprisal function are quite poor. The rotational state distributions are simply too sharply peaked at too high J' for them to be represented by the temperaturelike parameter θ_R . The inadequacy of a linear surprisal function description of the H₂ product rotational state distributions for the H + HBr reaction and even more the H + HI reaction implies dynamical constraints that cannot be accounted for by the simple energetic statistical constraints incorporated in the surprisal approach; other constraints must be at least as important. For the HCl reaction the adequacy of the surprisal description indicates that energetic statistical constraints predominate in determining the rotational state distributions.

Applications of the surprisal analysis also yields some interesting observations about the vibrational state distributions in these abstraction reactions. The H_2 product vibrational distributions, obtained by summing the rotational populations in each vibrational level, are shown in Figs. 8–10. For the HCl and HBr reactions the H_2 product is very cold. We can quantify this using a linear surprisal description,¹⁴

$$P(v') = P^{0}(v') \exp\left[-\lambda_{0} - \lambda_{u} f_{v}(v')\right], \qquad (12)$$

where, as in the rotational surprisal description, $P^0(v')$ is the prior distribution, $f_v(v')$ is the fraction of the available energy in vibration for state v', and λ_v is the vibrational surprisal parameter. The vibrational distributions described by this



FIG. 8. Vibrational state distribution for H_2 from the H + HCl reaction at 1.6 eV. The symbols with error bars give the measured distribution. The solid line gives the linear vibrational surprisal description of the data, with the surprisal parameter given.

linear surprisal function are given by the solid lines in Fig. 8 and 9. For $H + HCl \rightarrow H_2 + Cl \lambda_v$ is 6.0 ± 1.8 , and for $H + HBr \rightarrow H_2 + Br$ it is 4.0 ± 2.4 . Since the vibrational distribution for H_2 from H + HI is inverted, it cannot be fit to a linear surprisal function. It is surprising not only in the infor-



FIG. 9. Vibrational state distribution for H_2 from the H + HBr reaction at 1.6 eV. The symbols with error bars give the measured distribution. The solid line gives the linear vibrational surprisal description of the data, with the surprisal parameter given.



FIG. 10. Vibrational state distribution for H_2 from the H + HI reaction at 1.6 eV. The symbols with error bars give the measured distribution. The solid line simply connects the data points.

mation theoretical sense, but also in the common sense of the word, that the 0.72 eV excergic (cf. Table I) H + HBr reaction gives such a cold H₂ product vibrational distribution, particularly since the vibrational distribution in the 1.4 eV excergic $H + HI \rightarrow H_2 + I$ reaction is so strongly inverted. However, the vibrational state distribution in the H + HBrreaction, $P(v') = 0.65 \pm 0.08$, 0.30 ± 0.03 , and 0.05 ± 0.01 in v' = 0, 1, and 2, respectively, is almost exactly the same as the mean of the vibrational state distributions in the H + HCl and H + HI reactions, $P(v') = 0.60 \pm 0.08$, 0.27 ± 0.07 , and 0.11 ± 0.05 in v' = 0, 1, and 2. Note that in terms either of exoergicity or total available energy the H + HBr reaction has energies that are nearly identical to the mean of the H + HCl and H + HI reaction energies. Viewed in this way the H + HBr reaction does not appear anomalous.

Despite the product vibrational population inversion in the H + HI reaction, the average fraction of energy partitioned to vibration, f'_v , is modest, 0.25 ± 0.05 . The cold H₂ vibrational distributions in the H + HBr and H + HCl reaction yield very small f'_v values, 0.09 ± 0.01 and 0.02 ± 0.01 .

For ease of comparison we summarize important parameters of the H₂ product vibrational and rotational state distributions for all three reactions in Table III. Comparison of the H₂ vibrational state distributions of Figs. 8–10 and the data in Table III reveals that for all three reactions there are several H₂ product vibrational states that are energetically accessible but in which we observe no product. In H + HCl these are v' = 2 and 3, in H + HBr v' = 3, 4, and 5, and in H + HI v' = 5, 6, and 7. Our failure to observe products in these states allows us only to set an upper limit on the relative populations in them. For $v' \ge 5$ in H + HI this upper limit is

TABLE III. Parameters of the product quantum state distributions in the $H' + HX \rightarrow H'H + X$ reactions at 1.6 eV collision energy.

	HC1	HBr	HI
$\overline{E'_{\rm tot}}(eV)$	1.6	2.3	3.0
f'_{ν}	0.02 ± 0.01	0.09 ± 0.01	0.25 ± 0.05
f'_{t}	0.21 ± 0.01	0.19 ± 0.02	0.18 ± 0.03
$f_1^{\prime a}$	0.77 ± 0.01	0.72 ± 0.02	0.57 ± 0.06
$\sigma_{\rm tot}({\rm \AA}^2)$	2 ± 1	3 ± 1	2 ± 1
(v')	0.08	0.40	1.10
v'max]b	3	5	7
$\langle J' \rangle (v'=0)^c$	5.5	7.9	13.1
$\left[J_{\max}'(v'=0)\right]^{d}$	15	19	23

^a Determined by f'_{r}, f'_{v} and energy conservation.

^b The maximum energetically accessible product vibrational state.

^c The average rotational quantum number for product in the ground vibrational state.

^d The highest energetically accessible product rotational state for product in the ground vibrational state.

0.004, that is less than 0.4% of the products can be in any one of these vibrational states. The limit is the same for $v' \ge 3$ in H + HBr, while for H + HCl no more than 1% of the products can be in v' = 2 or 3.

Included in Table III are values for f'_i , the fraction of the available energy that appears in product translation. This value is determined by our direct measurements of f'_i and f'_v and the application of energy conservation. Our detailed v', J' product distributions actually allow us to derive the detailed product translational energy distributions. These are shown in Figs. 11–13. In all three reactions the H₂ + X translational energy distribution is narrow, full width at half maximum (FWHM) of about 0.5 eV, and peaks near the 1.6 eV reactant translational energy. The most probable (average) product translational energy is 1.4 (1.3) eV, 1.6 (1.7) eV, and 1.7 (1.7) eV for H₂ + Cl, H₂ + Br, and H₂ + I, respectively.

The surprisal parameters, the f'_i , and f'_v values in Table III, and the product translational energy distributions in

C.M. TRANSLATIONAL ENERGY DISTRIBUTION



FIG. 11. Product center-of-mass translational energy distribution for the reaction $H + HCl \rightarrow H_2 + Cl$. The distribution is obtained by inverting the measured H_2 quantum state distribution.

Figs. 11-13 all require specification of the total energy for their determination. Since there are two H + HX collision energies in our experiments, 1.6 eV and 0.68 eV, associated with the two HI photolysis channels, $H + I({}^{2}P_{3/2})$ and $H + I({}^{2}P_{1/2})$, respectively, there is in principle some ambiguity in the values of these parameters that describe the product energy disposal. In practice, however, this ambiguity is not very important. First, the quantum yield⁸ for the $H + I({}^{2}P_{3/2})$ channel is almost twice that of the $H + I({}^{2}P_{1/2})$ channel. Second, in our signal-collision experiments the 1.6 eV H atoms, by virtue of their greater velocity, are much more likely to undergo a collision than the 0.68 eV H atoms. Together, these two factors imply that if the abstraction reaction cross sections are energy-independent the 1.6 eV collisions contribute 75% of the product and the 0.68 eV collision only 25%. However, the contribution of the 0.68 eV collisions is probably significantly less than this, since the $H + HX \rightarrow H_2 + X$ cross sections are probably larger at 1.6 eV collision energy than at 0.68 eV. Although

C.M. TRANSLATIONAL ENERGY DISTRIBUTION



FIG. 12. Product center-of-mass translational energy distribution for the reaction $H + HBr \rightarrow H_2 + Br$. The distribution is obtained by inverting the measured H_2 quantum state distributions.





FIG. 13. Product center-of-mass translational energy distributions for the reaction $H + HI \rightarrow H_2 + I$. The distribution is obtained by inverting the measured H_2 quantum state distributions.

both collision energies are greater than the collinear barrier height for all three abstraction reactions, the increasing barrier height with decreasing HHX angle (cf. Table I) much more significantly restricts the range of reactive geometries at 0.68 eV than at 1.6 eV collision energy. Using the dependence of the barrier height on HHX angle from the Baer and Last potential energy surfaces¹ and the simple line-ofcenters model¹⁴ cross section dependence on barrier height, $\sigma_{tot} \alpha \int [1 - E_b(\theta)/E_{rel}] (\sin \theta) d\theta$, it is clear that all the H + HX abstraction reaction cross sections should be significantly larger at 1.6 eV collision energh than at 0.68 eV. The ratio $\sigma_{tot} (1.6 \text{ eV})/\sigma_{tot} (0.68 \text{ eV})$ is 2.7, 1.7, and 1.4 for the HCl, HBr, and HI reactions, respectively. Such a cross section energy dependence would reduce the contribution of the 0.68 eV H atoms to 11%–19% of the total H₂ product yield.

Note that trajectory calculations carried out by Thompson *et al.*¹⁵ give results that are consistent with these expectations. They computed $\sigma(E)$ for $D + DCl \rightarrow D_2 + Cl$ and $D + HCl \rightarrow HD + Cl$ for collision energies up to 2.4 eV. They used an approximate potential energy surface with a collinear barrier height of 0.17 eV, rising to 1.1 eV at $\theta = 90^{\circ}$. This closely resembles the H + HBr surface of Baer and Last, described in Tables I and II.¹⁴ Thompson *et al.*¹⁵ found $\sigma(1.6 \text{ eV}) = 0.5 \text{ Å}^2$ and $\sigma(1.6 \text{ eV})/\sigma(0.68 \text{ eV}) = 1.3$.

IV. DISCUSSION

A. Total reaction cross sections

Comparison of our measurements on the $H + HX \rightarrow H_2 + X$ reactions for X = Cl, Br, and I reveals some surprising similarities as well as some surprising differences. Among the similarities is the near equivalence of the total reaction cross sections show in Table III. The uncertainty in these measured total cross sections is significant, $\pm 33\%$ -50%, but even taking this into consideration, the cross sections are remarkably similar. Since both the collinear barrier heights and the HHX-angle-averaged barrier heights (cf. Table I) increase in the order H + HI,

H + HBr, H + HCl, one expects the cross sections to decrease in this order. This expectation of a dependence of σ_{tot} on the identity of X must be put in quantitative terms in order to compare our expectations with the experimental observations. We can do so by incorporating the angle-dependent barrier heights of the Baer and Last HHX surfaces into a simple line-of-centers model as described in the previous section. If we make the reasonable assumption that the variation of the H + HX \rightarrow H₂ + X cross sections with identity of X is due only to differences in barrier heights, we find that at 1.6 eV relative energy the cross sections are in the ratio 1.9:2.6:3.1 for HCl, HBr, and HI, respectively. This ratio agrees with our measurements within experimental uncertainty.

For the $H + HI \rightarrow H_2 + I$ reaction our 1.6 eV collision energy is large enough that E_{rel} is significantly greater than $E_{h}(\theta)$ for HHX angles θ as small as 90° [$E_{b}(90^{\circ}) = 1.0$ eV]. In the context of the line-of-centers model and to the extent that the Baer and Last surface accurately describes this reaction this means that at 1.6 eV we are approaching the maximum possible value of $\sigma_{\rm tot}$, specifically 82% of the limiting cross section. For H + HCl and H + HBr the lineof-centers model and the Baer and Last surface indicate that we are at only 51% and 72% of the limiting cross sections. These differences are not significant in a comparison of total cross sections measured for the reactions, because of the limited accuracy of the measurements, but, they are very important when comparing the H₂ rotational state distributions for the different reactions. However, before we can take up this issue we must consider the H₂ vibrational state distributions.

B. Product vibrational and rotational state distributions

The product vibrational state distributions of the $H + HX \rightarrow H_2 + X$ reaction, shown in Figs. 8–10 display the most obvious differences among this homologous series of H atom abstraction reactions. However, it is the similarities in the P(v') for these three reactions that provides the clue to understanding the differences among them. In all three cases the only appreciably populated [P(v') > 0.1]H₂ vibrational states are those accessible as a result of the reaction exoergicity alone. For the HI reaction those states are $v' \leq 2$, while for the HBr reaction those states are $v' \leq 1$, and for the nearly thermoneutral HCl reaction only v' = 0. In each reaction the 1.6 eV collision energy opens several additional product vibrational channels (cf. Table III), but only 6-8% of the products appear in them. In the $H + HI \rightarrow H_2 + I$ reaction the energy added by the H + HI reactant translational motion more than triples the number of vibrational states accessible, opening v' = 3, 4, 5, 6, and 7, yet only 6% of the H₂ products appear in these states, and then only in v' = 3 and 4. In H + HBr the reactant translational energy opens v' = 2, 3, 4, and 5, but of these only v' = 2 is actually produced in the reaction, and only 6% of the products are in this vibrational state. In H + HCl the reactant translational energy adds v' = 1, 2, and 3, but only v' = 1 is actually produced, and with only 8% of the product. Apparently, the transfer of reactant translational energy to product vibration in the H + HX reactions is inefficient in the extreme. In fact, the vibrational distributionis we observe imply that at most onehalf of the collision energy is available to product vibration, for the highest vibrational state that we observe in each reaction is the highest vibrational state for which the energy does not exceed the reaction excergicity plus 0.8 eV.

A consideration of the potential energy surfaces and the kinematics of these reactions can explain the behavior. To incorporate both the energetic and kinematic features of these reactions we plot the Baer and Last collinear potentialenergy surfaces for the three $H + HX \rightarrow H_2 + X$ reactions in mass-scaled coordinates¹⁴ in Figs. 14-16. For the lightlight-heavy mass combination of these reactions the skew angle, ¹⁴ γ , is approximately 45° for all X. For such a small skew angle reactant translation will not couple very effectively to product vibration, for two reasons. First, a simple projection of reactant translation onto product vibration, given by $\sin^2 \gamma$, is only 0.5. Second, for a collision at high energy to "turn the corner" from the reactant valley into the product valley requires that the trajectory be sharply "steered" into the exit valley by the curvature of the inner corner of the potential energy surface. This further reduces the projection of the reactant translation onto product vibration, strongly coupling reactant and product translation. The latter effect is impossible to quantify without running trajectory calculations. The skew angle influence, on the other hand is easy to quantify, and should in fact provide a reasonable upper limit on the contribution of reactant translation to product vibration. Since $\sin^2 \gamma$, is 0.5, this upper limit is 0.8 eV in our experiments, precisely as we have observed.

For noncollinear trajectories rotational excitation of the H_2 product must also be considered, and the generalization of this restriction should preclude states for which the total internal energy is more than the sum of the exoergicity plus one-half the collision energy. In fact, we do observe a restriction on the populated rotational states to those for which the sum of $E_{vib} + E_{rot}$ does not exceed the reaction exoergicity plus 0.8 eV. For the H + HI reaction the 1.4 eV exoergicity plus 0.8 eV of translational energy allows J' = 19 in v' = 0, J' = 17 in v' = 1, J' = 14 in v' = 2, J' = 11 in v' = 3, and

J' = 7 in v' = 4. The highest observed rotational states are J' = 17, 17, 15, 11, and 5 in v' = 0, 1, 2, 3, and 4, respectively. For the less excergic H + HBr reaction the states accessible as a result of the excergicity plus one-half the collision energy are J' = 15, 12, and 9 in v' = 0, 1, and 2, while the highest J' observed are 13, 11, and 5, respectively. For H + HCl we should be able to get up to J' = 11 and 7 in v' = 0 and 1, respectively, while we observe up to J' = 11 and 7.

Assuming that the same kind of restriction applies to the product state distributions of these reactions at 0.68 eV, we can estimate what H₂ quantum states contain contributions from reaction of the slower photolytically generated H atoms in our experiments. For H + HI these are $J' \leq 17, 14$, 11, 7, in v' = 0, 1, 2, and 3. For H + HBr these states are $J' \leq$ 12, 9, and 3 in v' = 0, 1, and 2, while for H + HCl we expect population in $J' \leq 7$ in v' = 0. Thus, there are many states for which both the 0.68 eV and 1.6 eV H atoms can be expected to contribute. We expect then that while the product state distributions we measure have a 10-20 % contribution (see Sec. III) from the 0.68 eV collisions, this contribution will not shift the distributions much from the true 1.6 eV collision energy values, probably only 1 to 3 \hbar lower in J', and only very slightly to lower v'. However, only the experimental measurements at lower collision energy can determine this unambiguously.

The $H + HX \rightarrow H_2 + X$ potential energy surfaces depicted in Figs. 14–16 suggest that for high H + HX translational energy the turning point in reactive encounters will occur near the inner corner of the surface, where both r_{HH} and r_{HX} are small and the reactant translational energy has been spent climbing the repulsive inner wall of the surface. The HHX will then move rapidly into the product channel, driven by the large gradient of the potential energy at the turning point. From this turning point into the product channel the gradient of the potential along r_{HH} is much greater than that along r_{HX} , a situation that should make the product separation vibrationally adiabatic but rotationally impulsive. That is, the H₂ product vibrational state would be determined by the value of r_{HH} at the turning point, where



COLLINEAR H + HBr -> H, + Br



FIG. 14. Collinear potential energy surface for the $H + HCl \rightarrow H_2 + Cl$ reaction, plotted in mass-scaled coordinates, from the DIM-3C calculations of Baer and Last, Ref. 1. The contours are given every 6 kcal mol⁻¹ with the outermost contour at 42 kcal mol⁻¹, with energies measured relative to the bottom of the asymptotic H + HCl well.





FIG. 16. Collinear potential energy surface for the $H + HI \rightarrow H_2 + I$ reaction, plotted in mass-scaled coordinates, from the DIM-3C calculations of Baer and Last, Ref. 1. The contours are given every 6 kcal mol⁻¹ with the outermost contour at 42 kcal mol⁻¹, with energies measured relative to the bottom of the asymptotic H + HI well.

the transition from H + HX to $H_2 + X$ occurs. This is simply a modification of the Franck–Condon model of reactions.¹⁶

As used previously to describe the $F + H_2 \rightarrow HF + H$ and $H + Cl_2 \rightarrow HCl + Cl$ reactions, this Franck-Condon model assumes that the transition from reactants to products is sudden (with respect to the nuclear motions), occurring in a small region of coordinate space, which is generally taken to be located at the saddle point. Thus it is the geometry of the saddle point (in particular the internuclear distances) that determines the vibrational distribution in the product, and as the products separate this vibrational distribution is preserved. Thus, the Franck-Condon model assumes vibrationally adiabatic exit channel dynamics. In these applications of the Franck-Condon model it has been assumed that the velocity of the reacting system at the saddle point is small. For the $F + H_2$ and $H + Cl_2$ systems this is a reasonable assumption because the reactions were studied only for the case where the collision energy was comparable to the barrier height,¹⁶ and thus the system expends its kinetic energy climbing the barrier to reaction. We invoke a Franck-Condon description of these H + HX reactions at our high collision energy with a turning point not at the saddle point, but rather at small H-H separation, where all the collision energy has been expended in climbing the repulsive inner wall of the potential energy surface. At this H-H separation a Franck-Condon-like transition from H + HX to $H_2 + X$ that is sudden with respect to $H_2 + X$ separation would occur.

For the H + HI reaction the potential energy surface is such that the H-H separation at this turning point can be much *smaller* than the equilibrium H₂ bond distance for collisions at 1.6 eV, so one expects the H₂ will be formed with considerable vibrational excitation. For the H + HBr and H + HCl reactions what appear to be only slight differences in the potential energy surface move the turning point out to sufficiently larger $r_{\rm HH}$ that product vibrational excitation is much less likely. We could quantitatively apply this Franck-Condon description using the Baer and Last surface to calculate P(v'), but uncertainties in the surfaces at these high energies make such a detailed calculation of dubious value. It does not take detailed calculations to explain, at least semiquantitatively, the rotational distributions that we observe. In the context of the Franck–Condon model, these are simply determined by rotationally impulsive energy release in the half-collision of $H_2(v') + X$ separation. The rotational state of the H_2 is determined by the HHX geometry, specifically the HHX angle, θ , and the energy available to the $H_2(v')$ and X, E_{avl} ,¹⁷

$$E_{\rm rot} = (m_{\rm H} m_{\rm X} E_{\rm avl} \sin^2 \theta) / [(m_{\rm H} + m_{\rm H})(m_{\rm H} + m_{\rm X}) - m_{\rm H} m_{\rm X} \cos^2 \theta] . (13)$$

We have previously applied this model to describe the energy disposal in the A + BC half-collision accompanying ABC photofragmentation.¹⁷ For photodissociation Eq. (13) is easy to implement, since ABC is stable and its geometry (range of θ) well determined. For a transition state like HHX the geometry is not well determined. However, the possible values of θ are restricted both by the HHX bending potential (cf. Table I), and by simple geometric constraints imposed by the size differential between X and H.

We have carried out a simple calculation to predict the rotational state distribution assuming that the energy release is rotationally impulsive, incorporating the effect of the bending potential in terms of a simple line-of-centers model, and interpreting the size differential as restricting reaction to those encounters in which the attacking H atom strikes the H of HX with zero H–H impact parameter. This gives a one-to-one correlation between the H–HX impact parameter, b, and the HHX angle, θ , specifically

$$\theta = \sin^{-1} \left[(b/r_{\rm HX}) (m_{\rm X} + m_{\rm H})/m_{\rm X} \right], \qquad (14)$$

where m_i is the mass of particle *i*, and r_{HX} the HX bond length. For a given angle θ there must be reaction taking place with impact parameters both larger and smaller than this, so the model should yield a rotational distribution that is narrower than the actual one. Note that in the context of maximum value this model the of b is $r_{\rm HX} [m_{\rm X} / (m_{\rm X} + m_{\rm H})]$. The model conserves angular momentum, and in fact the reactant orbital angular momentum transforms completely into product orbital angular momentum. For a given b, Eq. (14) specifies θ , and Eq. (13) gives $E_{\rm rot}$ for a particular H₂ (v'). The probability of this $E_{\rm rot}$ is determined by the probability of reaction at impact parameter b, given by

$$P(E_{\rm rot}) = P(\theta) = P(b) = 2\pi b \times \left[1 - E_b(\theta)/E_{\rm rel}\right],$$
(15)

where the last factor is the line-of-centers reaction probability,¹⁴ with $E_{rel} = 1.6 \text{ eV}$ and $E_b(\theta)$ taken from the Baer and Last potential surfaces.¹ Thus Eqs. (13)–(15) specify the H₂ product rotational distribution. The results of these model calculations are compared with the rotational distributions actually observed in Figs. 17–19. As expected, the calculated distributions are narrower than those actually observed, but the peaks in the distributions are reproduced quite well, as are the general shapes of the distributions. Not much more should or could be expected of the model. The results do, however, confirm the physical reasonableness of the model, and suggest that more detailed calculations be carried out to



FIG. 17. Comparison of rotational state distributions for the H_2 product of the H + HCl reaction. The symbols with error bars are the experimental results, while the solid lines give the distributions predicted by a rotationally impulsive model. See the text for details.

explore further the description of the reaction in terms of a Franck–Condon model with rotationally impulsive energy release.

The model also helps explain why a linear surprisal function cannot adequately describe the rotational distributions of the H₂ product of the H + HI and H + HBr reactions, but can do so for the H₂ product of the H + HCl reaction. This surprisal description invokes a prior distribution that is constrained by energy conservation, but not by angular momentum conservation. It works well as long as the dynamical bias in a reaction is not based simply on total angular momentum conservation, but rather on some feature of the potential energy surface. The model calculations show that in the H + HCl reaction the product rotational distribution is restricted to relatively low J' by the steep rise in the HHCl bending potential, which restricts reaction to



FIG. 18. Comparison of rotational state distributions for the H_2 product of the H + HBr reaction. The symbols with error bars are the experimental results, while the solid lines give the distributions predicted by a rotationally impulsive model. See text for details.



FIG. 19. Comparison of rotational state distributions for the H_2 product of the H + HI reaction. The symbols with error bars are the experimental results, while the solid lines give the distributions predicted by a rotationally impulsive model. See the text for details.

small θ , and therefore small H₂ rotational energy. For the H + HBr reaction and even more for the H + HI reaction, the high collision energy of the experiments allows the reaction probability to be near unity for almost the entire range 180° to 90°, so the H₂ rotational distribution is restricted significantly (HBr) or almost completely (HI) by total angular momentum conservation.

In each of the $H + HX \rightarrow H_2 + X$ reactions there is enough energy to form the halogen atom X in the excited spin-orbit state, ${}^{2}P_{1/2}$, which lies 0.11, 0.46, and 0.94 eV above the ground ${}^{2}P_{3/2}$ state for Cl, Br, and I, respectively. Infrared chemiluminescence studies of the $H + HI \rightarrow H_2 + I$ reaction, ¹⁸ carried out with a room-temperature thermal distribution of collision energies, show that 2% of the reactive events lead to the formation of $I({}^{2}P_{1/2})$, but the collision energy dependence of the branching ratio is not known. Similar studies¹⁹ of the thermal $H + HBr \rightarrow H_2 + Br$ reaction showed $Br({}^{2}P_{1/2})$ production, but the branching ratio was not determined. There is no way to tell from our measurements the extent of production of excited spin-orbit states $X({}^{2}P_{1/2})$.

In a previous CARS experiment²⁰ H_2 from the H + HBr reaction at a nominal collision energy of 2.6 eV was detected and found to be rotationally excited in the v' = 1 and 2 states. Our measurements are not inconsistent with these previous observations, but a direct comparison with them cannot be made, in part because of the difference in collision energy, but also because the previous experiments were done under conditions that allow many H + HBr and $H_2 + HBr$ collisions. Deconvolution of the measured state distributions to remove the effects of these multiple collisions is not feasible.

V. CONCLUSION

Reaction of translationally excited H atoms with HX (X = Cl, Br, and I) at 1.6 eV produces H₂ with quite characteristic rotational and vibrational state distributions that vary significantly with the identity of the halogen. These

differences reflect the dramatic changes in thermochemistry and hence potential energy surface that accompany changes in the identity of the halogen. However, there are also persistent similarities in the H_2 product state distributions, which reflect the extreme light-light-heavy kinematics of the reactions, and the near independence of the kinematics from identity of X. It appears that a simple model of the reaction that has vibrationally adiabatic, rotationally impulsive exit channel energy release with Franck-Condon factors determining the H_2 vibrational distribution can account for the observed product state distributions.

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- ¹M. Baer and I. Last, in *Potential Energy Surfaces and Dynamics Calculations*, edited by D. G. Truhlar (Plenum, New York, 1981).
- ²K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

- ³D. P. Gerrity and J. J. Valentini, J. Chem. Phys. 79, 5202 (1983).
- ⁴D. P. Gerrity and J. J. Valentini, J. Chem. Phys. 81, 1298 (1984).
- ⁵D. P. Gerrity and J. J. Valentini, J. Chem. Phys. 82, 1323 (1985).
- ⁶D. P. Gerrity and J. J. Valentini, J. Chem. Phys. 83, 2207 (1985). ⁷For a review of CARS see J. J. Valentini, in Spectrometric Techniques,
- edited by G. A. Vanasse (Academic, New York, 1985), Vol. 4, Chap. 1.
- ⁸R. D. Clear, S. J. Riley, and K. R. Wilson, J. Chem. Phys. **63**, 1340 (1975).
- ⁹From thermal conductivity measurements in *CRC Handbook of Chemistry and Physics* (CRC, Cleveland, 1975), 55th Ed., p. F195.
- ¹⁰E. A. Rohlfing, H. Rabitz, J. Gelfand, R. B. Miller, and A. E. DePristo, Chem. Phys. 51, 121 (1980).
- ¹¹D. W. Chandler and R. L. Farrow, J. Chem. Phys. 85, 810 (1986).
- ¹²D. K. Veirs, G. M. Rosenblatt, and J. J. Valentini, J. Chem. Phys. 83, 1605 (1985).
- ¹³C. Schwartz and R. J. LeRoy, J. Mol. Spectrosc. 121, 420 (1986).
- ¹⁴R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford University Press, London, 1987).
- ¹⁵D. L. Thompson, H. H. Suzukawa, and L. M. Raff, J. Chem. Phys. 62, 4727 (1975).
- ¹⁶G. C. Schatz and J. Ross, J. Chem. Phys. 66, 1021 (1977).
- ¹⁷H. B. Levene and J. J. Valentini, J. Chem. Phys. 87, 2594 (1987).
- ¹⁸P. Cadman and J. C. Polanyi, J. Phys. Chem. 72, 3715 (1968).
- ¹⁹J. R. Airey, P. D. Pacey, and J. C. Polanyi, *11th Symposium on Combustion* (The Combustion Institute, Pittsburgh, PA, 1967), p. 85.
- ²⁰C. R. Quick, Jr. and D. S. Moore, J. Chem. Phys. 79, 759 (1983).